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Towards silver fluoride quantum materials

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Abstract

Motivated by the analogy of Ag^{2+} fluorides with high- T_c cuprate superconductors, this work investigates the synthesis and characterization of silver fluorides. A custom ultra-high vacuum (UHV) chamber was developed for the fluorination of surfaces. We discovered a protocol that allows the production of monatomic fluorine in an ultra-clean environment. We used the chamber to study the interaction of $\text{Ag}(100)$ and $\text{Ag}(110)$ surfaces with atomic fluorine using scanning tunneling microscopy (STM) supported by density functional theory (DFT) calculations. The preferred fluorine adsorption sites were identified. We estimated an anomalously low initial sticking coefficient of monatomic fluorine for the $\text{Ag}(100)$ ($S_0 \approx 10^{-5}$) and the $\text{Ag}(110)$ surfaces ($S_0 \approx 10^{-4}$). At higher fluorine coverages, we found that the sticking coefficient grows by more than an order of magnitude. Furthermore, the system phase separates into fluorine-poor and fluorine-rich disordered regions. This phenomenon was modeled using a two-dimensional Van der Waals theory. The $\text{Ag}(100)$ surface has a stronger tendency to phase separation compared to the $\text{Ag}(110)$ surface, which could be related to an attractive fluorine-fluorine interaction potential deduced from the low-coverage correlation functions. These results pave the way to the synthesis and engineering of two-dimensional silver fluoride quantum materials. Furthermore, to characterize bulk silver fluoride phases, powder samples of the two-dimensional antiferromagnet (AF) AgF_2 and the one-dimensional AF AgFBF_4 were examined using X-ray absorption spectroscopy and resonant inelastic X-ray scattering. We found that spectral features—such as dd and charge-transfer excitations—closely resemble those of La_2CuO_4 . These findings highlight AgF_2 as a promising platform to mimic the physics of cuprates without copper and to investigate correlated electron physics and unconventional superconductivity in silver fluorides. With this perspective, we collaborated with a company in the design of a custom-made chamber for pulsed laser deposition of silver fluorides.

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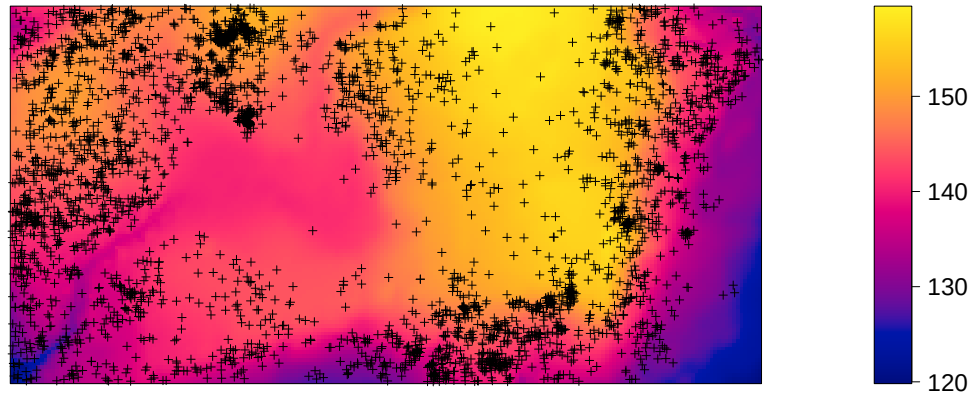


Figure 1: Tropical rainforest data. Locations of *Beilschmiedia pendula* trees (+) and terrain elevation (colorscale) in a 1000×500 meter survey plot in Barro Colorado Island (near Panama). Elevation is measured in meters above sea level (the colorbar is shown in the right part of the image). Part of a larger dataset containing the positions of hundreds of thousands of trees belonging to thousands of species. Data is from [1–3].

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Chapter 1

Introduction

1.1 Motivation and outline of the thesis

The discovery of high-temperature superconductivity (HTS) in copper oxide (cuprate) materials by Bednorz and Müller in 1986 [4] became the "revolution" in condensed matter physics. Before that, the material with the highest critical temperature was Nb_3Ge , which has been known since 1973 with the record at 23 K, and there was not so much improvement over NbN discovered in 1941 with $T_c=15\text{K}$ [5]. So, the widespread pessimism about the discovery of HTS, circulating among scientists at that time, was clearly understood. Moreover, according to the theory of conventional superconductivity (Bardeen-Cooper-Schrieffer (BCS), 1957 [6]), cuprates were considered the least promising candidates for a scientific breakthrough. Indeed, after a small alteration of their chemical composition, cuprates become highly insulating antiferromagnets, which is not compatible with ideas of conventional superconductivity.

Magnetism in cuprates springs from a strong repulsion between electrons, whereas BCS theory relies on the mechanism of "Cooper pairs", in which electrons bind due to interaction with lattice vibrations (phonons). For conventional superconductors, it was predicted that the highest achievable $T_c = 30\text{K}$ [7]. These values are much less than the maximum T_c for cuprate compounds (with the current record of more than 130K). Ironically, even the predicted bound for maximum T_c for conventional superconductivity was disproved in 2001 with the experimental discovery of superconductivity in the simple metal MgB_2 with $T_c = 39\text{K}$, showing that the conventional theory still has some drawbacks [8].

In recent years, hydrogen-rich materials have emerged as a new class of high- T_c superconductors, exhibiting record-breaking critical temperatures under extreme pressure. These materials follow the conventional phonon-mediated BCS mechanism, with superconductivity driven by strong electron-phonon interactions. The breakthrough discovery of H_3S in 2015 marked the first instance of superconductivity above 200 K (203 K at ~ 150 GPa), confirming that hydrogen-based systems can sustain superconductivity at unprecedented temperatures [9]. This was followed by the discovery of LaH_{10} (lanthanum decahydride), which pushed T_c to 250–260 K (near 0°C) at ~ 170 –200 GPa, making it the highest- T_c superconductor confirmed to date [10]. The key to their high T_c lies in their clathrate-like structures, which stabilize dense hydrogen sublattices that promote high-frequency phonon modes and strong electron-phonon coupling. However, a major challenge remains—the extreme pressures required to stabilize these phases make them impractical for widespread applica-

tions. Therefore, the search for new superconducting materials that can surpass cuprates continues.

Since the discovery of graphene by Novoselov and Geim in 2004 two-dimensional (2D) materials [11] have attracted a lot of attention due to significant promise for future applications (particularly in electronics and quantum computing). Though, despite all the expectations, the technological revolution hasn't happened yet, these materials provide unique opportunities to study fundamental physical principles and reveal properties, sometimes very different from their bulk counterparts. Superconductivity was also discovered among 2D materials. Notable examples include monolayer FeSe on SrTiO₃, which exhibits dramatically enhanced superconducting transition temperatures [12], and twisted bilayer graphene, where superconductivity arises in a moiré superlattice structure [13]. These systems provide valuable insight into unconventional pairing mechanisms and the interplay between electronic interactions, topology, and superconductivity.

Coming back to cuprates, one can try to mimic their physics in different materials. One successful route has been the replacement of Cu by Ni. Normally Ni has a valence +2 like in NiO. This leads to a d^8 electronic configuration and a total ionic spin $S = 1$. In contrast, cuprates have $S = 1/2$, which implies larger quantum fluctuations. However, it is possible to stabilize the d^9 configuration of Ni (valence +1). This has led to superconductivity in nickelates similar to cuprates [14–16].

Another possibility is the replacement of Cu by Ag, as they both belong to the coinage metals group in the Mendeleev table. As will be explained in more detail below, this requires the replacement of oxygen by fluorine to compensate for the stronger electronegativity of silver [17].

Silver fluorides have already been extensively studied, which has exposed many similarities with cuprates. The magnetic ground state of AgF₂ has been determined long ago [18]. It is a canted antiferromagnet with a weak ferromagnetic component larger than the analogous phenomena in parent cuprates. This can be understood as due to the larger buckling of planes of AgF₂ and larger spin-orbit coupling leading to a stronger Dzyaloshinskii–Moriya interaction. The Néel temperature of AgF₂ (163 K) is half that of La₂CuO₄ (325 K), which hints at a moderately large antiferromagnetic interaction. Indeed, the antiferromagnetic interaction has been measured with two-magnon Raman scattering and inelastic neutron scattering [17], yielding a value $J = 70$ meV compared to $J = 100 \sim 130$ meV in the Cu-based siblings.

In cuprates, empirical as well as theoretical arguments have shown that the maximum superconducting T_c achievable with doping scales with the antiferromagnetic interaction of the parent insulating compound [19–21]. It has been proposed [21] that the antiferromagnetic interaction of AgF₂ could be enhanced by growing a flat layer on appropriate substrates. This, in addition, has the advantage of reducing polaronic tendencies, which could hamper metallicity [22]. This strain engineering approach predicts a maximum superconducting T_c of nearly 200 K (Fig. 1.1). However, it relies on a close analogy between AgF₂ and parent cuprates, which calls for an in-depth comparison, which will be part of the aim of this thesis.

This thesis is also devoted to the development of methods towards the synthesis of 2D silver fluorides, ideally doped AgF₂. It is part of a broader effort to experimentally investigate and compare the physical properties of fluorides and cuprates. Along the way, we uncovered several intriguing physical phenomena, useful for synthesis but not directly related to superconductivity and highly interesting from an experimental perspective.

The work begins with a brief overview of the current state of fluorides and cuprates, providing a modern perspective in the field (Chapter 2). We emphasize similarities between fluorides and

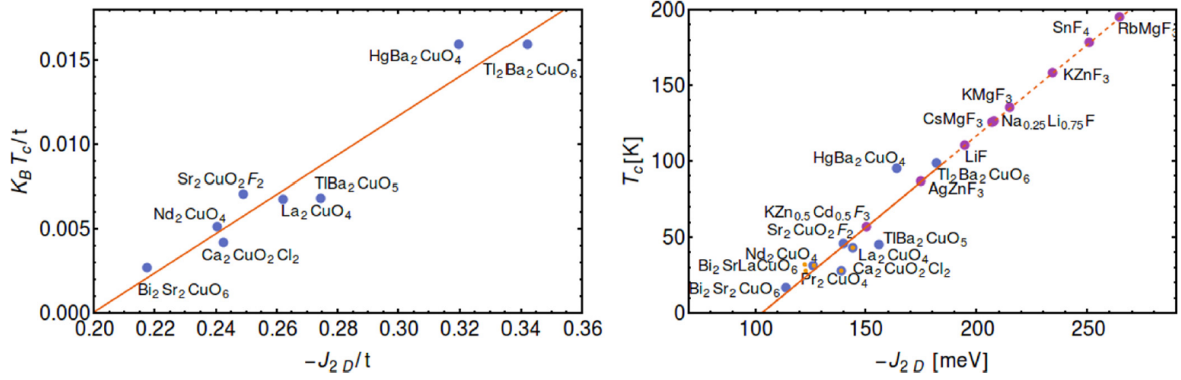


Figure 1.1: Left panel: The maximum T_c value of each cuprate family (in units of t) as a function of J_{2D} in the same units. The line is the linear fit. Right panel: The maximum experimental T_c value of each cuprate family in Kelvin vs J_{2D} in meV for various monolayer bulk cuprates and a single AgF_2 layer labeled by the substrate. Blue dots correspond to the J_{2D} computed in Ref. [23] while small orange dots are experimental J_{2D} from two-magnon data [24–27]. Notice that for La_2CuO_4 , Nd_2CuO_4 , and $\text{Ca}_2\text{CuO}_2\text{Cl}_2$ both Raman and the quantum chemistry determination of J_{2D} are available. The almost perfect overlap of the points serves as a test of the accuracy of the quantum chemistry computations. The line is the linear regression over the cuprate data with slope 1.2 K meV^{-1} . The purple dots are the expected values of the maximum T_c of the AgF_2 monolayers in the different substrates. The image is from [21].

cuprates from both theoretical and experimental points of view, based on available up-to-date data.

Chapter 3 is dedicated to the design and construction of an Ultra High Vacuum (UHV) chamber for fluorination of surfaces with the aim of synthesizing two-dimensional silver fluorides. Despite its apparent simplicity, this method shows great promise, as it allows for controlled studies of F-adatom interactions with Ag surfaces. We developed an innovative fluorination methodology in which reactions occur exclusively with monoatomic fluorine (as opposed to molecular fluorine)—opening new possibilities for surface chemistry and materials research. One common method to grow two-dimensional cuprates is Pulsed Laser Deposition (PLD). Unfortunately, silver fluorides are very reactive, and the conventional chambers can not be used. Aiming at expanding the synthesis possibilities, we collaborated with a private company in the design of an innovative PLD chamber for silver fluorides.

Chapter 4 presents Scanning Tunneling Microscopy (STM) investigations of individual fluorine atoms adsorbed on crystalline silver surfaces. We also provide a thermodynamic analysis of fluorination at higher surface coverages, along with density functional theory (DFT) simulations of the apparent topographies (AT) of adsorbed F atoms.

In Chapter 5, we demonstrate that it is possible to grow fluorinated overlayers on Ag surfaces. We observed an amorphous overlayer structure and propose a simple mean-field model based on a two-dimensional Van der Waals gas to describe the phase separation phenomena we encountered in the experiment.

Finally, in Chapter 6, we compare three-dimensional pellet samples of AgF_2 and AgF_2BF_4 with a well-known cuprate reference, La_2CuO_4 , using advanced spectroscopy techniques—specifically X-ray Absorption Spectroscopy (XAS) and Resonant Inelastic X-ray Scattering (RIXS). This includes the results of the first RIXS experiment conducted at the Ag L_3 edge, complementing earlier studies performed at the ligand edges. With this new data, we provide a comprehensive comparison of the electronic structures of AgF_2 and La_2CuO_4 .

The concluding chapter summarizes the results presented in this thesis and outlines potential future directions for both experimental and theoretical investigations in the field of high T_c superconductivity and exotic quantum behavior in silver fluorides.

1.2 Personal contribution of the author

The research presented in this thesis is the result of collaborative efforts carried out within several research groups and in close cooperation with external partners. In what follows, I outline my specific personal contributions to the different parts of the work, structured according to the corresponding chapters of the manuscript. My role encompassed both experimental and theoretical aspects, as well as the design and realization of custom-built apparatuses, data acquisition and analysis, and contributions to publications arising from this work.

Chapter2: Quantum materials and state-of-the-art of silver fluorides

This chapter is based on a brief review conducted by the author. I collected, organized, and critically analyzed the state-of-the-art research on quantum materials, with particular emphasis on silver fluorides and their analogies with cuprates. The review serves as motivation and the framework for the experimental investigations presented in the subsequent chapters.

Chapter 3: Custom-built ultra high vacuum chambers for advanced synthesis of fluorides

i) Fluorination apparatus

I actively participated in the design and mechanical construction of the fluorination apparatus at Roma Tre University (laboratory of Prof. Monica De Seta). I participated in the experiments that led to the development of a novel fluorination protocol and maintained a detailed logbook of all experimental activities performed with this equipment. I am also one of the inventors named in the international patent application for the novel fluorination method and apparatus.

ii) PLD apparatus

I gained extensive practical experience with the Pulsed Laser Deposition (PLD) technique in the PLD group at Tor Vergata University, under the supervision of Prof. Daniele Di Castro. This work focused on learning the fundamentals of thin-film growth as well as developing experimental skills in characterization techniques such as Reflection High Energy Electron Diffraction (RHEED) and X-ray Diffraction (XRD).

In addition, I carried out a six-month internship at Ionvac s.r.l., an engineering company collaborating on my PhD project. My activities included the development of a detailed CAD design for an innovative PLD setup, based on modifications to an existing chamber, and participation in the mechanical construction of the apparatus.

Chapters 4 and 5: Low Temperature Scanning Tunneling Microscopy of fluorination

I contributed to the installation of the fluorination apparatus in the Low-Temperature Scanning Tunneling Microscopy (LT-STM) laboratory at Tor Vergata University (Prof. Luca Camilli) and performed preliminary experiments using XeF_2 as a fluorine source.

i) The initial stages of silver fluorination: a scanning tunneling microscopy investigation

I participated in the synthesis and LT-STM measurements (“short fluorination”). The subsequent data analysis and discussions with Adrian Gomez Pueyo on the theoretical interpretation of the results led to Ref. [28]. I collaborated with Jazmin Aragon Sanchez and Prof. Luca Camilli’s group on the analysis of the experimental manuscript published in [29]. I contributed to the revision of both manuscripts.

ii) Fluorine overlayers studied by scanning tunneling microscopy

I contributed to the synthesis and LT-STM measurements (“long fluorination”), carried out data analyses, prepared STM images, and studied correlation phenomena between F-adatoms leading to the identification of a stabilized amorphous fluorine phase on Ag. I effectively modeled the phase separation in the system using a two-dimensional van der Waals gas framework. The article is currently in preparation.

Chapter 6: Resonant Inelastic X-ray Scattering for silver fluorides: comparison with cuprates

I took part in the experiment at ESRF (Grenoble, France) under the supervision of Prof. Giacomo Ghiringhelli and Prof. Marco Moretti Sala. My responsibilities included mounting samples, data acquisition, and data analysis. I developed algorithms to process the detector signals, which were initially not optimized for RIXS measurements, thereby enabling this exploratory experiment. I also carried out the comparison of the measured spectra with reference cuprate data and with theoretical computations carried on by Adrian Gomez Pueyo. I wrote the original draft of the article, which is now in preparation.

1.3 Research Output

Publications

- **I. Degtev**, D. Jezierski, A. Gómez Pueyo, L. Di Gaspare, M. De Seta, P. Barone, G. Ghiringhelli, P. Glatzel, W. Grochala, M. Moretti Sala, and J. Lorenzana,
Silver fluorides: electronic clones of cuprates revealed by resonant inelastic x-ray scattering, [in preparation]
- J. Aragón Sánchez, A. Caporale, **I. Degtev**, L. Di Gaspare, L. Persichetti, M. Sansotera, A. Gómez Pueyo, M. De Seta, J. Lorenzana, and L. Camilli,
The initial stages of silver fluorination: a scanning tunneling microscopy investigation,
J. Phys.: Condens. Matter **37**, 185002 (2025)
- A. Gómez Pueyo, J. Aragón Sánchez, **I. Degtev**, M. E. Temperini, D. Jezierski, C. Hogan, A. Caporale, L. Di Gaspare, L. Persichetti, M. De Seta, W. Grochala, P. Barone, L. Camilli, and J. Lorenzana,
How orbitals and oxidation states determine apparent topographies in scanning tunneling microscopy: The case of fluorine on silver surfaces,
Phys. Rev. B **110**, 235407 (2024)

Patents

- J. Lorenzana, L. Di Gaspare, M. De Seta, L. Persichetti, L. Camilli, **I. Degtev**,
Method for Producing Monatomic Fluorine for the Fluorination of Target Materials and Apparatus Thereof, Italian Patent Application #102024000015871, extended as **International Patent** Application PCT/EP2025/069560

Industrial collaboration

- Six-month **internship** in an engineering company, Ionvac s.r.l. (Pomezia, Italy) (2023)
Developed CAD design of an innovative Pulsed Laser Deposition (PLD) system for silver fluoride synthesis and contributed to its mechanical construction

1.4 Acknowledgements

I am very grateful to my advisor, José Lorenzana, for his support at all the stages of my PhD work and for giving me the chance to gain this experience in my life.

I've participated in a very collaborative project, and therefore, I also want to thank all the groups involved in it. Particularly, Monica De Seta and Luciana Di Gaspere from Roma 3 University for the new experience in UHV and warm welcome; Luca Camilli, Luca Persichetti, and Daniele Di Castro from Tor Vergata University for the chance to work in their labs. Giacomo Ghiringhelli and Marco Moretti Sala for the short, but very interesting trip to ESRF.

I would like to thank Gianfranco Sabbatella and Nello Vittulano from IonVac s.r.l. where I made my engineering internship, for the help with CAD and interesting experience in a real company that projects and produces scientific equipment.

Moreover, I am grateful to the evaluators of this thesis, Alessandro Ruocco and Marina Putti. Your suggestions and small criticisms made this work better.

I am very grateful to all the students of the PhD program in physics at La Sapienza, and in particular the Condensed Matter Theory group with whom I had the privilege to lunch together and follow joint seminars. With my background, it was a very interesting and useful activity. I am grateful to each of them and also to all professors of the CM theory group. Particularly, to Sergio Caprara, who allowed me to do this PhD together with José, and was part of the committee to get the scholarship when I arrived in Rome.

Additionally, I am very grateful to Andrey Varlamov, as I spent a lot of time in his office at Tor Vergata University and used his personal library (it covered all my needs!).

Special thanks go to Moscow, to the Institute of Crystallography (RAS), where I studied before. Particularly to my former advisor, Tatiana Bukreeva, who supported me after many years, and my colleague Bogdan Parakhonskiy for his useful advice and for sharing his broad experience in research. I had the privilege to be mentored by L.A. Feigin, who had already been an emeritus professor in the group by the time I started my Master thesis, but I remember his attitude to science in general, and it helps me a lot.

I have recently realized that I was very lucky with my school teacher of physics N.F. And I am very grateful to her. It was a bit of a shame to meet her last time, but now I can meet and show this thesis to prove that I have also done something, and all her efforts to spark interest in science have not been lost.

And finally, I am very grateful to my parents who put up with me and find so much optimism every day. Thanks a lot for your support!

Ilya, Rome, 02/09/2025

Chapter 2

Quantum materials and state-of-the-art of silver fluorides

Quantum materials or strongly correlated electron systems are defined by having macroscopic properties like magnetism and superconductivity, which crucially depend on quantum mechanical effects. These materials often exhibit emergent phenomena and functionalities not found in conventional materials, stemming from the strong interactions between their constituent electrons. A prototypical family of quantum materials is superconducting cuprates and their parent compounds. In this chapter, we introduce the main characteristics of quantum materials, the main characteristics of cuprates, and the state-of-the-art of silver fluorides as quantum materials.

2.1 Mott Hubbard and Charge Transfer insulators

To understand insulating behavior in *strongly correlated materials*, one must go beyond the non-interacting band picture. A minimal model that describes such interactions is the *Hubbard model* [31], which extends the tight-binding description by including an on-site Coulomb repulsion U_{dd} between two electrons occupying the same orbital with opposite spins. The corresponding Hamiltonian in

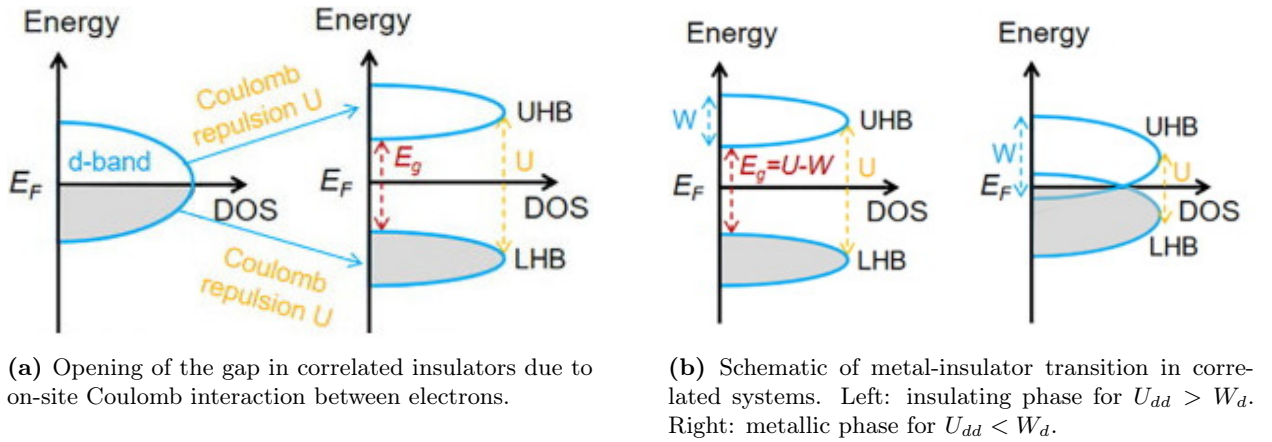


Figure 2.1: Illustrations of correlation effects in transition metal compounds. Both images are reproduced from [30].

the case of 1D tight-binding chain reads:

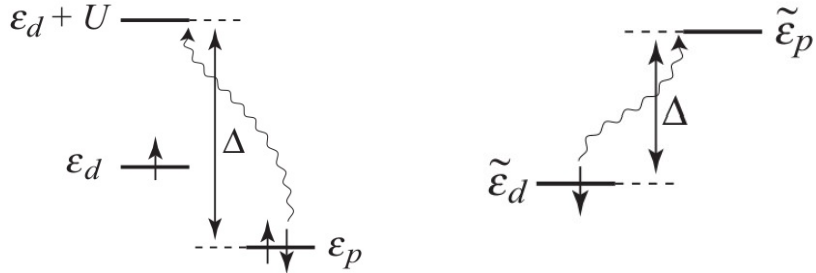
$$\hat{H}_{dd} = \varepsilon_d \sum_{i,\sigma} \hat{d}_{i,\sigma}^\dagger \hat{d}_{i,\sigma} - t_{dd} \sum_{i,\sigma} \left(\hat{d}_{i,\sigma}^\dagger \hat{d}_{i+1,\sigma} + \text{h.c.} \right) + U_{dd} \sum_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow}. \quad (2.1)$$

Here, $\hat{d}_{i,\sigma}^\dagger$ and $\hat{d}_{i,\sigma}$ are the creation and annihilation operators for an electron with spin σ at site i in a d orbital, and $\hat{n}_{i,\sigma} = \hat{d}_{i,\sigma}^\dagger \hat{d}_{i,\sigma}$ is the corresponding number operator. The parameter ε_d sets the on-site energy of the d orbital, t_{dd} is the hopping amplitude between neighboring sites, and U_{dd} describes the on-site Coulomb repulsion between two electrons occupying the same site.

At half-filling (one electron per site), and in the limit of strong interaction $U_{dd} \gg t_{dd}$, the energy cost of placing two electrons on the same site suppresses their mobility. In this regime, an excitation that moves an electron to an already occupied site (creating a doublon) while leaving a hole behind costs an energy:

$$d_i^1 d_j^1 \rightarrow d_i^0 d_j^2 \quad i \neq j \quad \Delta E = E_A - E_I = U_{dd}. \quad (2.2)$$

Here, d_i^n denotes a d orbital with n electrons on site i , while E_I and E_A are the ionization and electron affinity energies, respectively. This process leads to the opening of a gap between the energies needed to remove or add an electron. As a result, two separate bands appear in the spectrum — the lower Hubbard band (LHB) and the upper Hubbard band (UHB) — each accommodating up to N electrons in a chain of N atoms, unlike the non-interacting case, which allowed $2N$ electrons (Fig. 2.1 (a)).



(a) Typical energy level scheme for the simplest case with one d electron and a filled p shell; Δ is the CT energy defined in Eq.(2.5) and U is the Coulomb interaction between electrons of the d orbitals. The symbols $\uparrow$ and $\downarrow$ refer to the spin of the electrons. The wavy line indicates the lowest electronic excitations allowed, whose energy is written in Eq.(2.7)

(b) Energy level scheme concerning the left panel in the hole formalism. This panel is a one-hole energy diagram where $\tilde{\varepsilon}_d$ and $\tilde{\varepsilon}_p$ represent TM and ligand hole energies, and $\uparrow$ and $\downarrow$ refer to the spin of the holes. The wavy line indicates the lowest hole excitations allowed, whose energy is written in Eq.(2.8).

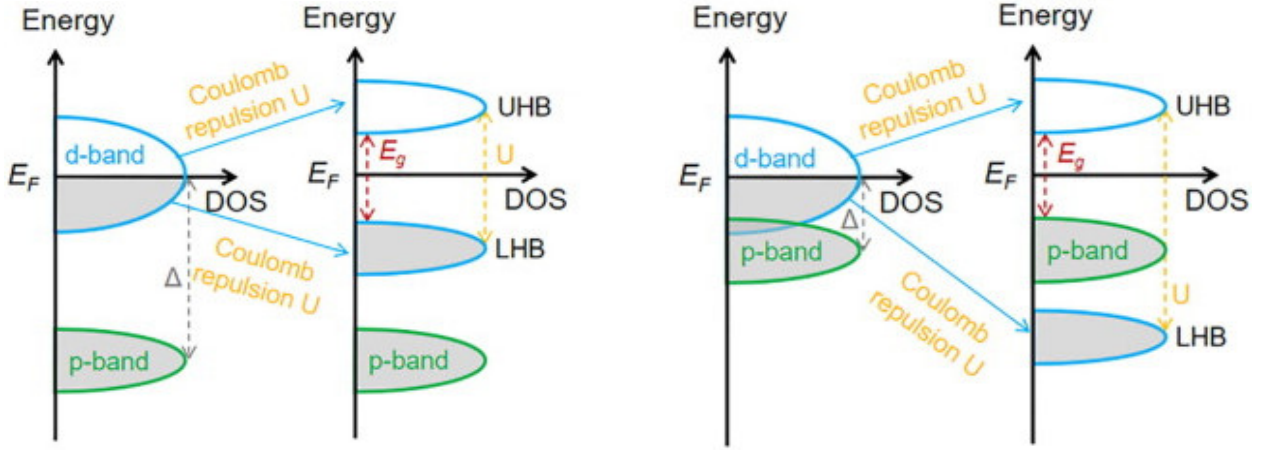
Figure 2.2: Illustration of the definition of the charge transfer energy given in electronic (panel a) and hole representation (panel b). Image is from [32]

When the atoms are brought closer together, the hopping t_{dd} increases (it is given by the hopping integral, which increases at small distances due to the overlap of orbitals), making the doublon-hole pair mobile. The competition between Coulomb repulsion and kinetic energy then determines the size of the gap:

$$E_{\text{gap}} \approx U_{dd} - W_d = U_{dd} - 2z t_{dd}, \quad (2.3)$$

where $W_d = 2zt_{dd}$ is the bandwidth and z is the coordination number. The system remains insulating if $U_{dd} > W_d$, but becomes metallic when the kinetic energy dominates, i.e., $U_{dd} < W_d$. The transition from insulator to metal is known as the *Mott transition* and occurs at a critical interaction strength $U_c \approx 2zt_{dd}$ (Fig. 2.1 (b)).

This framework explains why materials containing transition-metal (TM) atoms — which often have partially filled and spatially localized d orbitals — can exhibit strong correlation effects. When such TM atoms form compounds with ligands (e.g., O or F), the full physics also involves hybridization with ligand p states, requiring more elaborate models that include both electron hopping and charge-transfer processes.



(a) In MH insulators, the ligand band is far in energy from the d levels, and the gap is of order U_{dd} .

(b) In CT insulators, the ligand band is close to the d levels, and the gap is of order Δ_{pd} .

Figure 2.3: Two types of correlated insulators: Mott-Hubbard (left) and Charge Transfer (right). Figures adapted from [30].

Assuming the Hubbard model in Eq. (2.1) describes a chain composed entirely of transition-metal (TM) atoms, we now generalize it to a binary system by alternating TM atoms with ligand atoms along the chain. To keep the model minimal, we include only one relevant orbital per site: a $d_{x^2-y^2}$ orbital for each TM atom and a $p_{||}$ orbital for each ligand atom. The resulting Hamiltonian is:

$$\hat{H}_{pd} = \varepsilon_d \sum_{i,\sigma} \hat{d}_{i,\sigma}^\dagger \hat{d}_{i,\sigma} + \varepsilon_p \sum_{i,\sigma} \hat{p}_{i,\sigma}^\dagger \hat{p}_{i,\sigma} - t_{pd} \sum_{i,\sigma} \left(\hat{d}_{i,\sigma}^\dagger \hat{p}_{i+1,\sigma} + \text{h.c.} \right) + U_{dd} \sum_i \hat{n}_{i,\uparrow}^{(d)} \hat{n}_{i,\downarrow}^{(d)} \quad (2.4)$$

The operator $\hat{d}_{i,\sigma}^\dagger$ ($\hat{d}_{i,\sigma}$) creates (annihilates) an electron with spin σ in the transition-metal (TM) orbital at site i , while $\hat{p}_{i,\sigma}^\dagger$ ($\hat{p}_{i,\sigma}$) does the same in the ligand $p_{||}$ orbital. The number operators are defined as $\hat{n}_{i,\sigma}^{(d)} = \hat{d}_{i,\sigma}^\dagger \hat{d}_{i,\sigma}$ and $\hat{n}_{i,\sigma}^{(p)} = \hat{p}_{i,\sigma}^\dagger \hat{p}_{i,\sigma}$, and they count the number of electrons with spin σ on the respective orbitals. The hopping terms, such as $\hat{d}_{i,\sigma}^\dagger \hat{p}_{j,\sigma}$, describe a movement of an electron from a ligand site to a TM site (or vice versa).

We use the same notation d_i^n to denote a TM site hosting n electrons in its d orbital (p_j^n defines the same for a ligand site). Here, t_{pd} denotes the hopping amplitude between TM and ligand orbitals, and ε_d , ε_p are their respective on-site energies. In this model, local excitations of the type $d^n \rightarrow d^{n+1}$ on TM atoms still cost the Coulomb energy U_{dd} , as in Eq. (2.2). However, the presence

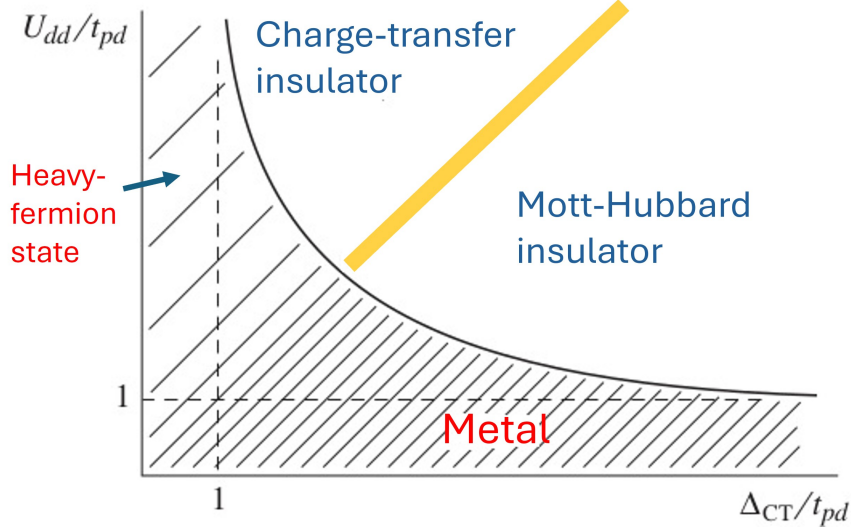


Figure 2.4: ZSA phase diagram. The unhatched region comprises two distinct insulating regimes: the MH and CT phases. The bottom right part of the hatched area refers to non-correlated metal (shown as Metal), while the upper left part refers to the heavy-fermion phase. Δ_{CT} is called Δ_{pd} in the text. This image is adapted from [33].

of ligand atoms introduces an additional type of excitation: an electron can transfer from a ligand p orbital to a neighboring TM d orbital, leading to a so-called *charge-transfer* (CT) excitation with corresponding energy Δ_{pd} :

$$d_i^n p_j^6 \rightarrow d_i^{n+1} p_j^5 \quad i \neq j \quad \Delta E = \Delta_{pd} \quad (2.5)$$

This is often written using the ligand-hole notation as:

$$d_i^n \rightarrow d_i^{n+1} \underline{L}_j \quad \Delta E = \Delta_{pd} \quad (2.6)$$

where $\underline{L}$ denotes a hole in the ligand shell, this shorthand is widely used in the literature. The charge-transfer energy associated with this process is:

$$\Delta_{pd} = \varepsilon_d - \varepsilon_p + U_{dd} \quad (2.7)$$

Alternatively, the model can be reformulated in terms of d and p *holes* instead of electrons. In this picture, the hopping process corresponds to a d hole moving from a TM site to a ligand site that initially has no holes in its shell. The Hamiltonian retains the same as Eq. (2.4), but the operators $\hat{d}^\dagger$, $\hat{p}^\dagger$, $\hat{d}$, and $\hat{p}$ are now interpreted as creation and annihilation operators for d and p holes, rather than electrons. The corresponding single-particle energies must also be redefined to reflect hole energies, as illustrated in Fig. 2.2. In this representation, the charge-transfer energy becomes:

$$\Delta_{pd} = \tilde{\varepsilon}_p - \tilde{\varepsilon}_d \quad (2.8)$$

where $\tilde{\varepsilon}_d$ and $\tilde{\varepsilon}_p$ denote the on-site energies of TM and ligand holes, respectively.

Depending on the nature of the lowest charge-carrying excitations, correlated insulators are commonly divided into two classes: **Mott-Hubbard (MH)** and **Charge Transfer (CT)** insulators. The key parameters that determine this are the on-site Coulomb repulsion U_{dd} and the

charge-transfer energy Δ_{pd}

If the charge transfer energy $\Delta_{pd} > U_{dd}$, then the lowest energy excitation corresponds to creating a doublon-hole pair described by Eq. (2.2). The system is in the **Mott-Hubbard** regime (Fig. 2.3 (a)), where the gap is mainly determined by the Coulomb repulsion U_{dd} :

$$\text{MH insulator: } \Delta_{pd} > U_{dd} \Rightarrow E_{\text{gap}} \approx U_{dd} \quad (2.9)$$

On the other hand, when $\Delta_{pd} < U_{dd}$, the lowest energy excitation involves moving an electron from a ligand p orbital to the TM d orbital. Here, a hole is created in the ligand band, and an extra electron is added to the metal site (see Eq. (2.6)). This defines the **Charge Transfer** regime (Fig. 2.3 (b)), and the energy gap is set by Δ_{pd} :

$$\text{CT insulator: } \Delta_{pd} < U_{dd} \Rightarrow E_{\text{gap}} \approx \Delta_{pd} \quad (2.10)$$

These two regimes are summarized in the **Zaanen-Sawatzky-Allen (ZSA)** [34] phase diagram shown in Fig 2.4.

Let us look at the limiting cases:

- When $\Delta_{pd} \gg U_{dd}$ and $U_{dd} < W_d$: the ligand band is far from the metal d -bands, and the system behaves as a *non-correlated metal*.
- Increasing U_{dd} at fixed Δ_{pd} : the system undergoes a *Mott transition* into the *MH insulator* regime when $U_{dd} > W_d$.
- When $U_{dd} \gg \Delta_{pd}$: the system becomes a *CT insulator*. For $\Delta_{pd} \gg t_{pd}$, the system is a correlated CT insulator. Further decreasing Δ_{pd} widens the hybridized $p - d$ hole bands, leading to a metallic state with both strongly correlated d electrons and itinerant p electrons. In this regime, the itinerant quasiparticles acquire a strong renormalization due to the interaction with the localized moments, and the system is called a *heavy fermion*.

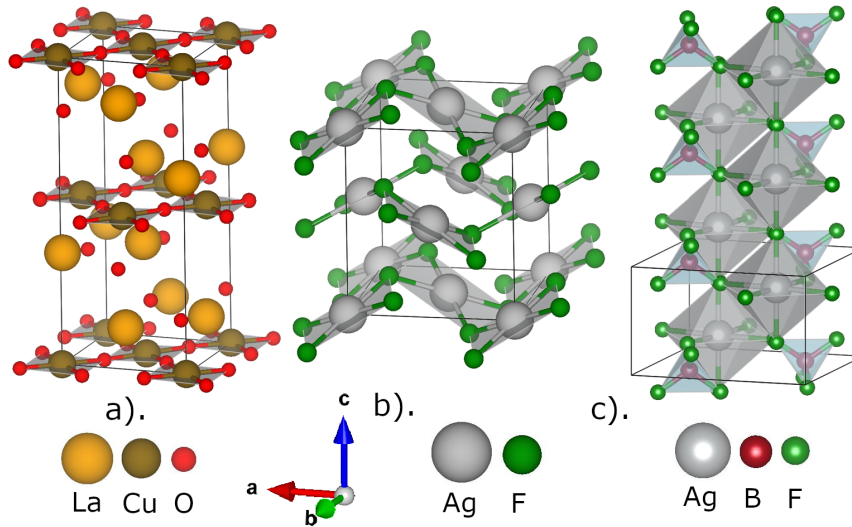


Figure 2.5: Crystallographic structures of La_2CuO_4 (a), AgF_2 (b) and AgFBF_4 (c).

2.2 High- T_c superconductivity in cuprates

As explained in the introduction, this thesis is part of a broader effort to mimic the physics of cuprates without copper. Here we discuss the main characteristics of cuprates.

Fig. 2.5 (a) shows the crystal structure of La_2CuO_4 , the parent compound of the cuprate high-temperature superconductors. A key structural feature is its pronounced two-dimensionality: the Cu and O atoms form extended CuO_2 planes, which are common to all known high- T_c cuprates. These planes are separated by La_2O_2 double layers that include apical oxygen atoms, resulting in a distorted octahedral coordination around each Cu atom. Notably, the Cu – O bond to the apical oxygen is significantly longer than the in-plane Cu – O bond, reinforcing the quasi-two-dimensional electronic character of the system.

In terms of valence, La_3^+ and O_2^- ions impose a Cu_2^+ oxidation state, leaving one hole in the Cu $3d$ shell per site. As a result, La_2CuO_4 behaves as an antiferromagnetic charge transfer insulator according to the classification of the previous section. The charge-transfer band gap is approximately 2 eV. Upon doping, for instance by substituting La_3^+ with a divalent cation such as Sr_2^+ , one obtains the doped compound $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

Fig. 2.6 presents a representative phase diagram for cuprate materials as a function of hole doping x , which corresponds to the number of added holes per CuO_2 unit. At $x \approx 0$, the material remains an antiferromagnetic insulator with a strong superexchange interaction between adjacent Cu^{2+} spins ($J \approx 0.1$ eV). As x increases, long-range magnetic order is rapidly suppressed, giving way to a spin-glass-like regime. At higher doping levels ($x \approx 0.05 - 0.25$), a superconducting phase emerges, reaching a maximum critical temperature around $x \approx 0.15 - 0.2$.

Perhaps even more intriguing than the high superconducting transition temperature are the anomalous properties of the normal (non-superconducting) state. Undoped cuprates are experimentally observed to be insulating, even though band theory predicts metallicity due to the half-filled Cu $3d$ band. This is explained by strong electron–electron correlations. According to the ZSA classification scheme, cuprates are charge-transfer correlated insulators. The metallic doped material is not a conventional metal due to the correlated insulating nature of the parent compound.

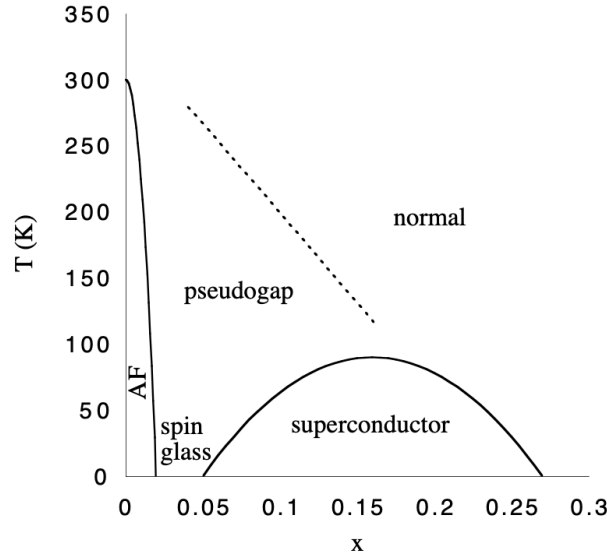


Figure 2.6: Phase diagram of the cuprates (x -represents hole doping). AF stands for antiferromagnetic insulator. The dotted line is a crossover line between the normal metal phase and the pseudogap phase. The image is from [35]

2.3 The Silver fluoride family

Although Cu and Ag might be thought to share the same electronic properties as they belong to the same group in the Mendeleev table, essential differences are evident. Because silver is more electronegative than copper, AgO has a negative charge transfer energy that ends up in a non-magnetic charge disproportionated state ($1+/3+$), instead of the expected $4d^9$ Ag^{2+} . This is in contrast to CuO, which is an antiferromagnetic charge transfer insulator with the $3d^9$ ground state of Cu^{2+} . (Fig. 2.7 (a) and (b)). The lack of magnetism in AgO can be solved by replacing oxygen with fluorine. The stronger electronegativity of fluorine compensates for the electronegativity of Ag and leads to the $4d^9$ configuration in silver fluoride. This is schematized in the ionic picture of Fig. 2.7 where the silver $4d$ levels (gray) are more bound than the copper $3d$ (red). Despite that, the relative position of p and d levels in panels (a) and (c) remains the same.

Based on the above, silver fluoride (AgF_2) has been proposed as an analog of the parent insulating materials of cuprate high-temperature superconductors[17]. As shown in Fig. 2.7 (c), AgF_2 is expected to be a CT insulator and a very close analog of cuprates from this perspective.

Contrary to the charged CuO_2 plane of cuprates [Fig. 2.5(a)], AgF_2 is already neutral due to the inherent F^- character instead of O^{2-} . Thus, AgF_2 does not need a charge reservoir [Fig. 2.5(b)] and can be considered the “012” equivalent of the 214 stoichiometry in a cuprate like La_2CuO_4 . Indeed, AgF_2 consists of neutral planes stacked one on top of each other, which have the same topology as the CuO_2 planes of cuprates but with much larger buckling [c.f. Fig. 2.5 (a) and (b)].

2.3.1 Density functional theory

The above ionic picture of the similarity among silver fluorides and cupates has been substantiated through density functional theory computations (DFT).

Fig. 2.8 shows the density of states (DOS) of AgF_2 and La_2CuO_4 [17]. UHB and LHB (marked

by vertical red arrows) with predominantly $d_{x^2-y^2}$ character are clearly seen on both panels, with p -bands lying between them. This picture suggests that in the ZSA classification scheme, both compounds are correlated CT insulators.

The splitting between Hubbard bands (9.4 eV for AgF_2 and 10.7 eV for La_2CuO_4) suggests that the U_d parameter, which is responsible for Coulomb repulsion in $d_{x^2-y^2}$ orbitals, is similar for both compounds. The computed charge transfer gap for AgF_2 is even smaller than the one for cuprates.

The simplest model of the electronic structure consists of one $d_{x^2-y^2}$ orbital on the TM site with two p orbitals on the F-sites: one is $p_{\parallel}$, parallel to the TM-TM bond, and another one is p_z , perpendicular to the bond. Due to substantial buckling, p_z also mixes with $d_{x^2-y^2}$ and should be considered. This is in contrast with cuprates, where taking only one orbital is enough in first approximation.

The hopping integral $t_{pd} = 1.38$ eV for a hypothetically straight Ag-F-Ag bond was computed from unpolarized DFT. This value is almost the same as for cuprates [37], but the effective hybridization is smaller, which leads to a narrower UHB of AgF_2 in comparison with La_2CuO_4 as can be seen from Fig. 2.8.

Overall, we can conclude that AgF_2 and La_2CuO_4 have very similar DFT electronic structures. Another conclusion is that AgF_2 is a very covalent compound that has a good agreement with

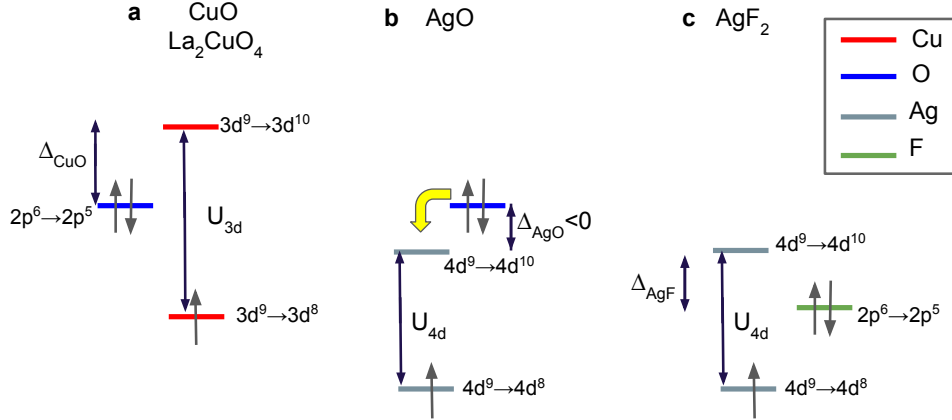


Figure 2.7: Schematic energy levels of cuprates and argentates in an ionic picture. All levels are assumed to be referenced to a common zero energy vacuum so that the $3d^9 \rightarrow 3d^{10}$ ($4d^9 \rightarrow 4d^{10}$) level is located at minus the second ionization energy of Cu (Ag). **a** Levels for CuO and La_2CuO_4 . Cu is in the d^9 configuration. Electron addition ($3d^9 \rightarrow 3d^{10}$) and removal ($3d^9 \rightarrow 3d^8$) energies from Cu correspond to the centroid of the upper and lower Hubbard bands, while removal from filled oxygen corresponds to the valence band. The charge-transfer energy Δ_{CuO} and the Hubbard U_{3d} parameter are indicated. **b** In the case of AgO , silver is formally d^9 . However, since the $4d^9 \rightarrow 4d^{10}$ levels are deeper than the $3d$ counterpart, the charge-transfer energy is practically zero or even negative, and the pictured filling is unstable towards more complex mixed valence behavior (yellow arrow)[36]. **c** Fluorine is more electronegative than O, which translates into deeper $2p^6$ removal states and restores a positive charge-transfer energy in AgF_2 . Image is from [17]

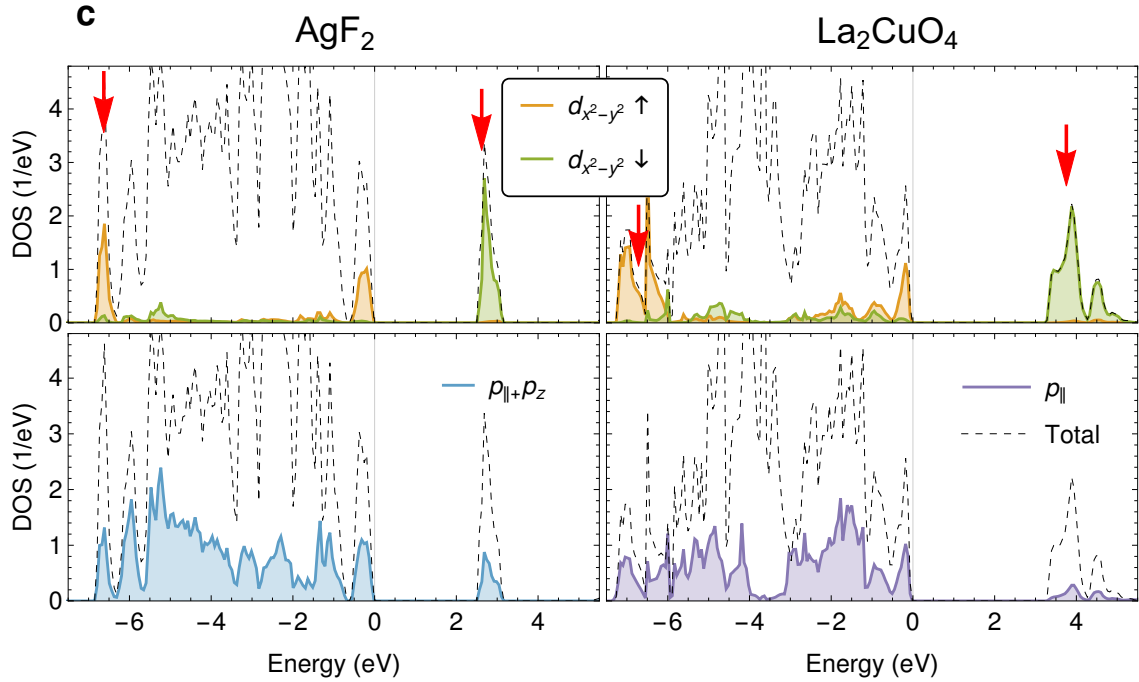


Figure 2.8: Comparison of the orbital resolved (upper panels $d_{x^2-y^2}$, lower panels $p_{||}$ and p_z) and total (dashed lines) density of states of the two compounds computed within hybrid-DFT in the antiferromagnetic state. The red arrows indicate the Hubbard bands. The image is from [17]

experimental results of core- and valence-level spectroscopy [38, 39].

2.3.2 Spectroscopic results

Raman scattering

The parent cuprates are insulating antiferromagnets, with spin- $\frac{1}{2}$ moments localized on copper sites in the CuO_2 planes. Their low-energy magnetic properties are well described by the two-dimensional spin- $\frac{1}{2}$ Heisenberg Hamiltonian,

$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j,$$

where J is the nearest-neighbor superexchange constant and the summation runs over adjacent copper sites on the square lattice. The magnitude of J sets the fundamental energy scale of the spin dynamics, giving rise to the high Néel temperatures and strong antiferromagnetic correlations characteristic of these compounds.

Raman spectroscopy provides a powerful means of determining J through the observation of two-magnon (bimagnon) scattering. In this process, the incident photon creates a pair of magnons with opposite momentum, leading to a broad spectral feature whose position directly reflects the superexchange constant. The involvement of two magnons is crucial, as it allows the coupling with light near the zone center of the Brillouin zone with zone boundary magnons, which have high energy (and therefore prove the scale J). In addition, the two-magnons satisfy the condition $\Delta S = 0$ for the total spin along the quantization axis. Therefore, angular momentum is conserved, and circularly polarized light is not needed.

Theoretical analysis[41, 42] yields the bimagnon peak energy at $\omega_p \approx 3J$, allowing a quantitative

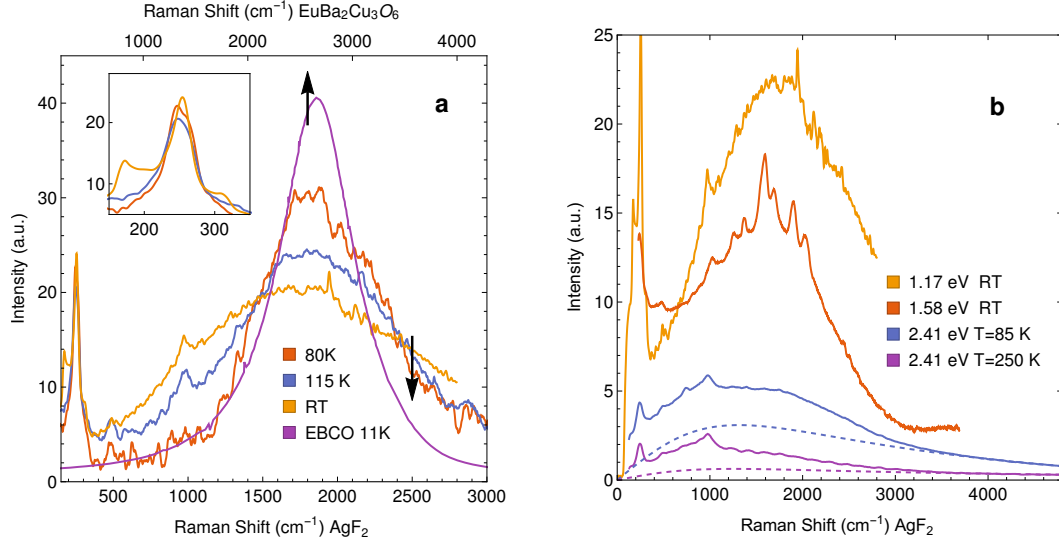


Figure 2.9: Two-magnon Raman spectra of AgF_2 . (panel a) Temperature dependence for excitation energy 1.17 eV. The low temperature two-magnon line shape for the parent cuprate compound $\text{EuBa}_2\text{Cu}_3\text{O}_6$ (EBCO) is shown following Ref. [40]. The upper scale corresponds to EBCO, while the lower scale corresponds to AgF_2 . Curves are labeled by the temperature in Kelvin. Comparing the energy scales in a it was obtained that $J_{AF} = 0.7J_{EBCO}$ which yields $J_{AF} = 70$ meV for AgF_2 . All the spectra are normalized with the phonon lines as shown in the inset. (panel b) Data for AgF_2 at various excitation energies. For the 2.41 eV laser line two temperatures are reported. Dashed lines are estimated non-magnetic backgrounds which are well defined at high energy but can not be uniquely defined at low energy. The image is from [17]

estimate of the exchange interaction strength J . These results establish Raman scattering as a benchmark technique for quantifying the superexchange interaction in cuprates, providing experimental confirmation of the Heisenberg description of their spin dynamics and precise estimates of J . As an example, with this method Ref. [40] established $J = 100$ meV for $\text{EuBa}_2\text{Cu}_3\text{O}_6$. The low temperature data of this work are shown in violet in Fig. 2.9(a).

Ref. [17] reported the two-magnon Raman spectra of AgF_2 . This appears as a broad band centered at 1750 cm^{-1} at room temperature, which hardens and narrows upon cooling (Fig. 2.9a). This feature closely resembles the two-magnon Raman signal observed in cuprates [40], confirming the two-magnon origin. Aligning the data in both compounds, they obtained that the magnetic interaction in AgF_2 (J_{AF}) is 70% of the one in the cuprate (J_{EBCO}), namely $J_{AF} = 70$ meV. This confirms the strong magnetic interactions. The Néel temperature of AgF_2 (163 K) is half that of La_2CuO_4 (325 K), which is in agreement with this conclusion (although a precise scaling is not expected, as also anisotropic terms in the Hamiltonian play a role in determining the Néel temperature).

The persistence of the two-magnon signal well above the Néel temperature further supports the presence of robust short-range antiferromagnetic correlations.

Fig. 2.9b also from Ref. [17] shows measurements of the two-magnon line using different excitation energies. The signal is most prominent at 1.17 and 1.58 eV, while for 2.41 eV it becomes more visible only at low temperatures. A weaker feature at 970 cm^{-1} is assigned to a two-phonon process. The excitation energy dependence suggests that the resonance profile of the two-magnon feature is shifted to lower energies compared to cuprates [43], consistent with the smaller charge-transfer gap predicted by DFT. As discussed below, spectroscopies predict a larger gap, but the difference may

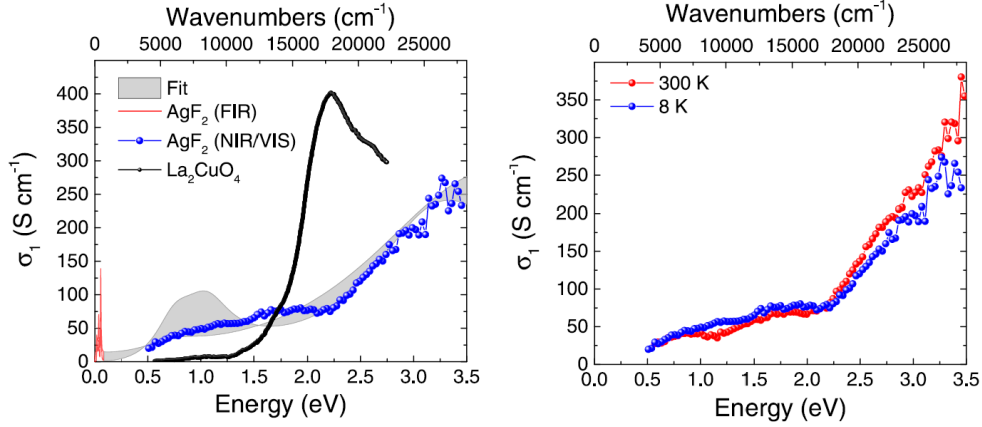


Figure 2.10: Real part of AgF_2 optical conductivity. The left panel shows experimental values of σ_1 measured at $T = 8$ K. The dots are obtained using both amplitude and phase information of the reflectivity extracted from ellipsometry data. The shaded grey region represents confidence boundaries obtained by fits using only amplitude or phase information. The AgF_2 data are compared with optical conductivity data reported in [44, 45] regarding undoped La_2CuO_4 (black line). AgF_2 data show an onset at about 1.75 eV associated with the charge transfer gap ($\Delta_{\text{peak}} \approx 3.4$ eV). Furthermore, they are compared with a charge transfer excitation peaking at $\Delta_{\text{peak}} \approx 2.2$ eV with an onset of ≈ 1.6 eV in the equivalent oxocuprates compound La_2CuO_4 . The right panel compares data recorded at 8 K and then 300 K, showing slight modifications of the different excitations in the charge transfer sector and the sub-gap sector. This image is from [46]

be due to larger excitonic effects in silver fluorides.

Optical conductivity

Although optical measurements are challenging due to the lack of AgF_2 single crystals, strongly compressed powder samples have been produced using explosives, which allowed the recording of optical spectra [46] (Fig. 2.10). The optical absorption shows an onset at 1.75 eV for charge-transfer excitations and a broad peak at 3.4 eV. These energies are somewhat higher than, for example, La_2CuO_4 , which shows an onset at about 1.6 eV and a peak at 2.2 eV. Hybrid density functional theory (DFT) calculations predicted a charge transfer parameter $\Delta = 2.7$ eV for AgF_2 [17]. High-energy spectroscopies combined with small cluster exact computations yield a somewhat higher value $\Delta = 3.5 \sim 4.1$ eV.

X-ray absorption (XAS)

Fig. 2.11 (panel a) shows the F K -edge X-ray absorption spectrum of AgF_2 from Ref. [46]. The sharp feature near 682 eV is attributed to excitations from F 1s into Ag 4d states, hybridized with F 2p orbitals, indicating a narrow upper Hubbard band [17]. Similar p - d hybrid features have been observed in F K -XAS of 3d metal fluorides [48], and a comparable structure is seen in the O K -XAS of La_2CuO_4 [47]. A broader feature peaking around 689 eV is assigned to transitions involving Ag 5s/5p states mixed with F 2p orbitals. These spectral assignments were supported by DFT results (Fig. 2.11 panel b)

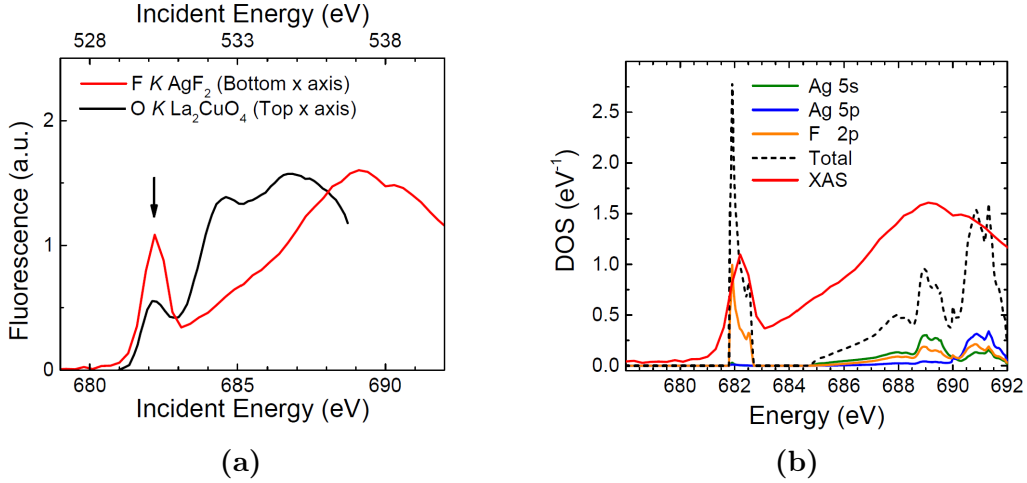


Figure 2.11: (panel a) Comparison of F *K*-XAS on AgF₂ and O *K*-XAS on La₂CuO₄ [47]. AgF₂ and La₂CuO₄ XAS energies correspond to the bottom and the top *x*-axes, respectively. (panel b): Orbital projected unoccupied DOS of AgF₂ from the unpolarized DFT computations. The Fermi level has been shifted to 681.8 eV to facilitate comparison with F *K*-XAS (red line). For the band at the Fermi level, it is nearly equal to the difference of the total and F 2p contribution. Image is from [46]

Resonant Inelastic X-ray Scattering

Resonant inelastic X-ray scattering (RIXS) is essentially a resonant Raman experiment performed at some X-ray absorption edge. Because the incoming photons are X-rays with very short wavelengths, an exploration of most of the Brillouin zone is possible, as opposed to optical Raman scattering, which is confined to the zone center. In addition, large energy loss values can be measured, which provides a complete exploration of the relevant electronic structure. As an additional advantage, because the intermediate state involves a core hole with strong spin-orbit coupling, magnetic excitations (spin-flip) are allowed. In the Chapter 6 we provide a detailed description of this technique.

In Ref. [46], a RIXS experiment was performed at F *K* edge (683 eV) of polycrystalline AgF₂ samples and compared with RIXS of O *K* edge of reference La₂CuO₄. Results are presented in Fig.2.12. Several characteristic features are clearly visible on the RIXS spectra (left panel), including elastic peak (0 eV), *dd*-excitations peaks (between 1 eV and 3 eV), and a broad and intense feature of charge transfer excitations (after 4 eV). Upon more careful review (right panel) after decomposition in the low-energy part of the spectrum, one can find phonons (0.041 eV) and their overtones, and a damped bimagnon peak (centered at 0.218 eV). Position of this peak coincides with the one observed in the Raman spectra in [17]. A peak around 2 eV decomposes after fitting into 3 excitations standing at 1.59, 1.86, and 2.33 eV (right inset in the right panel). The origin of these peaks was explained using DFT and cluster computation in [46]. Within DFT, the band corresponding to $d_{x^2-y^2}$ is antibonding, half-filled, and located away from the other *d* bands (Fig.2.13, left panel). Joint DOS represents transitions between the partially unoccupied $d_{x^2-y^2}$ orbital and occupied other ones with various symmetries (Fig.2.13, left panel). Summing the joint DOS for *dd* transitions resembles the experimental data. One can assign the lower shoulder to transitions of the $d_{x^2-y^2}$ hole to z^2 orbitals, the higher peak to transitions to mainly xz orbitals, and the intermediate band to a mixed character.

A cluster computation based on the results of Ref. [39] also allows for the identification of the

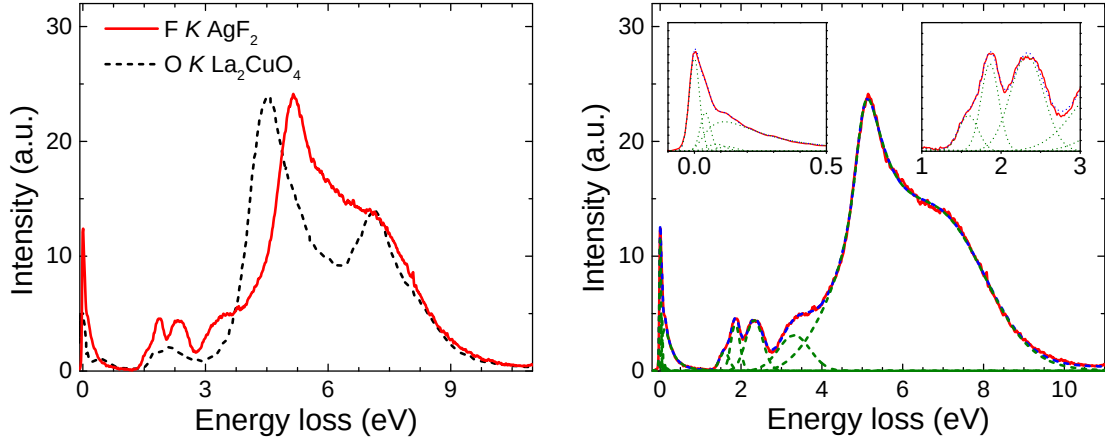


Figure 2.12: (Left panel) Comparison of F *K*-RIXS on AgF₂ and O *K*-RIXS on La₂CuO₄ [49]. (Right panel) F *K*-RIXS on AgF₂ fitted with multiple components. The left insets show the low-energy inelastic features, and the right inset shows the *dd* excitations with fitted profiles. Image is from [46]

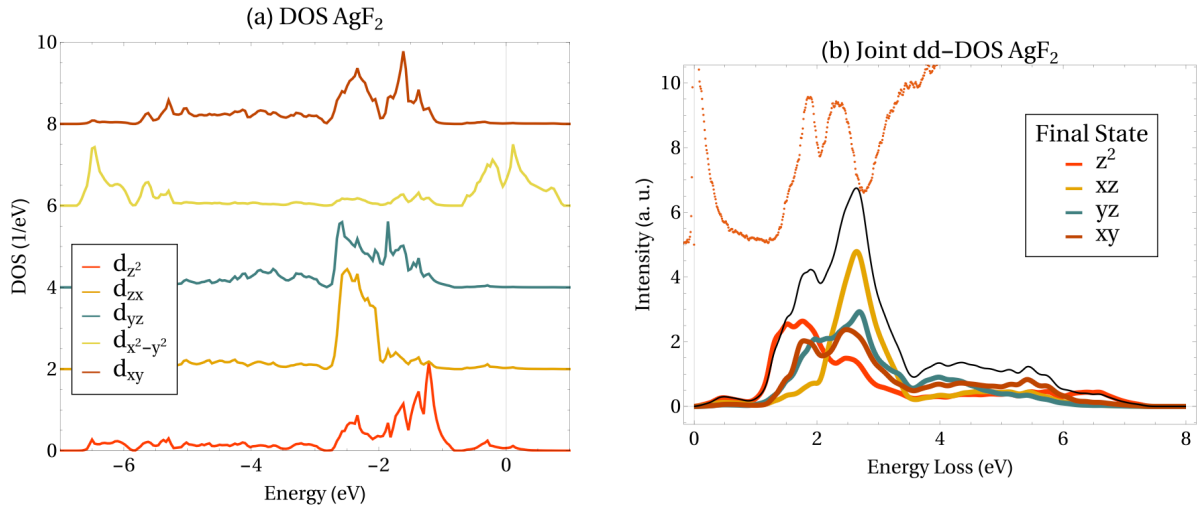


Figure 2.13: (a) DOS of AgF₂ projected on Ag *d* orbitals from the unpolarized DFT computations. (curves have been shifted by 2/eV for clarity). The Fermi level is at zero energy. (b) joint DOS between the unoccupied DOS of *d*_{x²-y² character and occupied DOS of different character representing *dd* transitions of a hole from the half-filled *d*_{x²-y² to a final state (labeled by the final state) character. The thin black line is the average of the different contributions. The dotted line is the experimental RIXS data. Image is from [46]}}

	La ₂ CuO ₄ (Theory)			La ₂ CuO ₄ (Exp.)	AgF ₂ (Theory)		AgF ₂ (Exp.)
	[50]	[50]	[50]		WB ZR	SB ZR	
z^2	1.42	1.28	1.20	1.70	0.96	1.51	1.5
xy	1.53	1.40	1.35	1.80	1.54	1.25	
xz	1.60	1.51	1.56	2.12	1.48	1.68	2.4
yz	1.60	1.51	1.56	2.12	1.50	1.70	
E_{gap}	1.20	1.80	2.40	2.20	3.60	3.10	3.4
n_d	0.60	0.66	0.72		0.80	0.67	

Table 2.1: Energies of dd -transitions $x^2 - y^2 \rightarrow \nu$ from [39], calculated under weakly bound (WB) and strongly bound (SB) Zhang-Rice (ZR) scenarios. For La₂CuO₄, theoretical values are from [50] and experimental data from [49]. For AgF₂, theoretical results are from [39] and experimental values from [44, 46]. Due to the lack of single-crystal samples, symmetry assignment for AgF₂ is not definitive. All energies are in eV. Table is from [39]

origin of the peaks as shown in Fig. 2.14. The initial state, consisting of a hole in the $x^2 - y^2$ orbital hybridized with the $d^{10}\underline{L}$ states, is represented as a line at zero energy. Peaks correspond to transitions from these states to excited states of the cluster. A very similar computation was performed in the early days of cuprates [50]. For both AgF₂ and La₂CuO₄ energies of transitions under several possible bounding scenarios are shown in Tab. 2.1.

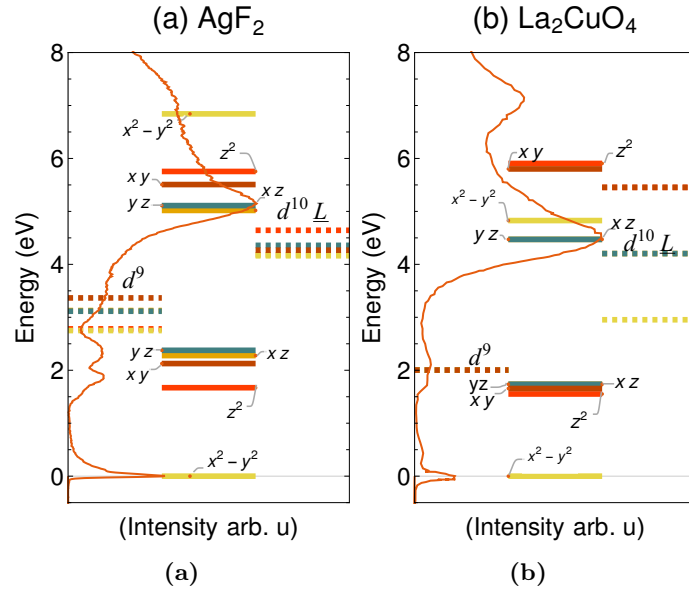


Figure 2.14: Energy level diagram for one hole states in the clusters considered for (a) AgF₂ with $\Delta = 1.29$ eV and parameters from Ref. [46] with a 20% increase of the T_{pd} matrix elements and $J = 70$ meV as stabilization energy [51] (b) La₂CuO₄ with $\Delta = 2.45$ eV and $J = 130$ meV. Dashed lines correspond to energies before hybridization in the d^9 configuration (left) and $d^{10}\underline{L}$ (right). Hybridization yields bonding and antibonding states (full lines). The ground state corresponds to the half-filled antibonding $d_{x^2-y^2}$ which was placed at zero energy so the vertical scale represents energies of transitions to states of majority d^9 character (i.e. dd transitions) around 2 eV and $d^{10}\underline{L}$ (i.e. charge transfer transitions) at higher energy. RIXS spectra have been superposed for comparison. The position of excited states is measured with respect to the $x^2 - y^2$ ground state and is plotted as a function of the renormalization of the T_{pd} matrix element with respect to the DFT value. The image is from [46].

2.4 Conclusion

In this Chapter, we have reviewed the fundamental concepts of correlated quantum materials, with a particular focus on Mott-Hubbard and charge-transfer insulators. Using the Zaanen–Sawatzky–Allen (ZSA) framework, we have discussed how the relative magnitudes of the Coulomb repulsion U_{dd} and the charge-transfer energy Δ_{pd} determine the character of the insulating state.

Silver fluorides, and in particular AgF_2 , have emerged as potential analogs to cuprates. We compared the structural, magnetic, and electronic properties of AgF_2 and La_2CuO_4 , showing that AgF_2 exhibits many of the same hallmarks of strong correlation—such as a comparable Hubbard U , charge-transfer gap, and two-magnon excitations—as seen in the cuprates. Spectroscopic data including Raman scattering, optical conductivity, XAS, and RIXS further support this analogy.

The identification of AgF_2 as a charge-transfer insulator with strong antiferromagnetic interactions and covalent bonding provides a compelling motivation for exploring silver-based compounds as analogs—or potentially alternatives—to cuprates in the search for new superconductors.

Chapter 3

Custom-built ultra high vacuum chambers for advanced synthesis of fluorides

3.1 Introduction

The controlled synthesis of fluoride-based quantum materials, such as AgF_2 , demands an experimental environment capable of handling highly reactive species with minimal contamination. Conventional material growth platforms are typically optimized for oxides or metals and are not readily compatible with the unique chemical challenges posed by fluorine chemistry. As such, the development of custom-designed ultrahigh vacuum (UHV) systems tailored to fluorination processes is a central prerequisite for the experimental objectives of this thesis and, more broadly, for the development of the field.

This chapter describes the design, construction, and integration of two complementary UHV systems developed for this purpose: i) A fluorination chamber optimized for clean, low-pressure gas-phase reactions with surfaces. ii) A pulsed laser deposition (PLD) chamber capable of growing layered fluoride-based thin films.

In the case of the fluorination chamber, we explore the thermodynamic and practical principles that govern surface fluorination under UHV conditions. We describe a new method that enables ultraclean fluorination. These considerations highlight the strong chemical potential of monoatomic fluorine and its advantage in enabling selective, low-pressure reactions. Meeting these requirements necessitates a custom-designed experimental environment with precise gas control, compatibility with highly reactive halogens, and minimal background contamination. The fluorination chamber forms the technical foundation for the experimental investigations presented in Chapters 4 and 5, where we explore fluorination thermodynamics and the structural evolution of silver fluoride systems at the atomic scale.

Additionally, to achieve the broader objective of synthesizing layered fluoride-based materials, particularly for quantum applications, it is essential to develop thin-film deposition capabilities, such as PLD. Special attention is given to innovations such as in situ substrate manipulation and compatibility with glove-box transfer systems and very reactive pellet targets.

3.2 Fluorination chamber

This section describes the development of a custom-built apparatus and a novel methodology for the fluorination of surfaces, developed for the synthesis of functional and quantum materials. The techniques uses monoatomic fluorine contrary to previous works, which rely on fluorine in some molecular form. This development led to an Italian patent application and the extension at the European level (still pending).

Fluorination of surfaces has a broad range of applications as it can functionalize surfaces and improve quantum materials. One notable example is the surface treatment of lithium metal with molecular fluorine under controlled temperature and pressure conditions, as described in Italian Patent Application [52]. This process was developed to form protective fluorinated layers on lithium anodes for battery applications. Vaney *et al.* [53] demonstrated topotactic fluorination of intermetallics using $c\text{-C}_4\text{F}_8$ as a fluorine source. The decomposition of this perfluorocarbon yields CF_2 radicals, reducing the overall reactivity of fluorine and enabling its slow and selective diffusion into the material. In another study, Antipov *et al.* [54] achieved the synthesis of high- T_c superconducting phases in $\text{YBa}_2\text{Cu}_3\text{O}_6$ using XeF_2 as a fluorinating agent. Likewise, Qiu *et al.* [55] investigated the self-limiting growth of FeF_2 thin films by exposing atomically clean iron surfaces to XeF_2 and SeF_6 under UHV conditions. These methods rely on molecular species as fluorine sources. By contrast, the approach developed in this work employs monoatomic fluorine, which, from a thermodynamic perspective, is significantly more reactive. This higher reactivity allows for effective fluorination at substantially lower partial pressures and dosages. Moreover, the technique enables ultraclean fluorination, as confirmed by the absence of contaminant signals in STM measurements discussed in Chapter 4.

3.2.1 Principle of Operation

The fluorination process is based on the in-situ generation and storage of monoatomic fluorine within a vacuum chamber. A fluorine-containing gas, such as F_2 diluted in He is introduced into a pre-evacuated chamber. Alternatively, other noble gases (Ne, or Ar) can be used for dilution, or one can use fluorine-containing molecules like XeF_2 or $\text{C}_{60}\text{F}_{48}$. The chamber walls, composed of stainless steel, have a catalytic role in the process. They promote molecular dissociation and incorporate fluorine as a surface fluoride.

Once the gas inflow is halted, the chamber is held under high vacuum (base pressure 10^{-10} to 10^{-7} Torr). Analyzing the gas in the chamber with a residual gas analyzer (RGA) we have found that this results in gradual desorption of monoatomic fluorine from the chamber walls, forming a chemically active environment suitable for fluorination.

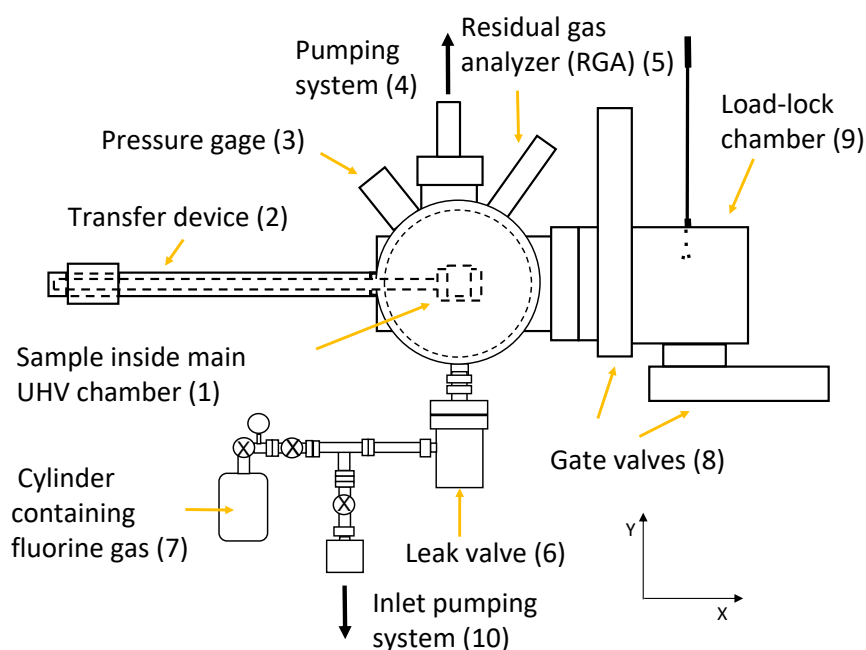
The mechanism of monoatomic fluorine production has not yet been fully investigated. We speculate that fluorine may be incorporated in the walls as FeF_3 , which then transforms according to $\text{FeF}_3 \rightarrow \text{FeF}_2 + \text{F}$. Halogens of iron are known to decompose in this way under vacuum and heat (Ref. [56] p. 1084). It is also possible that the presence of other contaminants found in the chamber, such as hydrogen (H_2 , which we also detect in the chamber), plays a role in the production of monoatomic fluorine.

Another interesting direction for future investigations in the field is how contaminants in the fluorine-rich atmosphere affect the growth of structures on the sample's surface.

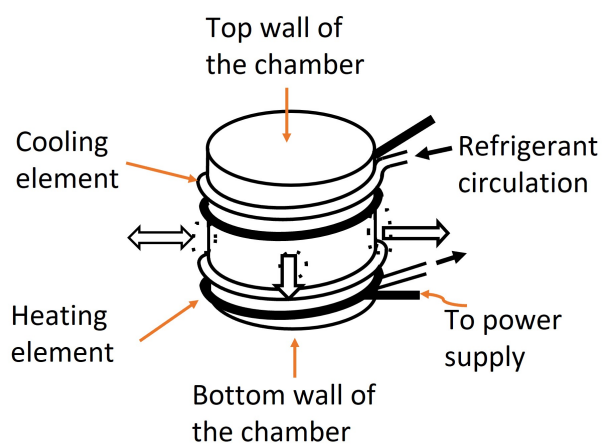
3.2.2 Apparatus Design

The fluorination apparatus includes several components configured to create and maintain a reactive fluorine environment, as well as to control the exposure of target samples to monoatomic fluorine. It was originally designed and constructed at Roma 3 University by Monica De Seta and Luciana Di Gaspare. However, the chamber is quite mobile and can be transferred and connected with various research facilities for postgrowth analyses (Scanning Tunneling Microscopy or X-ray Photoemission Spectroscopy for example). The apparatus is shown in Fig. 3.1 (principle scheme) and Fig. 3.2 (technical realization). It comprises the following key elements:

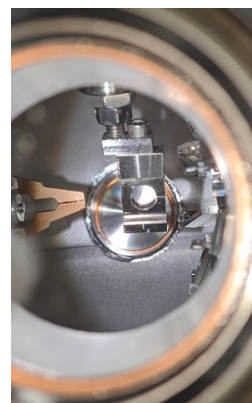
- **Processing Chamber:** In the current implementation, it is a stainless steel Ultra High Vacuum chamber. For in-situ gas composition analyses, the chamber is equipped with a *residual gas analyzer* (5)(RGA100 from Stanford Research Systems [57]). RGA works as a quadrupole mass spectrometer. It ionizes the gases present in the UHV chamber and separates sample ions based on their mass-to-charge ratio (m/z). It is possible to read all partial pressures of the gases in real-time. However, it provides only the aforementioned (m/z) ratio, though gas particles can be doubly or triply ionized (having charges 2^+ or 3^+ , for example), which should be taken into account. The main UHV chamber is connected with the load-lock chamber (9). Gate valves (8) provide vacuum integrity in the system and allow assembly of several chambers together. For example, in Chapters 4 and 5 the scanning probe chamber was directly connected with the load-lock mechanism (9), thus it was possible to measure topography of the samples immediately after fluorination.
- **Vacuum System:** A high-vacuum pumping unit operatively connected to the processing chamber (4), capable of evacuating it to pressures ranging from 10^{-10} to 10^{-7} Torr. The additional pumping system is connected with gas inlet line (10).
- **Fluorine Gas Source:** A source of fluorine-containing gas connected via a gas inlet line (it is shown as cylinder (7)). The gas inlet line is designed to introduce the gas directly into the processing chamber. The dosage of fluorine is controlled through a *leak valve* (6). It offers precise control, sensitivity, and stability with leak rates as small as 1×10^{-10} Torr-liters per second. Leak rate adjustment is controlled simply by rotating the knobs of the valve.
- **Transferring Device:** A mechanical system designed to load and unload target samples(2). It is equipped with a sample holder(1) with a specific shape (shown in panel c of Fig. 3.1) which enables the transport of samples into and out of the fluorination chamber from the associated load-lock chamber without breaking the vacuum. The load-lock chamber can connect to other chambers for further analysis and processing. For example, the sample preparation chamber of a scanning tunneling microscope.
- **Temperature Control System:** Heating elements are arranged in direct contact with the outer surface of the chamber (shown in panel b of Fig. 3.1) These elements are configured to raise the chamber wall temperature within a range of 30°C to 200°C . The patent application includes the possibility of cooling elements. Temperature control aids in the activation of fluorine adsorption and desorption.



(a) Principal scheme of the fluorination apparatus showing all built-in key components (top view)



(b) Large-scale view of the fluorination setup (z-axis is vertical in the image)



(c) Modified sample holder (1) with asymmetric connection to transfer arm inside load-lock chamber (9). This design allows transferring samples between various chambers.

Figure 3.1: Description of fluorination chamber

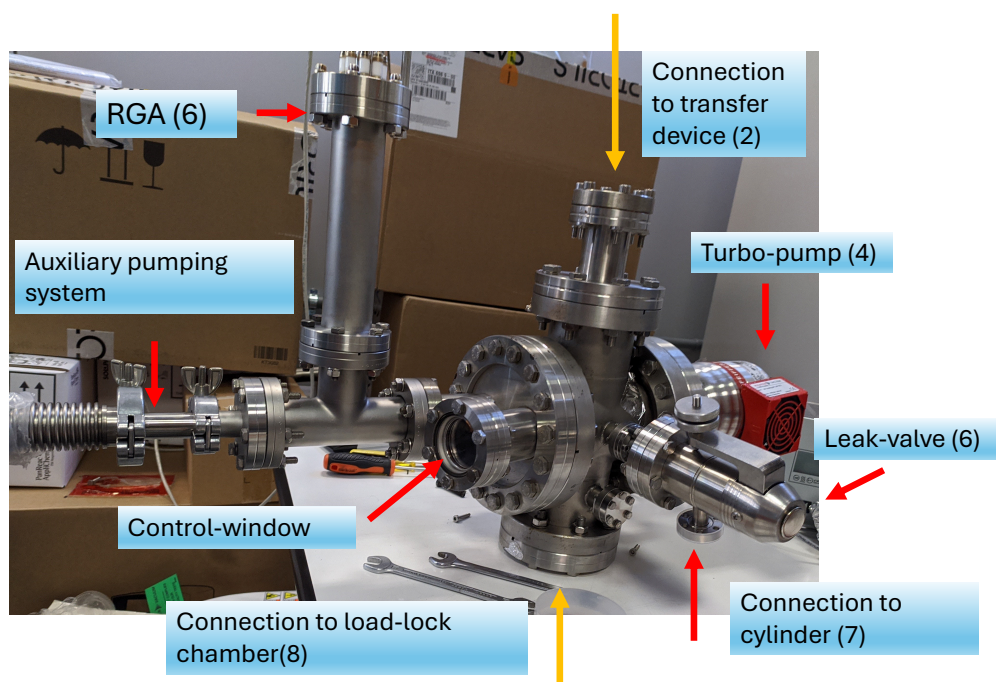


Figure 3.2: Technical realization: main UHV chamber of fluorination apparatus with the main parts installed. Transfer device(2), Gate-valve(8), Pressure gage(3) as well as Cylinder(7) are not shown. Numbers are correspondent to Fig. 3.1 panel (a)

3.2.3 Process Parameters and Control

The typical fluorination process consists of the following stages:

1. **Chamber Purging:** The chamber is evacuated to ultra-high vacuum levels (10^{-10} to 10^{-8} Torr), optionally enhanced by baking the walls at 100–180 °C to expedite degassing.
2. **Gas Introduction and monitoring:** A fluorine-containing gas is introduced at a controlled pressure (10^{-8} to 10^{-1} Torr) for a predetermined fluorination period (typically for several hours).

We used a 1:9 mixture of F_2/He at 10^{-6} to 10^{-5} Torr. The typical process of gas introduction into the chamber, when the partial pressures of gases were monitored in real-time by a RGA ((5) in the scheme). The partial pressure was measured for gas species with mass-to-charge ratios (m/z) ranging from 1 to 64, where m/z is defined as the ratio between the mass number of an ion and its charge number. The real-time evolution is shown in Fig. 3.3. Notice that several contaminant gases appear in the chamber, such as O_2 , H_2O , N_2 . This can also be seen in Fig. 3.4, where the complete mass spectrum is shown. Fluorination with the leak valve open would lead to contamination of the surface with these species. In contrast, our method avoids this effect.

3. **Stabilization:** Upon stopping gas inflow, residual molecular species are pumped out while fluorine remains adsorbed on the chamber surfaces.
4. **Mass Spectrometry:** The pressure of contaminants and monoatomic fluorine is measured again by the RGA. Fig. 3.5 illustrates a mass spectrometer spectrum of the interior of the processing chamber at ambient temperature, acquired after stopping the inflow of fluorinated

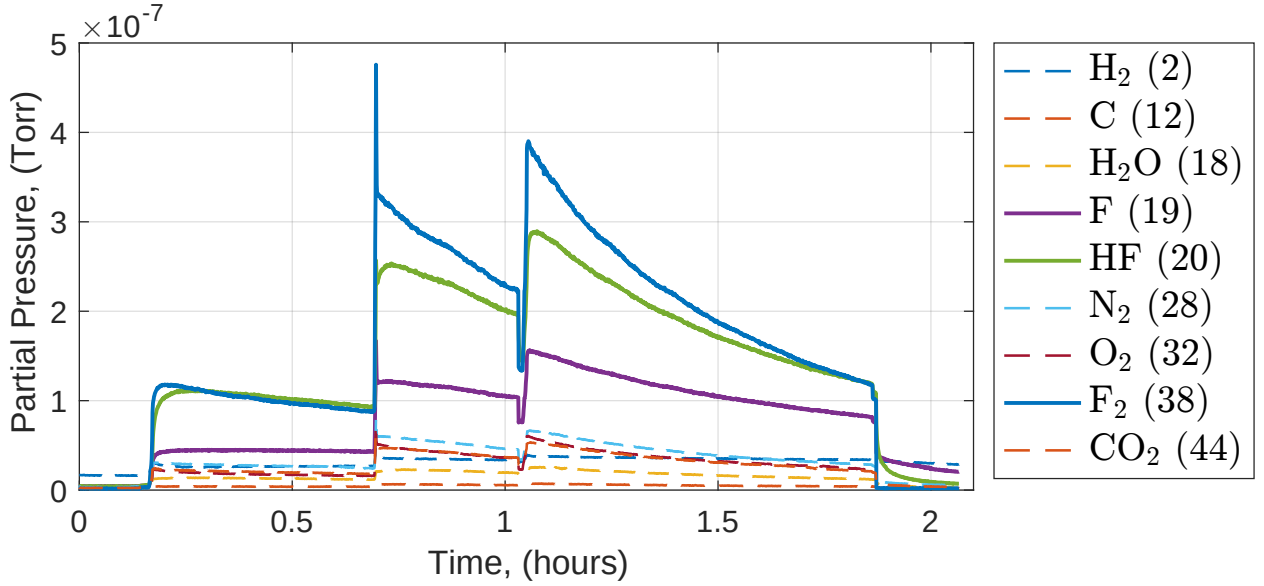


Figure 3.3: Evolution of partial pressures of the main gas species in the UHV chamber of the apparatus during a 2-hour test run with a 1:9 F_2/He gas mixture introduced from the supply cylinder. To avoid contamination of the bottle due to backflow, the gas line is used as a buffer. First, the line is filled with gas from the bottle through the rapid opening and closing of the bottle. Then this gas is used to fluorinate the chamber through the leak valve. The pressure in the chamber decreases gradually as the gas line is emptied. To compensate for the leak valve aperture is increased, leading to jumps in the pressure. The curve for Helium (4) is not shown as it has one order higher pressure than other gases and is not responsible for chemical reactions in the chamber. F_2 , HF, and F have the highest pressures among other gases throughout all the time and are shown by bold solid lines

gases (after several cycles similar to the one shown in Fig. 3.3). In the spectrum, monatomic fluorine ($m/z = 19$) shows a partial pressure of 6×10^{-9} Torr, while diatomic hydrogen is present with a partial pressure of 1.5×10^{-9} Torr. Other gas species exhibit a pressure below 5×10^{-10} Torr, considered within the noise level, i.e., below the maximum threshold partial pressure for impurities. Typically, diatomic hydrogen is not considered a relevant contaminant during the fluorination process. The monatomic fluorine-rich atmosphere at the end of the chamber fluorination is referred to as the “F atmosphere”.

If a desired minimal threshold concentration of monoatomic fluorine or a maximum threshold concentration of impurity gas is not met, an additional fluorination cycle can be triggered. We adopted the following criteria:

- Residual gases (excluding fluorine and hydrogen): $< 6 \times 10^{-10}$ Torr.
- Monoatomic fluorine: $> 3 \times 10^{-9}$ Torr.
- If these thresholds are not met, the fluorination and gas analysis steps are repeated.
- This iterative refluorination continues until the desired gas environment is achieved.

5. **Sample Loading and Exposure:** Target samples are loaded into the chamber and exposed for a defined time to the monoatomic fluorine gas atmosphere (i.e., with the leak valve closed).
6. **Post-Processing:** Following exposure, samples are removed, and the chamber walls may be cooled to $5\text{--}15^\circ\text{C}$ to preserve remaining fluorine for future experiments.

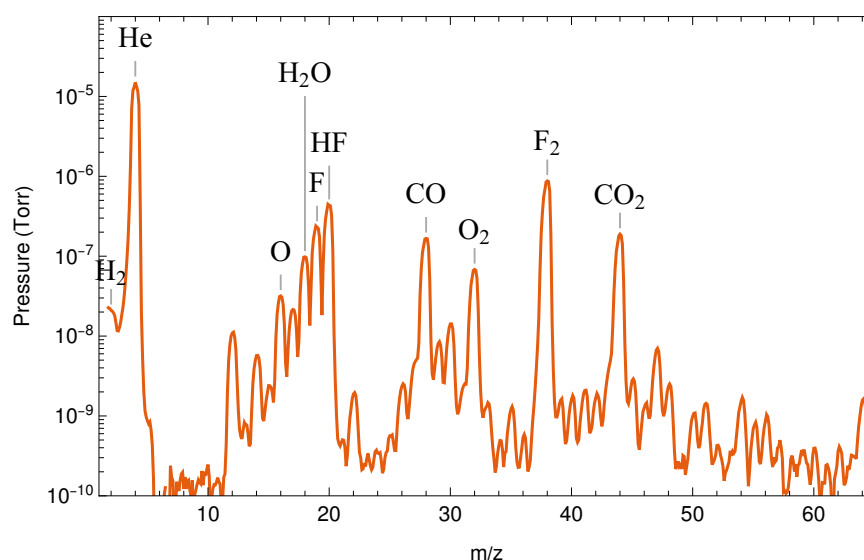


Figure 3.4: Mass spectrum of the processing chamber during exposition of the chamber to the gas from the bottle. Notice the presence of several contaminant gases (H_2O , CO , O_2 , CO_2 , etc.). The lower limit of the scale is near the limit of sensitivity of the instrument.

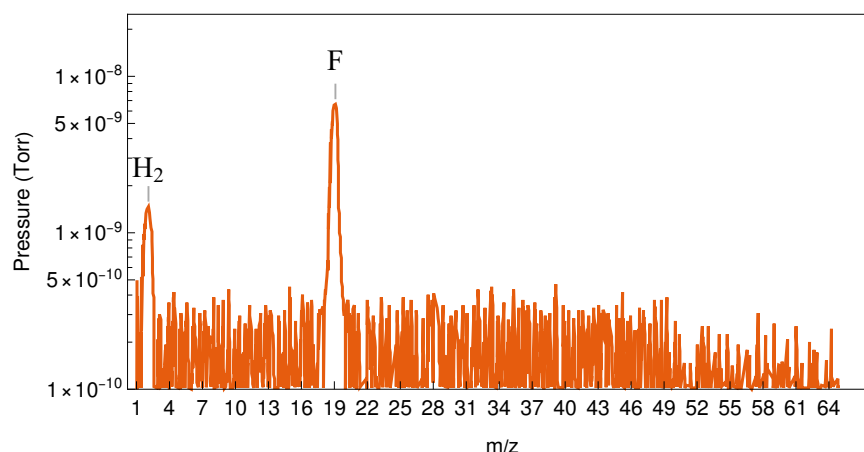


Figure 3.5: Mass spectrum of the processing chamber after stopping the inflow of fluorinated gases, showing the presence of monoatomic fluorine and diatomic hydrogen (corresponding peaks at 19 and 2 m/z) and the absence of other contaminants. Notice that the signal below 4×10^{-10} Torr is considered noise.

It has been observed that monoatomic fluorine continues to be released for several days following the fluorination step, provided vacuum is maintained. The release rate can be thermally modulated:

- Increasing the chamber temperature raises the partial pressure of monoatomic fluorine.
- Lowering the temperature reduces the release rate, allowing finer control or storage for future exposures.

This temperature-dependent behavior allows dynamic regulation of fluorine availability during sample processing. Moreover, the fluorine retained in the chamber walls provides a sustained source without continuous gas inflow, enhancing safety and working efficiency.

3.2.4 Summary of samples preparation

Samples

In the fluorination experiments performed during the thesis, we used two highly symmetric Ag-surfaces, namely, Ag(100) and Ag(110) (single crystals, purchased from Surface Preparation Laboratory). Before each experiment, the Ag sample was cleaned by (1-2) keV Ar⁺ sputtering cycles followed by annealing at 410°C in UHV.

Fluorine pressure and estimated doses

Particularly for longer treatments, we noticed that fluorine pressure can slightly decrease during the experiment. Therefore, to estimate doses, we used the average value of F-pressure between the starting and final points of reaction measured by RGA (Second columns in Tab. 3.1 and Tab. 3.2). The average fluorine pressure detected in the chamber during fluorination was in the range of 1.0×10^{-8} mBar and 6.3×10^{-8} mBar, depending on the experiment. All doses ($dose = time \times pressure$) were computed in Lengmuir units ($1L = 10^{-6}$ Torr $\times$ 1 sec= 1.33×10^{-6} mbar $\times$ 1 sec).

List of fluorination reactions

In the current research, we studied fluorination reactions, ranging from 30 minutes to 147 hours for Ag(100) surface (Table 3.1) and from 45 minutes to 3 hours for Ag(110) surface (Table 3.2).

Each time, the surface topography was studied by Low Temperature Tunneling Spectroscopy after fluorination (the fluorinated sample was transferred from the reaction chamber to the probe chamber under UHV conditions) These experiments are described in detail in the following chapters of this thesis. Chapter 4 focuses on the initial stages of fluorination (with fluorination times ≤ 3 hours for Ag(100) and 45 min experiment for Ag(110)), while Chapter 5 is devoted to the fluorination experiments with times between 4 and 15 hours for Ag(100) and 3 hour experiment performed on Ag(110). Fluorination experiments with times longer than 67 hours were also performed for Ag(100) surface, but the results are not included in this thesis and present an interesting direction for future investigations.

Fluorination time [h]	Average Pressure [Mbar]	Dose, L (10^{-6} Torr $\cdot$ s)
2.0	1.33×10^{-8}	70
3.0	1.5×10^{-8}	120
4.0	2.2×10^{-8}	240
5.5	3.0×10^{-8}	450
15.0	2.0×10^{-8}	810
67.5	3.2×10^{-8}	5850
132.0	5.1×10^{-8}	1.82×10^4
147.0	6.3×10^{-8}	2.50×10^4

Table 3.1: List of performed fluorinations on Ag(100) surface

Fluorination time [h]	Average Pressure [mbar]	Dose, L (10^{-6} Torr·s)
0.75	1.0×10^{-8}	20
3.0	1.0×10^{-8}	80

Table 3.2: List of performed fluorination on Ag(110) surface

3.2.5 Thermodynamic advantage of monoatomic fluorine use

As mentioned before, using monoatomic fluorine instead of molecular fluorine has the energetic advantage that the fluorine bond does not need to be broken. Here we quantify this advantage in terms of the thermodynamics of the system.

Take a hypothetical compound A. In a typical fluorination process, the outer surfaces of A are exposed to a fluorine-containing gas to obtain the fluorinated compound AF_n , where n is the number of moles of fluorine per mole of compound A that have reacted.

To analyze the free energy balance at equilibrium, we need the correct thermodynamic potential, which, when we control the pressure P and a temperature T is the Gibbs free energy. For a gas, the Gibbs free energy per atom or molecule can be directly related to the chemical potential.

When the fluorination process occurs at a pressure P and a temperature T in a processing chamber, if the gas is monoatomic fluorine (F), the Gibbs free energies per formula unit of the product compound, $g(AF_n)$, and of the reactant, $g(A)$, at equilibrium, satisfy the following relationship:

$$g(A) + n \mu_{\text{mono}}(P, T) = g(AF_n) \quad (3.1)$$

which can be rearranged as:

$$\Delta\mu_{\text{mono}}(P, T) = \left[\frac{g(AF_n) - g(A)}{n} \right] - \mu_0 \quad (3.2)$$

where $\Delta\mu_{\text{mono}}(P, T) = \mu_{\text{mono}}(P, T) - \mu_0$, $\mu_{\text{mono}}(P, T)$ is the chemical potential of atomic fluorine, and μ_0 is the energy of a single F atom at zero temperature. Both $g(AF_n)$, and $g(A)$ depend on pressure and temperature, which we omit for simplicity.

If instead, the gas is diatomic fluorine (F_2), at equilibrium, the Gibbs free energies satisfy the same equation (3.1) with the replacement $\mu_{\text{mono}} \rightarrow \mu_{\text{dia}}/2$. We can rearrange the equation as,

$$\frac{\mu_{\text{dia}}(P, T) - 2\mu_0}{2} = \left[\frac{g(AF_n) - g(A)}{n} \right] - \mu_0 \quad (3.3)$$

where $\mu_{\text{dia}}(P, T)$ is the chemical potential of molecular fluorine.

Eq. (3.3) can be rewritten as:

$$\frac{\Delta\mu_{\text{dia}}(P, T) - E_d}{2} = \left[\frac{g(AF_n) - g(A)}{n} \right] - \mu_0. \quad (3.4)$$

Here, $\Delta\mu_{\text{dia}}(P, T) = \mu_{\text{dia}}(P, T) - E(F_2)$, $E(F_2)$ is the energy of a fluorine molecule at zero temperature, and E_d is the dissociation energy of the fluorine molecule, i.e., which experimentally is $E_d = 2\mu_0 - E(F_2) = 1.6$ eV.

Equations (3.1)–(3.4) describe the balance of Gibbs free energy change in the reaction with

monoatomic gas ($\mu_{\text{mono}}(P, T)$) or diatomic gas ($\mu_{\text{dia}}(P, T)/2$). For convenience, the zero-temperature energy of the fluorine atom has been subtracted on both sides. All terms dependent on the initial and final product are placed on the right, while terms dependent on the type of gas are on the left.

Fig. 3.6 shows the left-hand side of Eq. (3.2) (monoatomic fluorine, dashed line) and the left-hand side of Eq. (3.4) (diatomic fluorine, solid line) as a function of the pressure within a processing chamber at ambient temperature. The data for $\Delta\mu_{\text{mono}}(P, T)$ and $\Delta\mu_{\text{dia}}(P, T)$ were obtained from the National Institute of Standards and Technology (NIST).

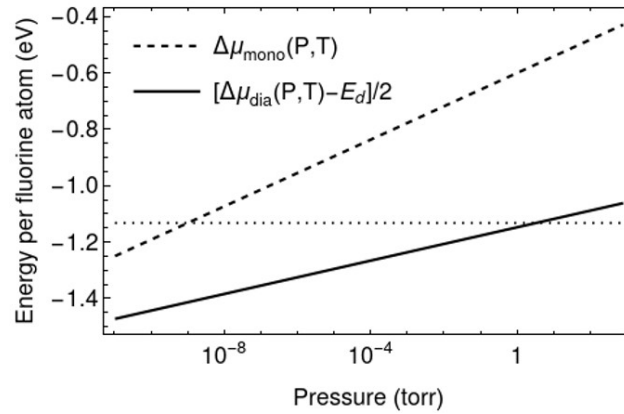


Figure 3.6: Temperature- and pressure-dependent contributions to the gas-phase Gibbs free energy per fluorine atom as a function of pressure inside the processing chamber. The solid line represents molecular fluorine (F_2); the dashed line represents monoatomic fluorine (F).

As an example, for a reaction characterized by a right-hand side Gibbs energy difference of -1.13eV (indicated by the dotted horizontal line), the equilibrium pressure required for reaction with molecular fluorine is approximately 3 Torr, whereas for monoatomic fluorine, the corresponding equilibrium pressure is on the order of 10^{-9} Torr.

This analysis indicates that the use of monatomic fluorine enables fluorination reactions to reach equilibrium at significantly lower pressures compared to those using molecular fluorine. As shown in Fig. 3.6, the required equilibrium pressure for a given Gibbs free energy difference is orders of magnitude lower when monatomic fluorine is employed. This finding suggests that monatomic fluorine can facilitate safer and more controlled fluorination processes by substantially reducing the need for handling high-pressure fluorine-containing gases. It should be emphasized that these thermodynamic arguments do not take into account the dynamics of the fluorination process. Often, fluorination does not occur at equilibrium, and the present considerations have to be taken with a pinch of salt.

Indeed, in Chapter 4 we show that the present method allows the production of very clean samples of silver fluorides. On the other hand, we also discovered anomalously small sticking coefficient; therefore, dynamical effects can not be neglected.

3.3 Innovative pulsed laser deposition chamber

In this section, we describe a pulsed laser deposition chamber for fluoride compounds. The contribution to the design and realization was done during the thesis in the framework of a stage at IONVAC Process S.r.l., a company specialized in the construction of custom-made high vacuum chambers. Prof. Daniele Di Castro supervised all the work as part of the QT-Fluo PRIN project.

3.3.1 The essence of method

Pulsed laser deposition (PLD) is a very simple technique for the growth of good-quality thin films. The typical experimental scheme is shown in the bottom part of Fig. 3.7. The basis of the method is the interaction between the radiation pulses of the laser and the target. The latter is usually a pellet with the same stoichiometry as the thin film one wishes to produce.

The laser produces ablation of the target inside a vacuum chamber with a controlled atmosphere. The chemical elements eject perpendicularly to the surface at the point heated by the radiation. The flux has a particular shape, denominated a plume. The ejected material is collected on the substrate, on top of which the thin film is deposited with each laser shot. The plume consists of ions, electrons, and macromolecules or small particulates with micrometric dimensions and usually preserves the stoichiometry of the target.

The concept of using laser radiation for thin film deposition was first demonstrated in 1965 [58], marking the early conceptual foundation of PLD. However, for several decades, the technique remained largely non-competitive compared to more established methods such as Sputtering and Molecular Beam Epitaxy (MBE). This was primarily due to limitations in laser technology: the lack of compact, reliable sources capable of generating ultrashort, high-intensity pulses with the temporal and spatial control required for reproducible thin film growth. Only with the later development of advanced laser systems—particularly those capable of delivering nanosecond pulses with high peak power—did PLD become a viable and versatile tool in thin film synthesis, enabling the deposition of complex materials with precise stoichiometric control.

A pivotal advance occurred in 1987, when superconducting thin films of $\text{YBa}_2\text{Cu}_3\text{O}$ were successfully synthesized using PLD techniques [59]. This was the first demonstration of superconducting cuprates grown by laser ablation, firmly establishing the method's ability to transfer complex multi-component oxide stoichiometry from target to film. This breakthrough accelerated the widespread adoption of PLD for research in superconducting oxides and other complex materials.

The equipment described in this section of the UHV chapter is designed to enable the successive application of the PLD technique—originally developed for the growth of cuprate superconductors—to the fabrication of layered AgF_2 thin films. This extension aims to reproduce the precise growth control and structural quality achieved in cuprates for a new class of fluoride materials.

3.3.2 Principal project of the chamber

Principal scheme of PLD setup aimed at syntheses of Fluoride materials are shown in Fig 3.7. Key parts are marked by numbers in the scheme and explained in details in the following list.

1. Main UHV Chamber

Dedicated to thin film deposition under ultra-high vacuum conditions.

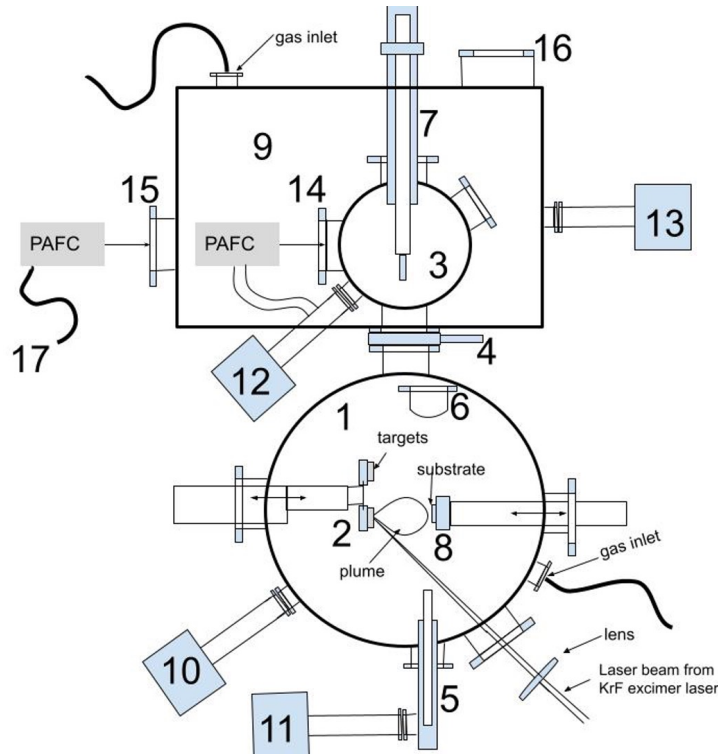


Figure 3.7: Scheme of innovative PLD system (image is taken from Quantum Transition-metal FLUOrides (QT-FLUO) project PRIN 20207ZXT4Z). The elements are explained in the main text.

2. Multitarget System Features linear and rotational movements. Enables fabrication of heterostructures based on different materials (e.g., $\text{LiF}|\text{AgF}_2|\text{LiF}$). Allows loading of air-sensitive targets from the load-lock chamber using the special manipulator (7).

3. UHV Load-Lock Chamber (Pre-Chamber) Facilitates sample and target loading/unloading without breaking vacuum in the main chamber. Can be coupled to the Fluorination chamber (depicted as **PAFC**) for in situ fluorination.

4. Gate Valve Isolates the main UHV chamber from the load-lock chamber to maintain vacuum integrity.

5–6. Reflection High Energy Electron Diffraction (RHEED) Composed of the electron gun (5) and the luminescent screen (6).

7. Special Manipulator Transfers both the substrate holder and the target holder to/from the deposition chamber. Allows secure handling of air-sensitive targets such as AgF pellets.

8. Heatable Sample Holder Supports the substrate holder and provides linear and rotational movements for optimal alignment. Ensures proper positioning during deposition, RHEED diagnostics, and loading/unloading operations.

9. Glove Box Maintains an electronically controlled inert atmosphere. Enables manipulation of highly air-sensitive materials (e.g., AgF_2). Can be directly coupled to the fluorination chamber for safe material transfer.

10–13. Vacuum and Pumping Systems Includes individual pumping units for:

- Deposition chamber (10)
- RHEED gun (11)
- Load-lock chamber (12)

- Glove box (13)

14–16. Ports and Interfaces

- Sample and target loading port / Fluorination chamber interface (14)
- Dedicated to Fluorination chamber connection port (15)
- Pre-glove box chamber for safe object transfer (16)

17. Safe Gas Line for Fluorination Supplies a diluted fluorine gas mixture (5 % F_2 in 95 % He). Multiple pressure sensors (not shown in the scheme) ensure safety and allow monitoring during fluorination.

3.3.3 Technical realization



Figure 3.8: The "Basis" chamber for the project of PLD setup (photos were done at Ionvac S.R.L.(Pomezia, Lazio) during my internship

The objective of this work was to prepare a PLD custom-made apparatus capable of growing thin films of fluorides, with a particular focus on silver fluoride (AgF_2) and related compounds. Due to the high chemical reactivity of these compounds, it is essential to operate within a UHV environment. As in conventional PLD setups, a pulsed laser beam is directed onto a target, in this case typically a pellet of AgF_2 . However, given the extreme sensitivity of AgF_2 to atmospheric exposure, the target cannot be handled in air. To address this challenge, we implemented a strategy in which the target is introduced into the deposition chamber through a dedicated load-lock pre-chamber, the same system used for substrate insertion. This process is carried out under inert conditions using a glove box.

The chamber used in this project was adapted from a pre-existing system. Although the original chamber shown in Fig. 3.8 had been constructed for different experimental techniques, it was extensively reconfigured and rebuilt specifically for PLD operation. Fig. 3.9 presents the corresponding CAD project. We omit the pumping system and glove box and demonstrate only the essential parts of the setup.

The apparatus consists of a main deposition chamber (1) and a preparation load-lock chamber (3), separated by a gate valve (4 in the scheme, not shown in Fig. 3.9). The reduced volume of the load-lock chamber allows for rapid evacuation to working pressure using its dedicated pumping system. Samples and targets are introduced through the load-lock and transferred into the main chamber via a magnetic manipulator arm (7), which provides precise linear and rotational motion.

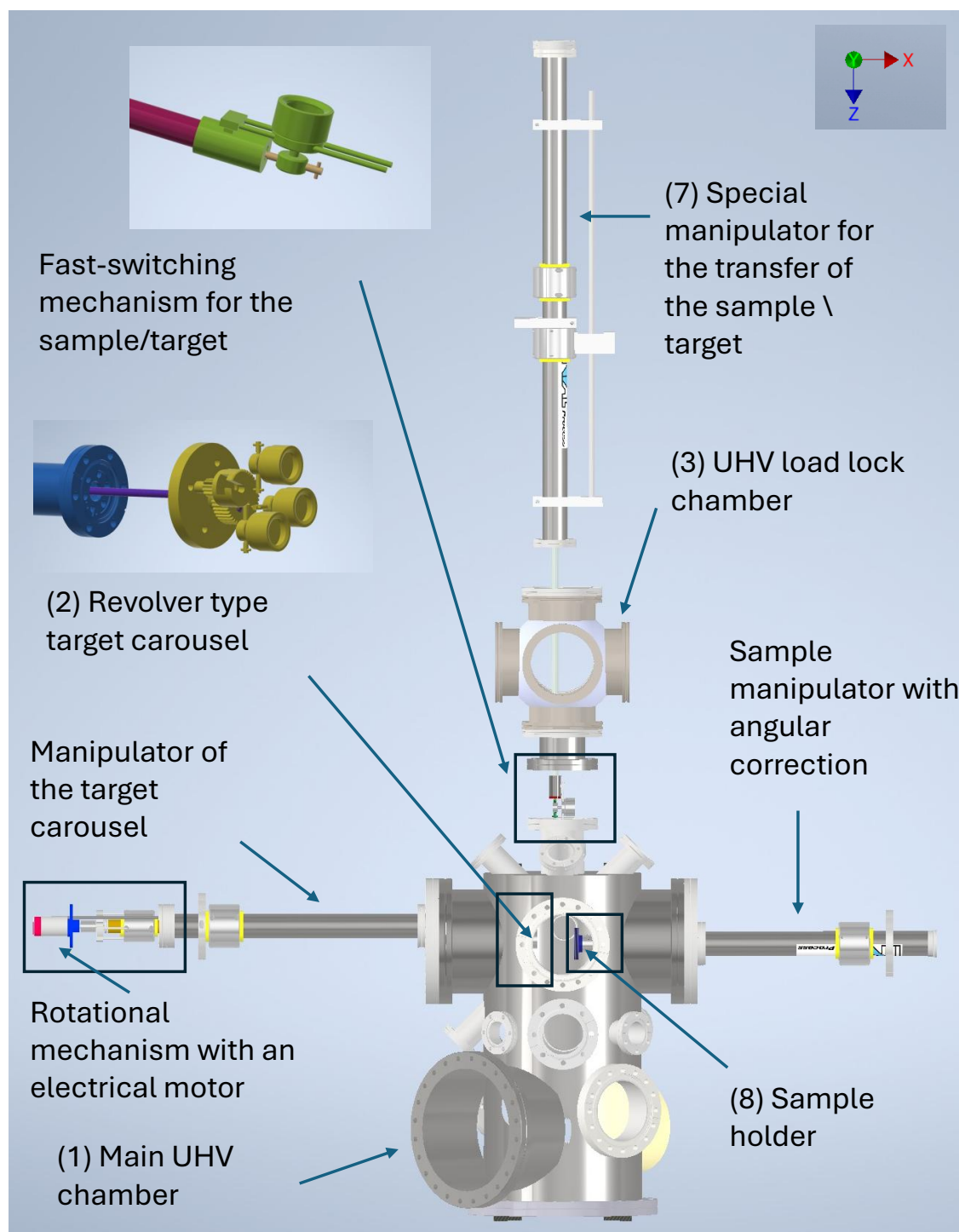


Figure 3.9: Principal CAD project of PLD custom-made setup adapted for existing chamber shown in Fig. 3.8. The main UHV chamber(1), load-lock chamber(3), and manipulator (7) are shown separately to illustrate the idea of the target transfer mechanism. Numbers depicting parts of the setup correspond to Fig. 3.7. Additional flanges are shown opened. Glove box (9) and RHEED system (5,6) are not shown in the current scheme.

Once inside, the substrate is mounted on the heatable sample holder (8), positioned directly opposite the multitarget carousel (2).

The target holder operates on a revolver-style mechanism, capable of accommodating multiple targets. This design allows for rapid switching between different materials during deposition by simply rotating the target wheel. Such flexibility enables the fabrication of multilayered structures and engineered heterostructures. In particular, this configuration allows for the deposition of sandwich-type films—such as a reactive AgF_2 thin film layer capped by a protective material (layer of LiF for example)—to preserve chemical integrity upon exposure to ambient conditions.

The project includes a mechanism for rapid target exchange (shown in the inset of Fig. 3.9) without breaking the vacuum. In conventional PLD setups, replacing a target often requires venting the entire main UHV chamber (1) to access the target carousel physically. This process significantly interrupts experimental continuity, as it necessitates re-establishing ultra-high vacuum conditions and performing a full chamber bake-out to remove residual gases and contaminants.

Keeping in mind that very often there is a demand to keep several different targets in the revolver carousel to make synthesis of heterostructures with several components, it can be a huge problem if only one target should be replaced (for example, because of its consumption or damage). The aforementioned fragility to ambient conditions of fluoride compounds additionally complicates the deposition and imposes more constraints on the construction of the equipment.

To overcome these challenges, the present design incorporates a load-lock-based mechanism (3) that enables the independent replacement of individual targets using the same manipulator (7) employed for substrate transfer. During this operation, a new target is mounted on the manipulator arm, transferred through the load-lock into the main chamber, and inserted directly into a designated position on the rotating carousel. The procedure takes approximately the same time as loading a new sample.

This mechanism, combined with glove box integration, is essential for the safe and efficient synthesis of fluoride-based materials. It not only improves the operational speed of PLD workflows but also enables the handling of highly reactive targets such as AgF_2 , expanding the range of accessible materials and heterostructure architectures.

The sample holder (8) is equipped with an integrated heating block, enabling substrate temperatures to exceed 500°C . Temperature control is achieved through a built-in thermocouple, allowing precise regulation during film growth. The distance between the sample and the target can be finely adjusted using the manipulator arm, which provides both linear and rotational degrees of freedom.

The main UHV chamber (1) is equipped with a vacuum system consisting of a scroll pump and a turbo molecular pump, which together enable film deposition at base pressures as low as 10^{-7} mbar. Additionally, the chamber has been designed with extra space and dedicated flanges to allow the integration of post-deposition analysis tools, providing flexibility for advanced characterization workflows.

Installation works are currently ongoing in the lab of Prof. Daniele Di Castro in Tor Vergata University (PLD group) and the system is almost ready for operation. It is important to emphasize that it is possible to connect the innovative PLD setup shown in Fig. 3.9 with the Fluorination apparatus Fig. 3.1a, using available flanges of UHV load lock preparation chamber (number 3 in the scheme). Indeed, the fluorination apparatus is quite mobile and can be transferred to PLD facilities that are associated with a heavy laser system. This new combined setup provides more

options and allows for the production of a wide spectrum of quantum materials not restricted only to ordinary AgF_2 thin films.

3.4 Conclusion

This chapter presented the conceptual design and technical realization of two UHV systems developed to advance the synthesis of fluoride-based quantum materials. The first, a custom-built fluorination chamber, enables the safe and efficient introduction of highly reactive monoatomic fluorine under controlled UHV conditions. This chamber integrates features such as a dedicated gas line with precise control of F-doses, in situ RGA monitoring, and a load-lock mechanism to connect it with other facilities. The apparatus enables atomic-scale fluorination of silver surfaces with unprecedented cleanliness and control. By enabling access to ultraclean, low-pressure fluorination, the constructed UHV system serves as a cornerstone for the experimental investigations presented in the subsequent chapters.

The second system is an innovative PLD chamber specifically engineered to accommodate the challenging chemistry of silver fluorides. Its revolver-type target carousel, inert gas handling infrastructure, and RHEED diagnostic tool will support the layer-by-layer growth of complex heterostructures. Notably, the design allows for the independent replacement of targets without breaking vacuum, a critical requirement for handling fragile fluoride compounds such as AgF_2 . This system will facilitate controlled synthesis and in situ diagnostics.

Together, these developments provide a versatile and robust experimental platform that bridges fundamental surface science and thin-film synthesis. These tools pave the way for engineering novel 2D fluoride systems relevant for studies of correlated electron phenomena and potential high-temperature superconductivity.

Chapter 4

The initial stages of silver fluorination: a scanning tunneling microscopy investigation

4.1 Introduction

A natural route to achieving silver fluoride two-dimensional quantum materials would be to fluorinate a thin silver film. However, before this can be achieved, it is necessary to understand the physicochemical parameters of the interaction of fluorine with a silver surface. The thermodynamics of silver fluorination and dynamic parameters, such as the sticking coefficient, have not been studied so far. The main purpose of this and the next chapter is to fill this gap. Part of this chapter has been published in Refs. [28] and [29].

Although adsorption studies of fluorine are scarce [60–65], due to challenges associated with handling this highly corrosive element, much is known about halogens in general. This is a group of chemical elements characterized by a remarkably high electronegativity, facilitating the formation of chemical compounds with a broad range of metals and the majority of nonmetals [66]. In fact, the interaction of halogens especially with metal surfaces has been the subject of extensive investigation also in light of their technological potential [60, 66–72], especially in the field of heterogeneous catalysis and microelectronics [73–75]. Previous research has considered the interaction between chlorine [69, 76, 77], bromine [62, 78] or iodine [79, 80] and transition metals, including Ag [70, 81, 82]. On many halogenated surfaces, a non-uniform arrangement of halogen adatoms has been observed at fractional mono-layer coverages, often accompanied by substrate reconstruction [62, 76, 77, 82].

An early experimental study [83] about the reaction of fluorine on silver samples was performed at high pressure of fluorine gas (50-600 Torr) and high temperatures (20-300°C), reporting the synthesis of Ag_2F , AgF or AgF_2 , depending on the synthesis conditions. Refs. [61, 62] report scanning tunneling microscopy (STM) studies of atomically smooth halogen adlayers, including F, on Ag(111). Unfortunately, the growth method used in these studies did not allow to finely control the amount of halogens deposited on the samples, thus limiting the investigation only to fully halogenated surfaces. Refs. [63, 64] used X-ray photoemission spectroscopy (XPS) to characterize the fluorination of several transition metals with a fine control of the gas exposure. However, the

case of silver was not considered. More recently, a study on the defluorination of $C_{60}F_{48}$ obtained silver fluorides as a byproduct[84]. Samples were studied by XPS and STM, but the surfaces were covered by the C_{60} molecules, which hampered a detailed characterization of the surface evolution as a function of fluorination. Therefore, as of today, a STM investigation of the first stages of fluorination of a metal substrate is still lacking.

From the experimental point of view, scanning tunneling microscopy (STM) provides unique information about an "apparent topography" (AT) of the surface. This, however, may be different from naive expectations based on the charge distribution. For example, operating in constant current mode, sometimes adatoms appear as protrusions, but depression is also possible, as well as a combination of both, yielding a Mexican hat or "sombrero" shape. Sombrero shapes are observed in the case of sulfur [85], and oxygen [86] on silver.

Given that halogens have a high sticking coefficient [74], they represent ideal elements for the study of the interaction between reactive gases and solid substrates [87] in ultra-high vacuum (UHV) conditions, where maintaining very low pressure is essential. However, most of the previously studied cases have been performed with diatomic gases, whereas little is known about the reaction with monoatomic gases.

To address all these questions, this chapter reports an experimental study on the adsorption of F atoms on low-index Ag surfaces performed by low-temperature (LT)-STM. The preferential absorption sites for F on the Ag(100) and the Ag(110) surface were determined. Furthermore, taking advantage of the new fluorination chamber developed, we could first study the interaction of a transition metal with monoatomic fluorine rather than the usual diatomic fluorine used in previous experiments. The extremely low values of the sticking coefficient of F on both silver surfaces were discovered. Possible causes of these anomalies are discussed.

The results were supplemented by Density Functional Theory (DFT) computations of F-adsorption on Ag surfaces [28] performed by Adrian Pueyo using guidance from the present experiments. These computations allowed us to estimate the range of fluorine gas chemical potential at which a given coverage or bulk phase is thermodynamically stable. Furthermore, the DFT energetics at small coverage allowed tentative assignments of the experimentally observed ATs to specific high-symmetry locations on the surfaces. A detailed comparison between experimental cross-section profiles over F-adatom and simulated ones provided further assistance on the assignment of adsorption sites.

4.2 Geometry of surfaces and definitions

For Ag(100) the atoms in the surface present a square unit cell with lateral dimension $a' = a/\sqrt{2}$ and area $(a')^2$, with a the bulk lattice constant. There are three highly symmetric sites for the adsorption of the fluorine atoms [Fig. 4.1 (a)]: hollow, bridge, and top site. The dimensions shown in the figure were obtained from the DFT computations as explained below.

The Ag(110) surface has a similar layout, albeit with a rectangular unit cell of area $a' \times b'$, with $b' = a$. Consequently, two types of bridge sites are present: a long-bridge site positioned between two Ag atoms along one of the longer sides of the rectangular lattice and a short-bridge site located between two Ag atoms along one of the shorter sides. This configuration yields a total of four highly symmetric sites suitable for the adsorption of fluorine atoms in ideal surfaces, as shown in Fig. 4.1 (c).

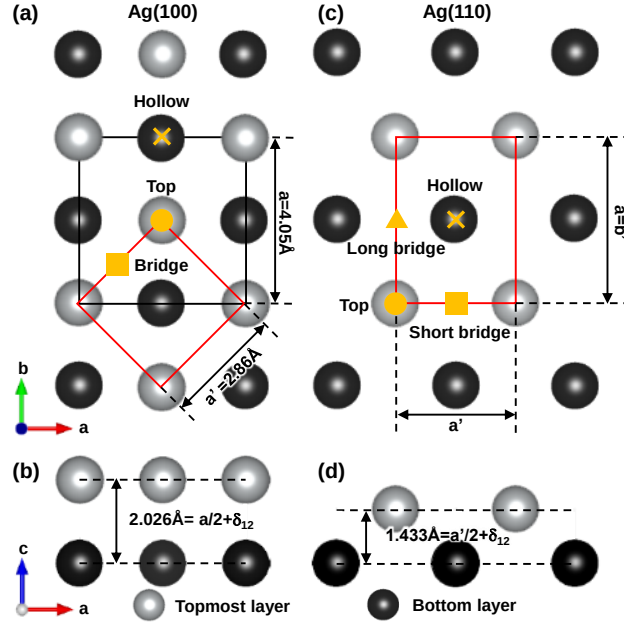


Figure 4.1: Geometry of the first two layers of the (a)-(b) Ag(100) and (c)-(d) Ag(110) slabs. The square and rectangle drawn with red solid lines in (a) and (c) show the unit cell considered for each surface. The crystallographic axis on the left indicates the orientation of the bulk crystal associated with the Ag(100) surface. For the 110 surface shown in (c), the horizontal direction corresponds to [110] while the vertical direction corresponds to [001]. The highly symmetric positions are indicated with yellow shapes for both surfaces. The light and dark gray spheres represent silver atoms from the topmost and the underlying layers, respectively. The distance between these two layers is indicated with an arrow in panels (b) and (d). The parameter δ_{12} characterizes the interlayer distance relaxation for the two topmost layers.

The surface coverage was defined as $\Theta = N_F/A$ (ML), where N_F is the number of fluorine adatoms on the surface and A is the surface area in units of the surface unit cell. For both surfaces, A corresponds to the number of each type of highly-symmetric sites in the pristine surface, and $\Theta = 1$ ML corresponds to the full occupation of all the available sites of one kind [considering bridges along the two perpendicular directions in the Ag(100) surface as distinct].

4.2.1 Theoretical structural and electronic parameters

Table 4.1 reports Density Functional Results for key structural and electronic parameters of the surface. We show the height of the F adatoms and their nearest Ag neighbor(s) relative to the surface of the clean silver slabs for all the highly symmetric sites of the Ag(100) and Ag(110) surfaces, as well as for the case where one F adatom occupies a vacancy on the clean silver surface. Notice that the bridge of the Ag(100) surface and the short bridge of the Ag(110) surface correspond to the same Ag-Ag distance a' . Indeed, the F height ≈ 160 pm is very similar in both cases. We also report the charge transfer δn between F and the nearest neighbor Ag atom on the surface.

4.3 Theoretical Adsorption Energies and Diffusion Constants

The surface can be exposed to monoatomic fluorine or diatomic fluorine, depending on the experimental conditions. If fluorination proceeds from exposing the clean Ag surface to the diatomic gas, the molecule must be dissociated during the reaction process. The zero-temperature dissociation

Table 4.1: Electron charge transfer, δn , and height d of the fluorine adatom and its silver nearest neighbor on the surface. d is measured relative to the (relaxed) topmost layer of the clean Ag(100) and Ag(110) slabs for each of the highly symmetric sites studied. δn for fluorine is defined as the difference in electron number relative to an isolated atom. For silver, the difference is relative to an atom of the pristine surface. The electron number are taken in spheres of radius 0.704 Å, 1.503 Å for F and Ag respectively. S/L stands for short/long. The table is from [28].

Site	Ag(100)				Ag(110)			
	F		Ag		F		Ag	
	d (pm)	δn	d (pm)	δn	d (pm)	δn	d (pm)	δn
Hollow	123.7	0.185	1.6	-0.019	94.9	0.173	2.0	-0.028
Top	205.6	0.185	1.7	0.025	200.5	0.163	-1.0	0.021
Bridge	160.7	0.197	6.0	-0.016	-	-	-	-
S bridge	-	-	-	-	163.8	0.199	5.4	-0.020
L bridge	-	-	-	-	112.4	0.188	3.7	-0.026
Vacancy	-15.7	0.155	-2.9	-0.028	-28.8	0.163	-2.0	-0.019

energy per atom reads,

$$E_d \equiv E(\text{F}) - E(\text{F}_2)/2, \quad (4.1)$$

where $E(\text{F}_2)$ being the energy of a F_2 molecule and $E(\text{F})$ the energy of a single F atom. Considering an ideal situation of N_F non-interacting atoms at zero temperature. This will be considered as an idealized "zero temperature gas". Of course in practice such an ideal situation does not exists as the atoms will crystallize but it is useful to consider it for the bookiping of the energies. The total energy of this system is $E_T(N_F) = N_F E(\text{F})$. Since the chemical potential is defined as $\mu_F^{(a)} = E_T(N_F + 1) - E_T(N_F)$, the zero temperature energy can be related to the chemical potential. In the case of diatomic molecules, one should use the equivalent definition $\mu_F^{(m)} = [E_T(N_F + 2) - E_T(N_F)]/2$. This leads to the identification of the molecular (m) and atomic (a) zero temperature chemical potentials namely,

$$\mu_F^{0(m)} \equiv E(\text{F}_2)/2, \quad (\text{F}_2) \quad (4.2)$$

$$\mu_F^{0(a)} \equiv E(\text{F}). \quad (\text{F}) \quad (4.3)$$

To fix ideas we consider a slab geometry in which N_F atoms from the gas are adsorbed in one of the two surfaces. This geometry was used in the experiments and DFT computations. We define the adsorption energy per atom as,

$$E_{ad}^{(g)}(\Theta) = (E_{\text{Ag:F}} - E_{\text{Ag}} - \Delta N_{\text{Ag}} \mu_{\text{Ag}}^0 - N_F \mu_{\text{F}}^{0(g)})/N_F, \quad (4.4)$$

where $g = a, m$ depending on the kind of gas exposure. $E_{\text{Ag:F}}$ and E_{Ag} are the total energy of the fluorinated system and the pure silver slab, respectively. μ_{Ag}^0 corresponds to the energy per atom of bulk Ag. In DFT these are computed as the total energies of fully relaxed systems. ΔN_{Ag} takes into account that the number of Ag atoms may change during the adsorption process. For example, a silver atom may be kicked off the surface and replaced by a fluorine atom (exchange reaction). Thus, $\Delta N_{\text{Ag}} = (N_{\text{Ag}} - N_{\text{Ag}}^0)$ is the difference of Ag atoms in the fluorinated slab (N_{Ag}) and the pristine slab (N_{Ag}^0). With these definitions $E_{ad}^{(g)} < 0$ indicates an exothermic reaction.

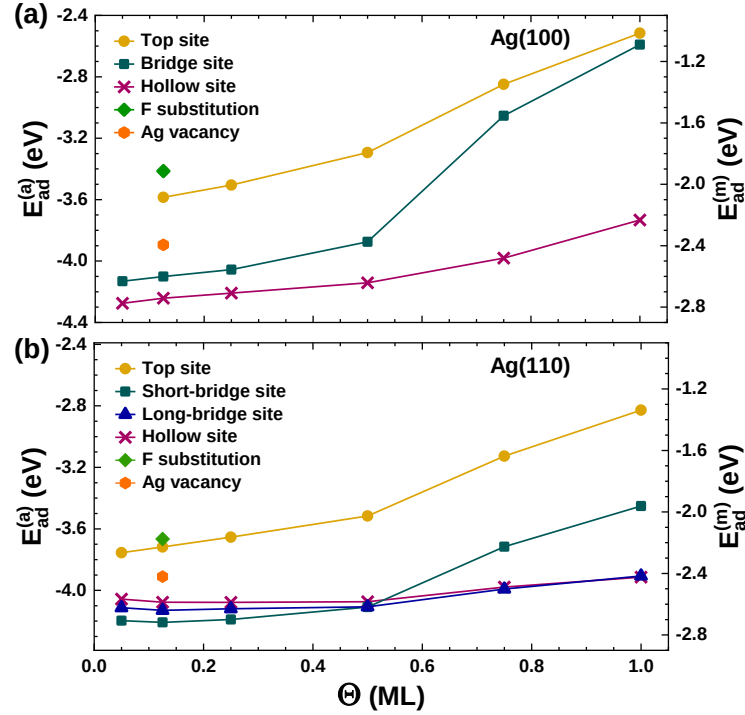


Figure 4.2: (a) Adsorption energies per atom for atomic fluorine (left scale) and molecular fluorine (right scale), as a function of the surface coverage, Θ , of the Ag(100) surface for the three possible highly-symmetric positions: hollow, bridge, and top. (b) The same plot for the Ag(110) surface, where we have four highly-symmetric positions: hollow, long bridge, short bridge, and top. The values labeled as "F substitution" correspond to an exchange reaction where an Ag atom is pulled from the surface and a fluorine adatom is adsorbed in the resulting vacancy, while in the "Ag vacancy" case, the vacancy in the surface already existed.

Often, experiments and theoretical works assume that Ag is exposed to F_2 gas, and therefore $E_{ad}^{(m)}$ is computed. The two adsorption energies are related by,

$$E_{ad}^{(a)} = E_{ad}^{(m)} - E_d. \quad (4.5)$$

Fig. 4.2 reports the adsorption energy, E_{ad} , for different levels of fluorine coverage for each type of highly symmetric site on both Ag(100) and Ag(110) surfaces. The lateral scales show the molecular and atomic adsorption energies, which differ by the theoretical value of $E_d = 1.49$ eV [Eq.(4.5)].

4.3.1 Ag(100) surface

The adsorption energies computed for the Ag(100) surface are plotted in Fig. 4.2(a). For the studied range of coverages, the most energetically favorable position is the hollow site, followed by the bridge, and finally, with a notable energy penalty, the top site. The smallest energy difference between the hollow and bridge sites is 140 meV, found at the two lowest coverages studied ($\Theta = 1/18$ and 0.125 ML). This result indicates that the hollow site is the preferred choice for F adatoms when the Ag(100) surface is fluorinated. The hollow sites also show the smallest increase in adsorption energy with Θ , indicating weak F-F interactions.

We can use the above result to estimate the surface diffusion constant. To jump from one hollow site to another the adatom should climb to the bridge site which determines the activation barrier $\Delta E_{ad} = 140$ meV corresponding to 1600 K. Although this value is quite large we can estimate a

room temperature jump hopping rate as $\Gamma = \nu \exp(-\Delta E_{ad}/k_B T) = 10^{10}$ jumps/sec, where, as an order of magnitude, we estimated $\nu = 15$ THz by a typical Ag-F stretching phonon frequency [17] in AgF₂. This indicates that at room temperature there is substantial diffusion and the system can equilibrate at least at the length scale of the STM experiment. At 53 K the jumps become of the order of one per second and, at the typical temperature of the STM experiment (10 K), the adatoms are essentially frozen.

4.3.2 Ag(110) surface

The adsorption energies for the Ag(110) surface are plotted in the Fig. 4.2(b). For the lowest coverage studied, the most favorable site is the short bridge. The long bridge and hollow sites have an energy penalty $\Delta E_{ad}^L = 90$ meV and $\Delta E_{ad}^H = 140$ meV respectively, similar to the energy penalty of the bridge site in the (100) surface. The energy differences reach a minimum at $\Theta = 0.5$ ML where the three sites become almost degenerate in agreement with Wang et al [88]. The adsorption energy of the top site is, once again, the less favorable one out of the four possible sites for every value of the coverage studied.

Since to escape from a short bridge the adatom has to pass through the hollow site, the lowest diffusion barrier at low coverage will be given by ΔE_{ad}^H (≈ 1600 K), which coincides with the Ag(100) surface. However, to move to the nearest neighbor short bridge in the horizontal direction in Fig. 4.1 requires the following passages: short bridge $\rightarrow$ hollow $\rightarrow$ long bridge $\rightarrow$ hollow $\rightarrow$ short bridge. In contrast, the movement in the perpendicular direction requires only one passage through a hollow site. This can make diffusion below 1600 K considerably anisotropic due to different prefactors of the activated (exponential) temperature dependence.

4.3.3 Exchange reactions and vacancy occupancy

We also considered the possibility that fluorine adatoms substitute surface Ag atoms, which are incorporated into the bulk. A viable path for such an exchange reaction process is that an Ag atom from the surface migrates to a kink along a step of the surface [89]. Since this only moves the kink by one lattice constant it is easy to see that the energy of the silver increases by μ_{Ag}^0 as dictated by Eq. (4.4).

Figure 4.2 shows the exchange reaction adsorption energy for the two surfaces at low coverages (green diamonds). From an energetic point of view, these reactions have a penalty that is similar to the top site although somewhat less favorable.

Another possibility is that the fluorine adatom occupies a vacancy site that is already present, saving the energy cost to expel the Ag. The energy in this case is given by the orange hexagons in Fig. 4.2 and it is still less favorable than the adsorption of the adatom on one of the highly-symmetric sites of the ideal surface, except for the top site.

4.4 Thermodynamics

One can use the DFT results to estimate the equilibrium pressures required to stabilize the various coverages. Similar estimations were done in [90], where the oxidation of silver was studied. The theoretical goal in Ref. [28] was to compute the equilibrium coverage Θ as a function of temperature

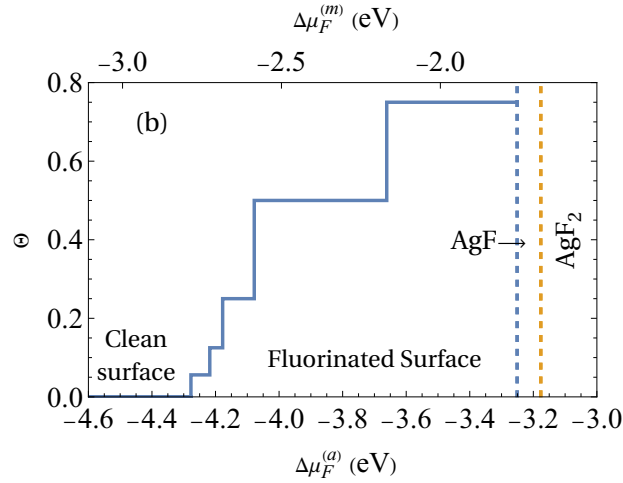


Figure 4.3: Most stable surface coverage for the Ag(100) surface. vs. fluorine chemical potential. The lower (upper) scale corresponds to the atomic (molecular) chemical potential. The dashed line indicates the limit of stability of the bulk phases: AgF between the dashed lines and AgF₂ to the right of the orange dashed line. (Adapted from Ref. [28])

T and pressure p , while the Ag surface is in contact with F₂ gas or F gas. In thermodynamics, one should use an appropriate potential depending on the thermodynamic variables of interest. In the experiments described below, the thermodynamic variables are the pressure p and the temperature T of the system. As mentioned in Chap. 3.2, the Gibbs free energy is the thermodynamic potential of choice in this case.

In Ref. [28] DFT was used to estimate the energies of formation of the different phases. This allowed an estimate of the Gibbs free energies [90–92] involved in the process, which could be compared with the Gibbs free energy of the gas. For gases, the Gibbs free energy can be directly related to the chemical potential. It is useful to write the gas chemical potential as a $T = 0$ contribution (which drops from the computation) plus a correction,

$$\mu_F(T, p) = \mu_F^0 + \Delta\mu_F(T, p). \quad (4.6)$$

In the computations, one first obtains the phase diagram as a function of $\Delta\mu_F(T, p)$ and then, knowing how $\Delta\mu_F(T, p)$ depends on pressure and temperature, allows one to obtain the result for arbitrary conditions.

The result of the computations of Ref. [28] for the Ag(100) surface is presented in Fig. 4.3. The horizontal axis is the term $\Delta\mu_F(T, p)$ in the case the surface is exposed to monoatomic fluorine (lower axes) or molecular fluorine (higher axes). The figure shows the equilibrium coverage as a function of the chemical potential.

Plateaus indicate that the corresponding structures will be stable in a certain chemical potential range. The silver surface is in a clean state for a large negative chemical potential. Increasing the chemical potential, a progressively larger fluorine coverage becomes stable. Notice that the plateau is particularly extensive for $\Theta = 0.5$ ML, hinting at a relatively large range of pressure and temperature where this phase is stabilized.

A similar analysis can be done for the Ag(110) surface using the reported values of adsorption energies [Fig. 4.2][28]. Similar computations for the oxide are shown in Fig. 7 of Ref. [90] where the x axis label should read $\Delta\mu_O$.

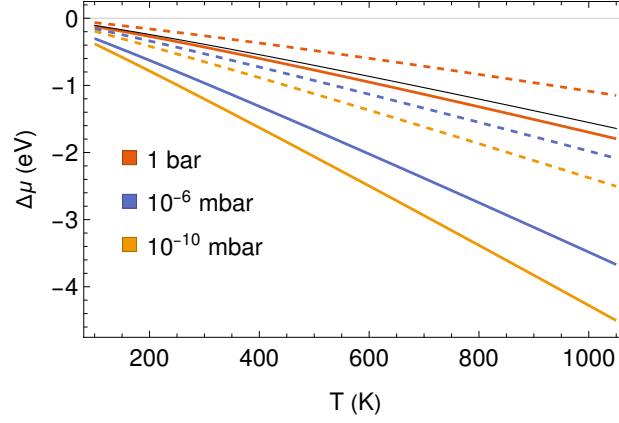


Figure 4.4: Temperature dependence of the chemical potential for different pressures using experimental data from the National Institute of Standards and Technology [93]. The full (dashed) lines correspond to the monoatomic (diatomic) fluorine gas. The thin line is the ideal monoatomic gas result (Eq. 4.9) for a pressure of 1 bar.

The size of the plateaus decreases as one approaches zero coverage. In the computations, a limited number of different coverages have been considered (1/18, 1/8, 1/4, etc.). Coverages with larger denominators require larger sizes and are computationally very costly. Ideally, considering all possible coverages, the curve would take a "Devil staircase" appearance approaching a smooth line when the coverage approaches zero. Similar behavior is expected near every rational coverage, rounding the sharp steps, but with large plateaus for commensurate coverages corresponding to small integer fractions.

The dashed lines in Fig. 4.3 indicate the range of thermodynamic stability of the bulk phases.

4.4.1 Gas chemical potential

To determine the equilibrium phase with the gas for each value of pressure and temperature, it remains to obtain the dependence of the chemical potential on these variables.

The pressure dependence of the chemical potential can be approximated by the ideal gas contribution ($k_B T \ln(p/p_r)$) with respect to a reference pressure p_r . Therefore $\Delta\mu_F^{(a)}(T, p)$ separates into a temperature dependence $\tilde{\mu}(T, p_r)$ and a pressure dependence, namely,

$$\Delta\mu_F^{(a)}(T, p) = \tilde{\mu}_F(T, p_r) + k_B T \ln(p/p_r), \quad (\text{F}) \quad (4.7)$$

$$\Delta\mu_F^{(m)}(T, p) = \frac{\tilde{\mu}_{F_2}(T, p_r) + k_B T \ln(p/p_r)}{2}. \quad (\text{F}_2) \quad (4.8)$$

For monoatomic fluorine, the temperature dependence can be estimated from the ideal gas expression,

$$\tilde{\mu}_F(T, p_r) = k_B T \ln \left[\frac{\hbar^3 p_r}{(k_B T)^{5/2}} \left(\frac{2\pi}{M} \right)^{3/2} \right]. \quad (4.9)$$

For $\tilde{\mu}_{F_2}(T, p_r)$ one should take into account rotational and vibrational contributions. Alternatively, one can use tabulated experimental data for both as shown in Fig. 4.4.

We show the chemical potential as a function of temperature for a pressure of 1 bar (≈ 0.99 atm) and typical pressures in ultrahigh vacuum experiments. At room temperature (300 K) for all reported pressures and gases the thermodynamic equilibrium is given by bulk fluorinated phases.

This means that in fluorination experiments reported below, the state of the surface is not dictated by thermodynamics but by kinetic factors such as the time of exposition and the sticking coefficient.

It is important to note that, even if the surface were exposed to the gas for a very long time, bulk compounds would not be formed due to the appearance of a passivating layer on the surface, which prevents a full fluorination of the bulk. This phenomenon, which is very familiar in alumina and other oxides, is a process by which the oxide itself creates a barrier that isolates the metal from the surrounding gas and prevents the reaction from proceeding, even though it is thermodynamically favourable. The effect is known as Mott-Cabrera barrier for their role in explaining the phenomenon[94]. In short, the mechanism attributes the self-limiting growth of ultrathin films to field-assisted ionic transport across the reaction product. Upon exposure to a reactive gas, charge transfer between adsorbates and the metal establishes an interfacial potential difference, generating an electric field across the thin film. This field lowers the activation barrier for ion migration, thereby sustaining rapid growth during the earliest stages. As the film thickens, however, the potential drop is distributed over a larger distance, leading to an exponential reduction of the field strength and, consequently, of the ionic flux. Once the driving field becomes too weak to overcome the diffusion barrier, further growth is effectively blocked, leaving only a few monolayers of product. This Cabrera–Mott blocking mechanism, originally applied to oxidation, has been shown to govern the fluorination of transition metals as well: in reactions with XeF_2 , the film growth terminates at nanometer-scale thicknesses in quantitative agreement with this model [55].

From Fig. 4.3, we see that a clean surface ($\Delta\gamma > 0$) requires a monoatomic chemical potential more negative than -4.3 eV, which, according to Figure 4.4, requires temperatures larger than 1000 K and minimal pressures. In contrast, the reaction with diatomic fluorine is stable at $T = 1000$ K and low pressure. Thus, this computation predicts that the surface will act as a molecule splitter at high temperatures. Molecular fluorine will be absorbed and atomic fluorine will be released.

4.5 Experimental methods

The fluorination was performed in the apparatus described in Chapter 3.2. This was connected to the UHV system through a gate valve and constantly evacuated by a turbo molecular pump, reaching a base pressure of 5×10^{-9} Torr. A cylinder with a mixture of He/ F_2 (nominal ratio of 9:1) was connected to the fluorination chamber via a leak valve. Before loading the samples, the chamber was exposed to the He/ F_2 mixture at room temperature and a pressure of 10^{-5} Torr for ~ 3 hours. As discussed in Chapter 3.2 this process passivates the walls but, more importantly, provides a fluorine-rich atmosphere to fluorinate the samples.

The chamber has a residual gas analyzer (RGA) (RGA100 from Stanford Research Systems). As reported in Fig. 4.5, in addition to the species typically found in UHV systems—namely H_2 , N_2/CO , CO_2 , and small traces of H_2O , with mass-to-charge ratios of 2, 28, 44, and 18, respectively—F and HF with mass-to-charge ratios of 19 and 20, respectively, can also be observed. If one excludes H_2 , monoatomic F (19) is the most abundant residual gas in the ancillary chamber, with its partial pressure (1×10^{-8} Torr) being at least almost an order of magnitude higher than the partial pressure of the other residual gases. Thus, samples were placed into the ancillary chamber and exposed at room temperature for different amounts of time to this fluorine-rich atmosphere. After fluorination, the samples were moved to the STM chamber for characterization.

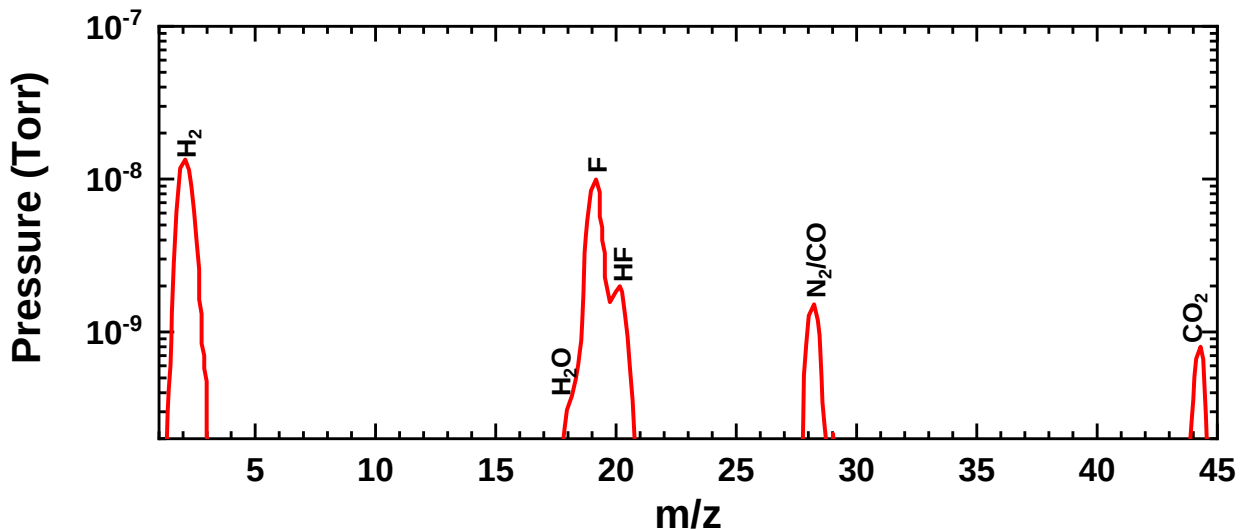


Figure 4.5: Residual gas analysis measured up to mass-to-charge ratio $m/z = 45$ in the ancillary chamber right after a passivation process. Notice that the lower pressure shown is near the limit of the sensitivity of the instrument.

STM experiments were performed in the laboratory of prof. Luca Camilli (University of Roma, Tor Vergata) using a commercial LT-SPM Infinity System (Scienta Omicron GmbH, Taunusstein, Germany) operating at ~ 9 K and a base pressure better than 4×10^{-11} Torr. Electrochemically etched W tips were used for all STM measurements. Data were collected in constant-current mode and calibrated using the lattice parameter values for Ag at the corresponding temperature as reported in Ref. [95]. Data were analyzed using Gwyddion software [96].

Unless otherwise specified, all coordinates presented in the experimental plots correspond to raw distances as recorded by the STM. These will be called "apparent lengths" as they do not correspond precisely to the physical length due to calibration errors. This problem is further discussed in Sec. 4.6.3, where we estimate the calibration constant and compute the sticking coefficient.

4.6 Results

4.6.1 Fluorine adatoms on the Ag(100) surface

After exposing the Ag(100) crystal to the fluorine-rich atmosphere for 1.9h corresponding to a dose of 70L (Tab. 3.1), we observe the presence of isolated F adatoms on the substrate surface (Fig. 4.6 (a)). As we will be shown later (Sec. 4.6.3), this corresponds to a coverage, $\theta \approx 0.001\text{ML}$.

It was found that at STM scans done with $V_B = -0.5\text{V}$ the fluorine atoms appear as protrusions surrounded by a dark halo less than 1 nm wide, forming a distinctive Mexican hat or *sombrero* shape. Incidentally, we note that a similar sombrero-like topography was also observed for chalcogen atoms adsorbed on Ag(100) [85, 86].

As previously discussed, three possible highly symmetric adsorption sites for the fluorine atoms are present for this surface: hollow, bridge, and top, as shown again for convenience in Fig. 4.6(b). In the current work, the split-image method was used to determine the adsorption sites of F adatoms. This method involves changing tunneling parameters while performing a scan and matching parts with different parameters between each other. To realize it, STM topography images as the one

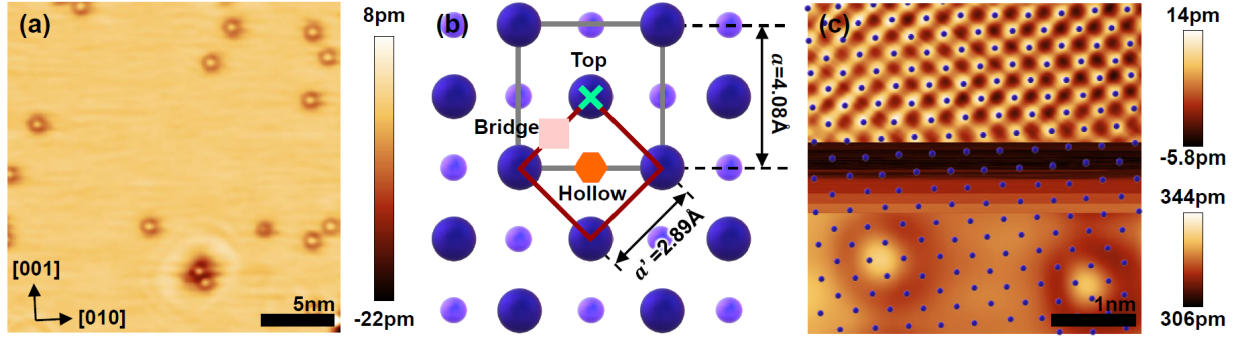


Figure 4.6: (a) STM image of the Ag(100) crystal exposed 1.9 h to a fluorine-rich atmosphere, acquired at 9.3 K with bias voltage $V_B = -0.5$ V and tunneling current 100 pA. The black arrows in the bottom left corner of the image indicate the crystallographic directions of the crystal surface. These directions are the same for all images related to Ag(100). The large, bright-contrast circle at the bottom of the image appears to be a defect of Ag. (b) Schematic representation of the first two atomic layers of Ag(100). Surface atoms are depicted with large spheres, while atoms in the underlying layer are shown with small spheres. The red square indicates the unit cell for this surface. The lattice parameters, a and a' , are based on experimental values obtained from X-ray diffraction at 9.3 K as reported in [95]. The three highly symmetric positions on this surface are marked with different shapes: hollow (hexagon), bridge (square), and top (cross). (c) STM image showing both the F adatoms and atoms of the Ag(100) surface acquired at $V_B = -0.5$ V. The tunneling current was set to 1 nA and 0.1 nA in the top and bottom halves, respectively. The scale bar corresponds to 1 nm.

displayed in Fig. 4.6(c) were analyzed. When collecting such an image, the bias was kept at a constant value in the whole scan. At the same time, the tunneling current was changed between a high setpoint (of the order of 1 nA), used for the top half without adatoms, and a low setpoint (of the order of 0.1 nA) for the bottom half where the adatoms were located. This allows us to bring the STM tip very close to the surface in the top half of the image, thus obtaining atomic resolution of the Ag surface atoms (visible as bright spots), while minimizing interaction with the adatoms in the lower half. The black lines at the center of the image are due to the change in tunneling current settings. The periodicity of the lattice was reproduced with blue dots in the bottom part of the image. Here, two fluorine adatoms are present, again with the *sombbrero* shape. The *sombbrero* apexes of both adatoms are located at the hollow sites of the Ag(100) surface. This experimental finding agrees with previous theoretical studies about the adsorption of halogen atoms on Ag(100) which find the hollow site as the energetically more favorable one [28, 97–100]. Furthermore, as it was shown in section 4.3, DFT calculations also predict the hollow site as the most favorable position of a fluorine atom adsorbed on Ag(100), which confirms the outcome of the split-image method.

The apparent STM morphology of isolated F adatoms on the surface strongly depends on the bias voltage, V_B . Panels (a)-(h) in Fig. 4.7 show consecutive images of the same isolated F adatom measured with tunneling bias ranging from -1 to 1 V and a tunneling current of $I_T = 750$ pA. The STM apparent shape of F adatoms is a *sombbrero* when $V_B < 0.75$ V and becomes a depression at 1 V.

At low tunneling currents, the STM topographic images show the same qualitative behavior but the threshold voltage for the disappearance of the *sombbrero* feature decreases. Fig. 4.9 shows a sequence of topographies measured at 10 pA. The appearance of an isolated F adatom on Ag(100)

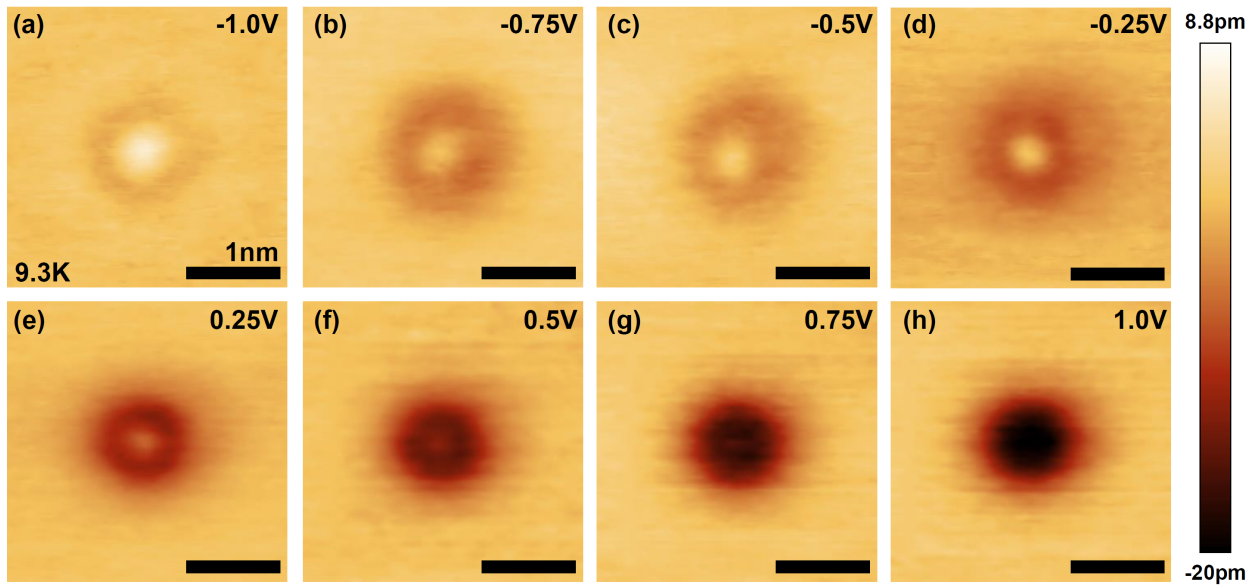


Figure 4.7: (a)-(h) STM images of the same F adatom on Ag(100) as a function of the bias voltage. The images were acquired at 9.3 K for an exposure time of 3 h. The tunneling conditions were set at 750 pA and $-1 \leq V_B \leq 1$ V. In all panels, the scale bar is 1 nm.

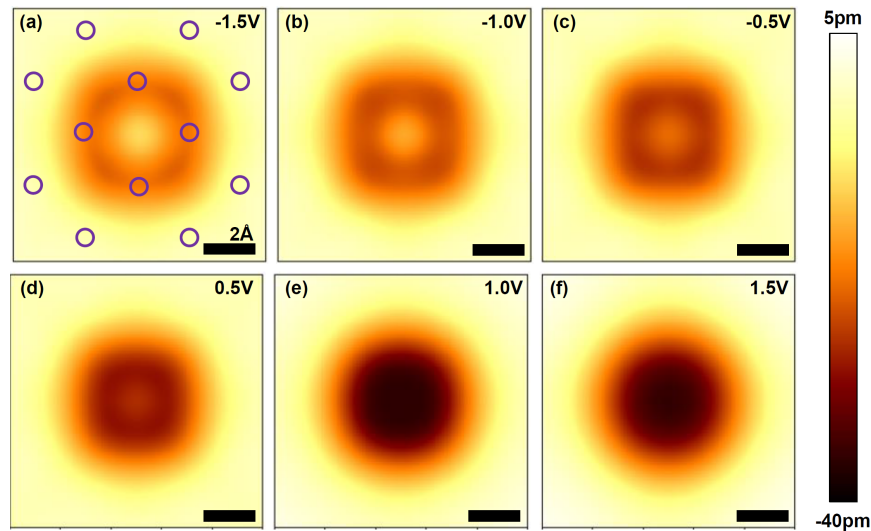


Figure 4.8: (a)-(f) Simulated STM topographies using DFT and the Tersoff-Hamann approximation for a F adatom in the hollow position of the Ag(100) surface. The simulated tunneling conditions: $-1.5 \leq V_B \leq 1.5$ V and a tunneling current of 5×10^{-7} a.u., corresponding to 3.3 nA. The superimposed purple circles on panel (a) correspond to the positions of silver atoms on the surface of the slab. Each panel's scale bar corresponds to 2 Å.

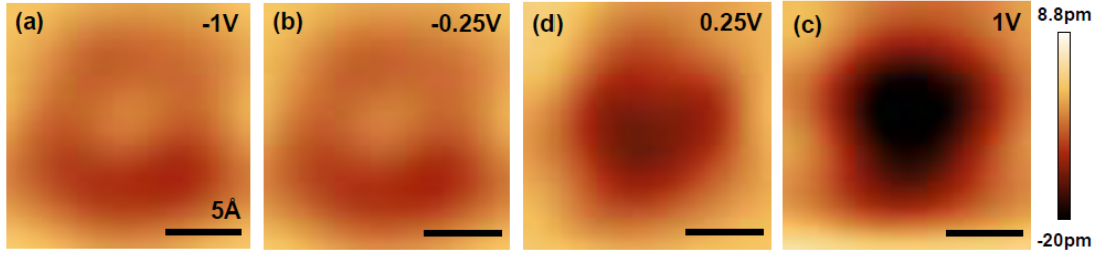


Figure 4.9: STM images of a fluorine adatom on Ag(100) after 3 hours fluorination experiments. Tunneling conditions: $-1 \leq V_B \leq 1$, 10 pA at 9.4 K. The scale bar corresponds to 5 Å in each panel.

surface changes from sombrero to depression when V_B is increased from negative to positive values. This behavior contrasts with the one observed in Fig. 4.7, where the F adatom is detected as a sombrero even for $0 < V_B \leq 0.75$ V.

To further confirm the experimental adsorption site assignment, the ATs of fluorine were simulated using DFT for various values of V_B (Fig. 4.8). Although fluorine was the dominant species in the fluorine-rich atmosphere of the reaction chamber, other gases, such as HF (at an order of magnitude lower pressure), are also presented. The comparison between experimental and simulated ATs provides additional evidence that the observed adatoms are fluorine.

Comparing Fig. 4.8 and Fig. 4.7 one can see that simulated ATs for F-adatom placed in the hollow site resemble very well experimental data. Simulated ATs are spherically symmetric as well as experimental ones, the trend to change the shape from sombrero to pure depression with an increase of V_B is observed in both cases.

The shape change is more evident by looking at the cross-sectional height profiles of the STM pictures in Fig. 4.10 (panel a). At $V_B = -1.0$ V, the apparent height profile shows the sombrero shape with a maximum in the apex, which protrudes out from the Ag surface (zero level in the apparent height of the topographies). It can be seen that, as V_B is increased, the height of the central protrusion of the sombrero is continuously reduced as well as the depth of the two depressions at each side of the central protrusion, until the sombrero feature is lost, resulting in a smooth depression at 1.0 V.

It is very interesting to compare experimental profiles with ones that can be derived from simulated AT. Indeed, cuts of the AT height profiles parallel to the horizontal axes were done to obtain theoretical cross-sectional profiles (Fig. 4.10 (panel b)). A clear sombrero-shaped AT is observed for negative bias with the apex of the sombrero suppressed as the bias increases. The "critical" value $V_B = 1.0$ V when central protrusion vanishes, transforming all the profile into a single depression exactly matches the one found experimentally. With a further increase in bias voltage (beyond the range studied experimentally), the depth of the depression decreases.

Overall, as one can see in Fig. 4.10 experimental and theoretical results don't match exactly for the chosen value of bias, but this wasn't expected due to limitations of the theoretical calculations. Indeed, Kohn-Sham [101] DFT maps the system to a non-interacting problem that has the same electronic density as the interacting one. In contrast to the density, the Kohn-Sham energies are auxiliary quantities without a priori correspondence to the binding energy of interacting quasiparticles. Typically, due to interactions, experimental quasiparticle bands are narrower than Kohn-Sham

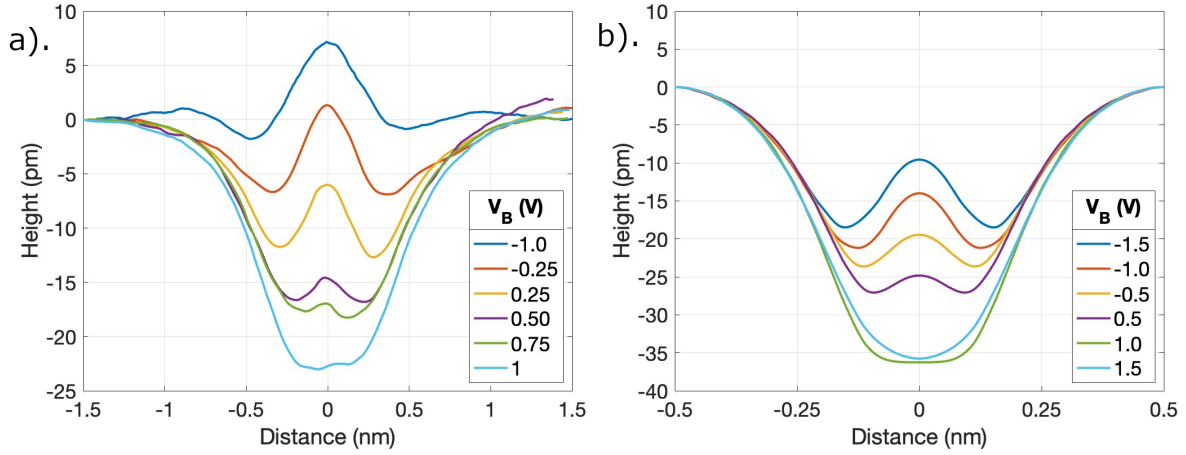


Figure 4.10: a) Cross-sectional height profile of the F atom in panels (a) to (h) in Fig. 4.7, evidencing the change in the apparent height as a function of V_B . b). Height profiles of F atoms for the studied bias values were computed as the cuts of simulated AT. The profiles were taken parallel to the horizontal axis of the topographies, crossing over the F adatom, with the reference value for the apparent height of the tip taken at the leftmost extreme of the profile curve. These reference values range from 3 to 5 Å, which compares well with typical distances for tunneling conditions. The DFT results are taken from [28]. Notice the very different absolute apparent height and width of the two structures. These problems are discussed in the main text, in particular in connection with Fig. 4.15.

bands. Therefore, we expect bias voltage magnitudes to be moderately overestimated in DFT. This may explain why for negative bias the protrusion appears less developed in the theory than in the experiment (a more negative theoretical bias is needed to match the experiment). For $V_B = 1.0$ V, both theory and experiment show a pure depression, suggesting this discrepancy is smaller.

While the behavior of the experimental STM ATs as a function of the bias voltage is well reproduced, we observe that the depth of the feature is overestimated, and its width is underestimated by approximately a factor of 0.5. This discrepancy can be attributed to the inherent simplifications in the Tersoff-Hamann approximation: *i)* the tip is modeled as a spherical s -wave, which may not accurately represent the tungsten tip used in experiments. In fact, the tip itself may have a silver termination due to a precedent contact with the surface. *ii)* states are assumed to be unaffected by the tip potential, whereas, in reality, the electronic cloud around fluorine can polarize substantially depending on the tip polarity [62]; *iii)* DFT maps the interacting problem to a non-interacting one, and using non-interacting wave functions and eigenvalues to model the tunneling conductance can be a crude approximation; *iv)* lateral resolution issues can also affect the apparent width and depth of the features. This issue will be further discussed in connection with the Ag(110) surface in Fig. 4.15 below.

It was also found in the DFT computations, that for an adsorbate in the bridge position, the sombrero shape of the AT is observed across the entire range of experimental current and bias voltage (not shown). This contrasts with the experimental findings, which show a depression AT for positive bias. Specifically, the depression was observed for bias values larger than 0.5 V and tunneling currents lower than 662 pA. These results further confirm that the observed AT corresponds to the hollow site.

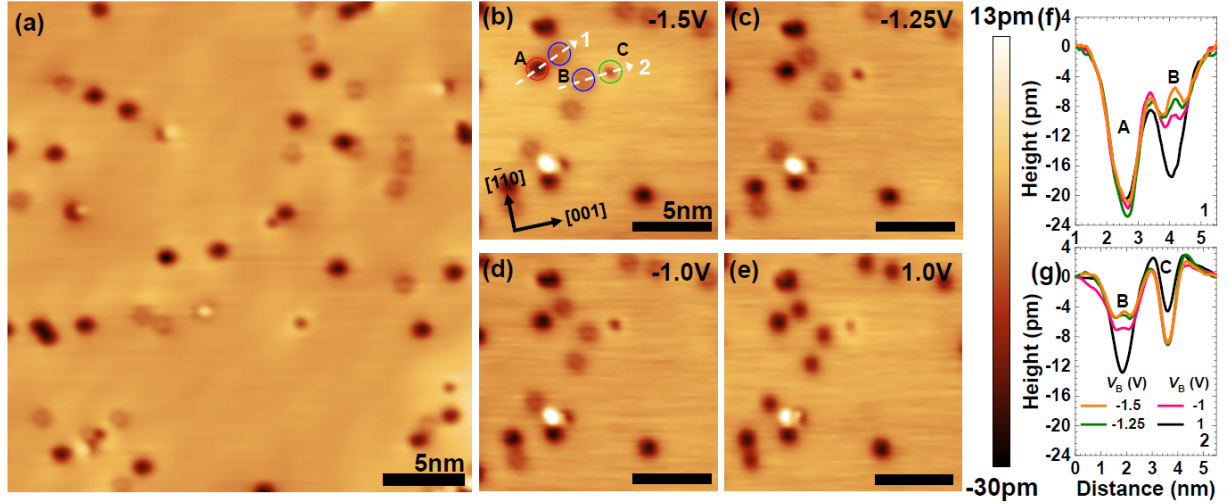


Figure 4.11: (a)-(e) STM image of the Ag(110) surface acquired at 9.3 K after exposure to a fluorine-rich atmosphere for 45 minutes. The tunneling conditions were set to $V_B = -0.5$ V and 80 pA in panel (a). The tunneling current was set to 35 pA and V_B varies from -1.5 to 1 V. The scale bar corresponds to 5 nm in all panels. Blue, red, and green circles in panel (b) highlight the different features observed in STM topographies at negative bias voltages. (f)-(g) Height profiles for different V_B values acquired along the white dashed arrows 1 and 2 indicated in panel (b), respectively. Letters A, B, and C in these panels indicate the different species indicated in panel (b).

4.6.2 Fluorine adatoms on the Ag(110) surface

As already discussed in Sec. 4.2, the Ag atoms on the (110) surface form a rectangular unit cell, as highlighted by a red frame in the schematic shown in Fig. 4.12 (a). The lateral dimensions of the unit cell are $b = 4.08$ Å and $b' = 2.89$ Å. This geometry presents four possible high-symmetry adsorption sites: hollow, top, short bridge, and long bridge. According to DFT calculations, the hollow and both bridges sites (short and long) are the most energetically favorable for F adatoms (see Fig. 4.2), with comparable adsorption energies, while there is a significant energy penalty for the top position [28, 88].

After exposing the Ag(110) crystal to the fluorine-rich atmosphere for 45 minutes, the surface results in being covered by adsorbates exhibiting different apparent topographies (Fig. 4.11 (a)). In Figs. 4.11 (b)-(e), the same area was measured using a tunneling current of 50 pA and voltage bias in the range $-1.5 \leq V_B \leq 1$ V. Specifically, three distinct types of apparent topographies are identified and marked in Fig. 4.11(b) as type-A (red circle), type-B (blue circles), and type-C (green circle). The bright-contrast feature in the bottom left part of the image is not considered as it appears rarely, thus, it is not statistically relevant. Height profiles for these adsorbates, recorded at different bias voltages along the lines indicated by the white arrows in panel (b), are shown in panels (f) and (g).

Type-A adsorbates appear as depressions, with their apparent shape largely independent of bias over the presented range ($-1.5 \leq V_B \leq 1$ V), (Fig. 4.11 (f), left feature). Type-B adsorbates (right and left features in Figs. 4.11 (f) and (g), respectively) exhibit a sombrero shape at negative bias, that is lost at $V_B = 1.0$ V. Type-C adsorbates are detected as depressions surrounded by a brighter halo, resulting in a distinctive volcano-like profile, with a central minimum and two lateral local maxima (right feature in Fig. 4.11 (g)). For $V_B < 0$, the depth of the depression and that of the

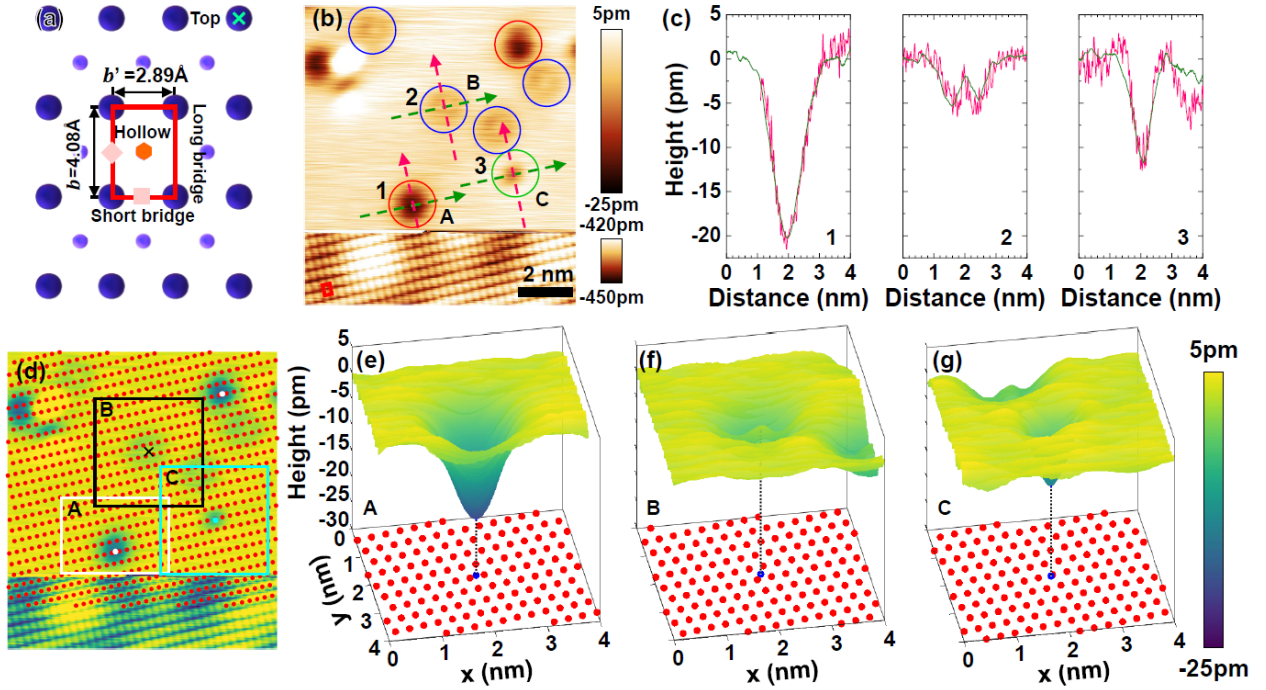


Figure 4.12: (a) Schematic representation of the first two surface layers of Ag(110). Large spheres represent surface atoms, while small spheres depict atoms in the subsurface layer. The red rectangle outlines the unit cell of the surface. Lattice parameters, denoted as b and b' , were determined from XRD patterns, reported in Sec. 4.2. The four primary high-symmetry adsorption sites are indicated: hollow (hexagon), shortbridge (square), long-bridge (rhombus) and top (cross). (b) STM image showing some adsorbates in the top part and atomic resolution of the Ag(110) surface in the bottom part, acquired at $V_B = -0.01$ V. The tunneling current was set to 0.1 and 1.0 nA in the top and bottom parts, respectively. The green and pink dashed arrows indicate the directions along which the height profiles shown in panel (c) were taken. (d) Flattened topography of the same region shown in panel (b), optimized for better visualization. Red dots mark the positions of surface silver atoms, while white circle, black cross, and cyan circle indicate the centers of a type-A, type-B, and type-C adsorbates, respectively. The areas marked by the colored frames A, B, and C are as 3D renderings in the panels (e), (f) and (g), respectively. In each plot, a blue dot at the bottom highlights the position of the corresponding adsorbate. Data is from 45 min fluorination experiment

surrounding region remain unchanged, but both of them increase at $V_B = 1.0$ V. At $V_B > 0$, type-A adsorbates have the deepest height (-24 pm), followed by the type-B (-16 pm), and type-C (-4 pm), as shown in Figs. 4.11 (f) and (g). However, for $V_B < 0$, type-C adsorbates appear deeper than type-B due to the central protrusion of the sombrero-shaped type-B feature.

To find the position of the adsorbates we used the same split image method as in the (100) case with two parts of the same image taken at different tunneling currents as shown in Fig. 4.12(b). In the top part of the topography, the three types of adsorbates are identified and marked: A (red circle), B (blue circles), and C (green circle). Since this image was acquired at $V_B < 0$, type-B adsorbates appear with a sombrero shape, while type-A and type-C adsorbates are observed as depressions with different depths. The deepest point for type-A and type-C adsorbates and the apex in the center of type-B adsorbates were determined from the left, right, and center height profiles in Fig. 4.12 (c), respectively, and taken as the position of the adsorbates.

To determine the position of the Ag surface atoms in the top part of the image, the lattice observed in the bottom part was reproduced and marked with red dots in Fig. 4.12 (d). In this panel, the positions of the centers of type-A, type-B, and type-C adsorbates, as extracted from the

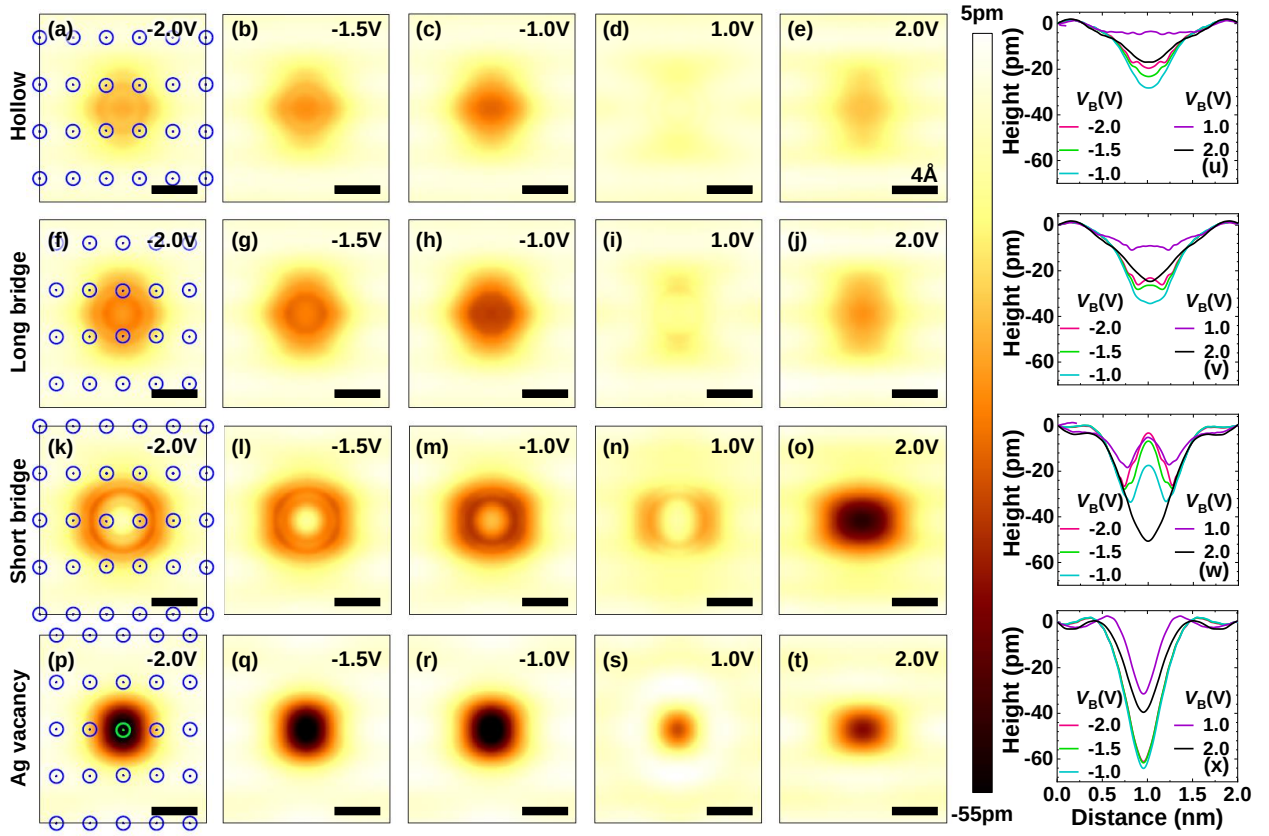


Figure 4.13: STM topographies simulated using DFT and the Tersoff-Hamann approximation for the Ag(110) surface for a fluorine adatom in the (a)-(e) hollow, (f)-(j) long-bridge, (k)-(o) short-bridge positions, and (p)-(t) F adatom on a surface Ag vacancy. The scale bar corresponds to 4 Å in each panel. The bias voltage values range from -2 to 2 V with a current of 1×10^{-8} a.u., corresponding to 66 pA. Blue circles overlaid on panels (a), (f), (k) and (p) indicate the positions of the silver atoms on the slab surface while the green circle in (p) indicates the substituted atom. The right-hand side panels display the corresponding profiles taken along diagonal lines with equal horizontal and vertical coordinates ($x = y$), passing through the fluorine position. We set the zero value for the apparent height of the microscope tip at the point in this line with the largest separation from the F adatom and its image in the neighboring supercells.

line profiles in panel (c), are visible as white dots, a black cross, and a cyan dot, respectively. This arrangement is better visualized in the three-dimensional representations displayed in Figs. 4.12 (e)-(g), and corresponds to the framed areas reported in panel (d). Here, the blue dot marks the position of each adsorbate, while the dashed line serves as a guide to the eye, projecting this position onto the Ag(110) surface atomic plane (red dots). This analysis suggests that type-A adsorbates are located at the short-bridge sites on the Ag(110) surface, type-B at the hollow sites, and type-C at the top sites. Unfortunately, due to the low statistical frequency of type-C adsorbates, the reproducibility of this analysis could not be checked. Also, the spatial resolution achieved in these measurements is not as good as in Fig. 4.6(c). Therefore, these should be considered preliminary results that need further confirmation.

Comparison with DFT results

A statistical analysis performed on several STM images reveals that the AT(A) adsorbates are the most abundant (60%), followed by AT(B) (35%), while AT(C) adsorbate is the least frequent, with

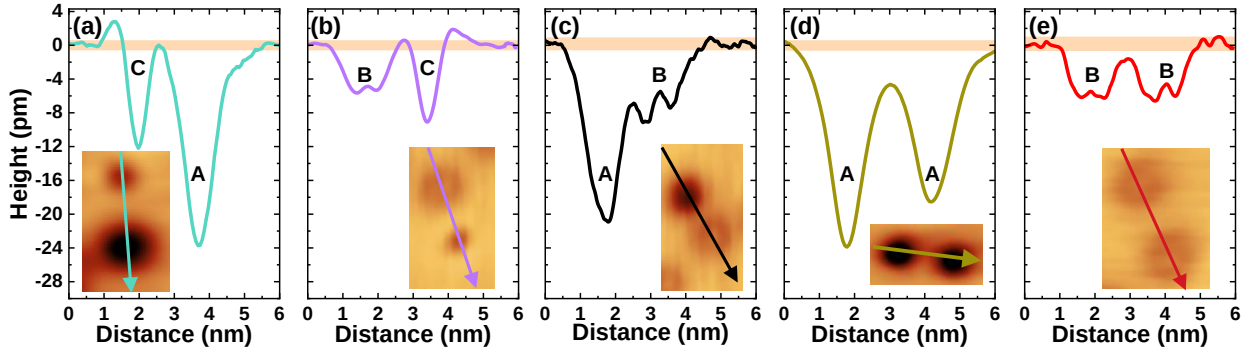


Figure 4.14: (a)-(e) Height profiles for different pairs of adatoms detected on the Ag(110) fluorinated surface. The profiles were acquired along the direction indicated by arrows in the STM image in each panel. Letters A, B, and C in these panels indicate the species of F observed adatoms. The dashed line indicates the zero level corresponding to the Ag surface and the highlighted region indicates the height values comprised between the maximum and minimum height values of Ag atoms. For all images $V_B = -1.5$ V. Data corresponds to 45 min experiment.

only 5% of relative abundance (here type of adsorbate is associated with the correspondent AT). Assuming as an order of magnitude that these experimental frequencies reflect thermal populations at room temperature we can write the population ratio in terms of the Boltzmann factors, for example for N_A and N_B populations we can write, $N_B/N_A = \exp[-(E_B - E_A)/(k_B T)]$. This allows us to estimate the difference in energy between two adsorbates $E_B - E_A$ by knowing the population ratio N_B/N_A . Using these considerations we obtain adsorption energy differences $\lesssim 60$ meV, of the same order as the energy difference found in DFT for the more stable adsorption positions, $\Delta E_{ad} \sim 90$ -140 meV as reported in Sec. 4.3. This assumes that the populations are established at room temperature during fluorine exposure and then are quenched rapidly to the temperature of the STM experiment, 9K. However, the populations may continue to evolve during cooling so the population estimate of the energy differences should be considered as an upper bound.

It is natural to assign the experimental ATs to the three more stable locations in DFT which are also close in energy (Fig. 4.2, (b)). Figure 4.13 shows the simulated ATs (first three rows). Comparing the profiles in the experiment and the theory (right panels in Fig. 4.13) and using the depth of the wells as a criterion AT(A) would be attributed to the short bridge, AT(B) to the long bridge and AT(C) to the hollow site. Assuming the lowest energy adsorbates would show the higher frequency leads to the same assignment.

This DFT assignment for AT(A) is in good agreement with the experimental finding made by the split-image method (both point to the short bridge), but for other adsorption sites, there is a contradiction between simulation and experiment. As it was discussed before in this section the second more abundant location AT(B) experimentally was assigned to the hollow site, and the relatively more favorable long bridge was not found. Instead, AT(C) was assigned to the top site which in DFT computations has significantly more energy [c.f. Fig. 4.2 (b)].

More insight can be obtained by comparing the topographies. The simulated AT for voltage biases ranging from -2 to 2 V and a tunneling current of 66 pA are presented on the left side of Fig. 4.13. While all sites exhibit a depression for all voltages shown, in the case of the long and short bridges, a protrusion appears at the depression's center for negative bias, giving the sombrero shape.

Among the three energetically more favorable locations, the short bridge has the deepest depression which is in agreement with the experimental assignment to the AT(A) having the deepest depression in the experiment (Fig. 4.14 shows experimental cross-sectional profiles, acquired over all possible different pairs of adatoms). On the other hand, the protrusion is not present in the experimental AT(A). For the hollow site, the well has a smaller depression in partial agreement with the experimental AT(B). Regarding the protrusion, the situation is reversed: it appears in the experimental AT(B) but not in the theory for the hollow site.

A simplified orbital model presented in Ref. [28] assigned the protrusion to the occupied F $2p$. Indeed, fluorine becomes a closed-shell system once it is allowed to oxidize the silver. Then the $2p$ state should be filled and at negative energies with respect to the Fermi level explaining the appearance of the protrusion mainly at negative voltages.

The model shows also that the protrusion is very sensitive to the competing role of F $2p$ and Ag $5s$ states. Its presence or absence depends on factors such as the relative strength of the symmetry-projected Density of States (DOS) in these channels, and the difference in decay length between F $2p$ and Ag $5s$ orbitals near the Fermi level. These aspects are susceptible to errors in DFT calculations. In contrast, according to the model, the depth of the depression is mainly determined by the oxidation state of the Ag atoms surrounding the central F atom. This feature is more robust in DFT given that the density plays the central role in this technique. Therefore, we find the assignment of the AT(A) and AT(B) to the short bridge and the hollow site, respectively, as compatible with the theory. The depth of the depression (excluding the protuberance) is overestimated, which we attribute again to the simplifications of the Tersoff-Hamann approximation and lateral resolution effects.

It remains to assign the less abundant AT(C). A plain top position would require a topography with a large protuberance for positive bias. For example, for a bias voltage $V_B = -2$ V and current as in Fig. 4.13, the computations predict a protuberance of 40 pm above the silver level (not shown), which is incompatible with the experimental observation of depressions for all ATs. This, together with the high energy cost [Fig. 4.2 (b)] allows us to exclude a simple top position.

Another possibility is that AT(C) corresponds to an exchange reaction (Sec. 4.3.3). The energy penalty is even larger than for fluorine on a top position [Fig. 4.2 (b)]. A third possibility is that F atoms fill already present vacant sites. Since the number of these sites is a small fraction of a small coverage, a tiny number of vacant sites would be enough to explain the observed abundance (of the order of $1/5000$ fraction of vacant surface sites). However, filling these sites is still not more favorable energetically than the three previous sites [see orange hexagon in Fig. 4.2 (b)].

Whether the vacancy was already present or not, the final configuration is the same. The last row in Fig. 4.13 shows the ATs for this final configuration. Interestingly, the experimental AT shows a rim around the depression (volcano shape) for the positive voltage, which is well reproduced by the theory [panels (s), (t), and (x)]. There are also other striking similarities between theory and experiment: for negative bias voltage, the depth of the ATs remains without significant changes, while for positive bias the well rises rigidly, enhancing the rim of the volcano [Fig. 4.11].

Unfortunately, the experimental AT(C) corresponds to the smallest depression for negative bias, while the theoretical one is the deepest. This is due to the depression being mainly determined by the silver $5s$ states, which here are retracted due to the vacancy.

Adding lateral resolution effects (which may also simulate a non-spherical tip) improves the

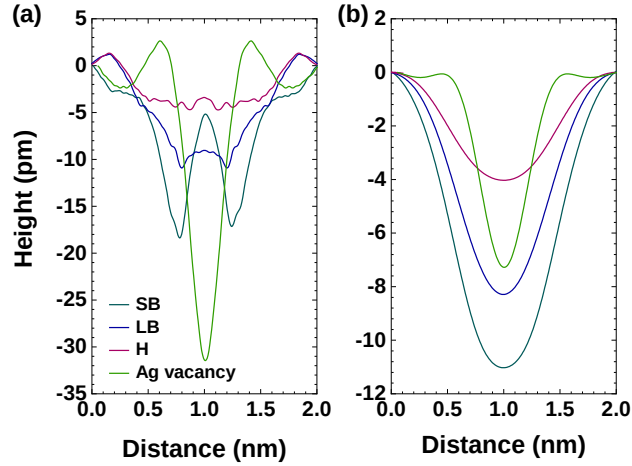


Figure 4.15: (a) Height profiles for a bias voltage of 1.0 V and the four studied locations: short bridge (SB); long bridge (LB); hollow (H) and Ag vacancy, taken as in Fig. 4.13. (b) The same profiles after convoluting with a two-dimensional Gaussian with a FWHM of 4.7 Å.

agreement. As an example, Fig. 4.15 compares the height profiles as resulting from the computations (a) and convoluting with a two-dimensional Gaussian with full width at half maximum (FWHM) of 4.7 Å (b). Several features improve the agreement with the experiment: i) Wells become shallower and wider. ii) The vacancy location (green) has a smaller well than the short bridge. iii) The short bridge loses the sombrero feature. Similar improvements are obtained for the Ag(100) case without fully losing the sombrero feature (not shown). On the other hand, for bias voltage -1.5 V (not shown), the vacancy still shows the deepest AT and the short bridge keeps the sombrero feature which contradicts the experiment. This problem casts doubts on the assignment of AT(C) to a fluorine substitution. Furthermore, it remains unexplained why the long bridge is not observed despite being energetically more favorable than the hollow site. Another possibility is that additional adatoms such as hydrogen or sulfur¹ are playing a role. More experimental and theoretical work is needed to resolve this issue.

4.6.3 Estimation of sticking coefficient

Following the definitions given in 4.2 coverage θ can be computed as

$$\theta = \frac{N_F}{N_H} = \left(\frac{N_F}{A} \right) a^2 = n a^2 \quad (4.10)$$

where N_F is the number of F adatoms on the area A and N_H is the number of hollow sites available for absorption (or any other type, say top). a^2 is the unit surface area and $n = \frac{N_F}{A}$ the two-dimensional density of fluorine adatoms. The surface area A was computed as a L^2 , where L is the apparent lateral scan size. The apparent Ag lattice constant $\tilde{a}$ was derived from STM measurement of the clean silver surface using Gwyddion software. It was found $\tilde{a} = 2.5\text{Å}$, which differs from a reference value $a = 2.89\text{Å}$ [95], because of distortion of the image acquired by STM and systematic calibration errors (the choice of unit surface area schematically shown in Fig. 4.16).

It is often assumed that one Langmuir corresponds to the completion of one monolayer; how-

¹We are in debt with Prof. Karina Morgenstern (Ruhr-University of Bochum) for pointing out this possibility given the difficulty to completely eliminate sulfur from silver crystals.

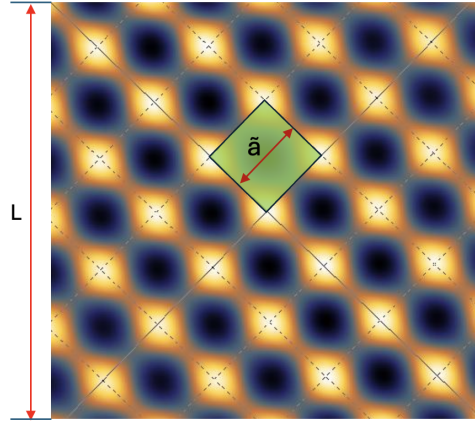


Figure 4.16: STM scan of Ag(100) surface, where L is the apparent size of the scan with correspondent area $A = L^2$ and $\tilde{a} = 2.5 \text{ \AA}$ is the apparent lateral size of the unit surface area (marked as a green rectangle), instead of the known value of $a = 2.89 \text{ \AA}$ [95]. As explained in Sec. 4.6.3, apparent sizes are raw STM data without an accurate calibration.

ever, this is correct as an order-of-magnitude estimate. A more precise estimate can be obtained by computing the flux arriving at the surface, which, according to the kinetic theory of gases, is given by[102]:

$$F = 3.51 \times 10^{22} P / (TM)^{1/2} \quad (4.11)$$

where P is the pressure in torr, T the temperature in K and M is the atomic or molecular weight in amu ($M = 19$ for F). For a pressure of 10^{-6} torr we get, $F = 4.7 \times 10^{14} \text{ cm}^{-2}\text{sec}^{-1}$. Multiplying by 1 sec, we obtain that 1L of dose, and assuming a sticking coefficient of 1, yields a surface density of $4.7 \times 10^{14} \text{ cm}^{-2}$. Dividing by the density of hollow sites, $1/(a')^2 = 1.2 \times 10^{15} \text{ cm}^{-2}$ we obtain that the theoretical coverage of a dose of 1L of monoatomic F over Ag(100) for a sticking coefficient of one is, $\theta_{1L} = 0.4$. Then, the actual sticking coefficient can be computed as

$$S = \frac{\theta}{0.4D} \quad (4.12)$$

where D is a dose in Langmuir units.

In general, the sticking coefficient depends on the coverage θ . We are interested in the sticking coefficient at zero coverage S_0 . To estimate its value, we choose experiments with the lowest possible coverages. This has the advantage that adatoms are well separated on the surface and can be easily identified and counted.

For Ag(100) we took a run with 2 hours of exposure to the fluorine-rich atmosphere starting from a clean surface ($D = 70 \text{ L}$). For Ag(110) we choose a 45 min experiment ($D = 20 \text{ L}$). For the images, we took several scans with various sizes. When an Ag-step was found within a scan, we noticed that F atoms were repelled from the step. To approximately take into account this effect, the total area was reduced by subtracting a stripe of $\sim 10 \text{ nm}$ times the length of the side more parallel to the step (Fig. 4.17).

These simple estimates indicate that both surfaces exhibit a very low sticking coefficient when exposed to monoatomic Fluorine, ranging from 10^{-4} to 10^{-5} , depending on the surface (Tab. 4.2). From previous results from other halogens, one expects that applied doses in the range of 10 Langmuir should lead to the formation of at least one monolayer on the surface. On the contrary, for

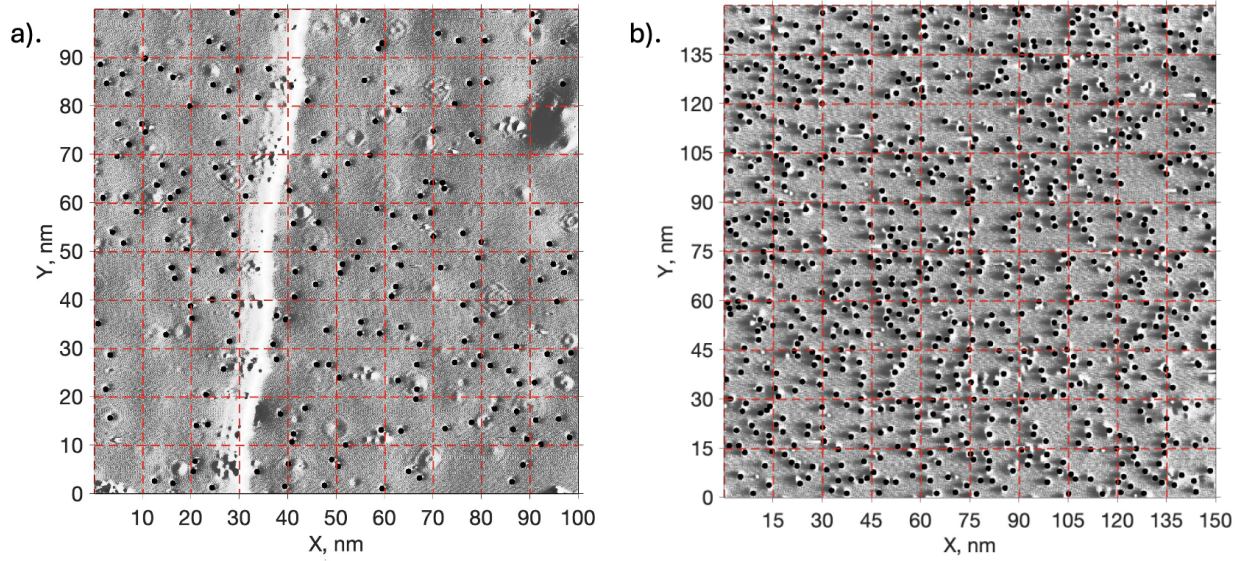


Figure 4.17: STM scans with F-adatoms depicted as black dots. (a) Ag(100) surface after 2 hours of exposure to the fluorine-rich atmosphere (70L, $\theta = 0.001$). Apparent scan size 100nm $\times$ 100nm, with 199 adatoms found. Notice the Ag step with $\sim$ 10nm width. (b) Ag(110) surface after 45 min (20L, $\theta = 0.002$) of exposure to fluorine-rich atmosphere. Apparent scan size 150nm $\times$ 150nm, with 827 adatoms found

Ag-surface	Number of adatoms	Apparent scan size (nm $\times$ nm)	Density (nm $^{-2}$)	Coverage ML	Sticking coefficient
100	57	50 $\times$ 50	2.3×10^{-2}	0.0015	7.0×10^{-5}
	110	75 $\times$ 75	2.2×10^{-2}	0.0012	6.0×10^{-5}
	199	100 $\times$ 100	2.3×10^{-2}	0.0012	6.0×10^{-5}
110	150	50 $\times$ 50	6.0×10^{-2}	0.0038	4.8×10^{-4}
	226	75 $\times$ 75	4.0×10^{-2}	0.0025	3.1×10^{-4}
	683	100 $\times$ 100	6.8×10^{-2}	0.0043	5.4×10^{-4}
	827	150 $\times$ 150	3.7×10^{-2}	0.0023	2.9×10^{-4}

Table 4.2: Estimation of coverage and sticking coefficient values. For Ag(100) surface data is from 1.9 hours experiment ($D = 70$ L), and for Ag(110) - from 45 min ($D = 20$ L). The lengths and the density are not corrected for calibration errors, but the sticking coefficient is independent of such errors.

both surfaces, coverages were found in the range of 10^{-3} ML for exposures up to 100L.

4.6.4 Possible explanations of the anomalously low sticking coefficient

The small value of the sticking coefficient is quite surprising, as halogens are generally expected to exhibit large sticking coefficients, typically around one, as mentioned in the introduction. Previous experiments[64] with XeF₂ do not report such a small sticking coefficient. This suggests that atomic and molecular adsorption can be qualitatively different.

Thanks to the fluorination chamber developed in Chapter 3.2, the present study is quite unprecedented. We are not aware of previous studies on fluorination with atomic fluorine on transition metals; therefore, no data are available for comparison.

At the same time, the difference in behavior between molecular and atomic fluorine can be an important clue to understanding the apparent discrepancy with precedent studies. At first glance, the difference makes the result even more puzzling. Thermodynamically, atomic fluorine should

be more reactive than the molecule: according to DFT computations, the adsorption energy per atom for atomic fluorine is $|E_B| = 4.2$ eV (Fig. 4.2), while the bond cleavage cost for F_2 is 1.6 eV. As a comparison, low values of the sticking coefficient are typical for the adsorption of molecular oxygen on metallic surfaces. For example, for O on Ag, the initial sticking coefficients were found in the range of 10^{-4} - 10^{-6} [103–105]. Such low values are understood because the experiments have been done with molecular oxygen O_2 , which adsorbs dissociatively at room temperature (300K). Such a process requires cleaving the molecular oxygen bond, which takes ≈ 5 eV. This affects the sticking coefficient because it reduces the thermodynamic drive of the reaction and creates a barrier for adsorption. The first effect was already discussed by comparing atomic fluorine and molecular fluorine in Fig. 4.4.

This explanation does not apply to the current experiment, because only atomic fluorine was found during the experiments (with no traces of molecular F_2 gas). Since the cleavage cost is not paid in the case of atomic adsorption, the thermodynamic drive should be larger than if molecular fluorine were used. Furthermore, the lack of a cleavage cost should make the adsorption barrierless.

An important difference which may help to explain the paradox is that the molecule offers many more degrees of freedom to dissipate the excess energy released upon adsorption, for example, the "fly" of hot atoms in the surface and atom abstraction, which are exemplified in the following. The phenomenon of transient "hot" motion is discussed in detail in the Appendix A and refers to dissociative adsorption of molecular gases on metallic surfaces.

For the adsorption of monoatomic fluorine on silver, in the absence of a partner, momentum conservation parallel to the surface would make the conversion of the adsorption energy into kinetic energy much more difficult, which may be an important ingredient to explain the different sticking coefficient of molecular and atomic adsorption.

Atom abstraction occurs on a diatomic gas when one atom of the molecule is adsorbed while the other atom is ejected carrying the excess energy. This process is known to occur in the case of silicon exposed to diatomic fluorine [106], and clearly it is not available in the case of a monoatomic gas.

The condition to get trapped by the potential of the surface is to dissipate the initial thermal kinetic energy of the fluorine (mass m) due to the velocity $v_\perp$ perpendicular to the surface, $\epsilon_T = m\langle v_\perp^2 \rangle / 2 = k_B T / 2 \approx k_B T / 2 \approx 13$ meV. How this occurs depends on the available excitations on the surface (phonons, particle-hole excitations) and the coupling of the incoming particle to the excitations.

The energy transferred to the surface lattice degrees of freedom, $\delta\epsilon$, can be estimated with a simple model due to Baule (see Ref. [107] and references therein). One assumes that the particle with incoming velocity perpendicular to the surface and kinetic energy ϵ far from the surface collides with only one atom of the surface with mass M .

For a particle with kinetic energy ϵ , associated with the motion perpendicular to the surface and the substrate at zero temperature, this simple model yields,

$$\delta\epsilon = \frac{4m/M}{(1 + m/M)^2} (\epsilon + |E_B|). \quad (4.13)$$

If the substrate is at finite temperature, the Baule formula becomes[107],

$$\delta\epsilon = \frac{4m/M}{(1 + m/M)^2}(\epsilon + |E_B| - k_B T/2). \quad (4.14)$$

Therefore, for a particle with thermal energy, the term ϵ_T cancels and the energy threshold for adsorption becomes

$$\delta\epsilon_0 = \frac{4m/M}{(1 + m/M)^2}|E_B|. \quad (4.15)$$

When $\epsilon_T < \delta\epsilon_0$, the energy loss in the collision is larger than the initial thermal energy, and adsorption occurs. Otherwise, the particle bounces back and thermalizes again with the gas.

Despite the small fluorine to silver mass ratio $m/M = 19/109$, for $|E_B| = 4.2$ eV one obtains $\delta\epsilon_0 = 2.1$ eV $\gg \epsilon_T$. Therefore, this model predicts that the sticking coefficient should be large. The Baule model, however, is considered as an upper bound[107] for the energy transfer since in reality the target is not a single silver atom but many interacting atoms.

Once the fluorine atom is trapped, it has to dissipate also this huge energy. If associated with one degree of freedom, it corresponds to a temperature of nearly 50000K. Of course, this energy will be distributed among several degrees of freedom available on the surface as phonons and particle-hole excitations. In any case, one can assume that there will be a strong local heating. One possibility is that this creates a temporary exclusion zone for other fluorine atoms to get adsorbed leading to a decrease of the sticking coefficient.

Another possibility, similar to atom abstraction, is the ejection of a silver atom. This would be essentially an elementary corrosion process. This is possible in principle as the atomization energy of silver (or the enthalpy of vaporization, ≈ 3 eV) is less than the energy that has to be dissipated, $|E_{ad}^{(a)}| + 3k_B T/2 \approx (4.2 + 0.39)$ eV. However, this requires the adsorption to happen near the kink of a step[89], otherwise the cost to extract the Ag atom would be higher. Since the density of these defects is small, it is unlikely that this plays a crucial role. A related process is that an AgF molecule is ejected, which can also be seen as an elementary corrosion process. If this process becomes very likely, it can explain the low sticking coefficient. However, one would expect the appearance of a large number of defects on the surface that have not been found.

Even if the lattice is found to fail to dissipate the excess energy of the incoming fluorine atom, one should understand why the electronic degrees of freedom do not do the job. A process analogous to atom abstraction is electron ejection[108]. This is very unlikely for silver as its work function (4.6 eV) is larger or nearly the same as the total energy that has to be dissipated.

Still, internal electronic excitations are possible [109]. One possible explanation of why they are not efficient is the following. The rate of energy dissipation will be limited by the density of final states according to Fermi's golden rule,

$$W_{i \rightarrow f} = \frac{2\pi}{\hbar} |\langle i | H' | f \rangle|^2 \rho(E_F)$$

where the total decay probability will be given by a sum over all possible final states, and H' describes the perturbative effect of the adatom. We can therefore hypothesize that if the resident time of the adatoms in the potential well is too small, there will not be enough time to dissipate the thermal energy of the adatoms. Treating the adatom as a classical particle, it is easy to see that for a fixed width of the well, the residence time decreases as the well becomes deeper. This is

simple because the deeper the well, the higher the velocity of the particle in the well. Therefore, it can happen that for very deep wells, the residence time is too small and the fluorine bounces back elastically.

The mechanism of energy dissipation during adsorption is not yet well understood. Simulations performed within the framework of molecular dynamics (MD) and DFT [110–112] so far could demonstrate that the large interpair distances observed for O on Al(111) are possible only for hyperthermal oxygen adatoms. In all other cases, adatoms may travel distances not more than a few lattice constants, which does not agree with the experimental data in those systems.

The computation of the sticking coefficient is a very challenging task, but it would be very interesting to make a molecular dynamics simulation to understand the present discovery of an anomalously low sticking coefficient of fluorine in Ag and the strong failure of the Baule model. Since fluorine is the most reactive element in the periodic table, this is quite a fundamental problem.

4.7 Summary and conclusions

This chapter reports the experimental study of the early stages of silver fluorination on the (100) and (110) surfaces and the comparison of the results with DFT simulations.

Neglecting thermal effects on the silver surface, zero-temperature DFT computations of adsorption energies were used to estimate the fluorine pressure and temperature regimes to stabilize the different coverages and the bulk phases *at thermodynamic equilibrium*. At typical conditions of fluorine experiments, thermodynamics predicts bulk fluorinated phases. This doesn't occur in practice because of kinetic factors such as a small sticking coefficient combined with a finite exposure time. Even for much larger exposures, Mott-Cabrera barriers[94] would prevent the formation of bulk phases beyond a certain depth.

During experiments, silver crystals were exposed to a fluorine-rich atmosphere at room temperature for various periods (≤ 3 h). Subsequently, the samples were characterized at low temperatures using STM.

On the Ag(100) surface, only one type of adsorbate is observed. The F adsorbates were found to be located in the hollow position of the lattice thanks to a split-image method.

The apparent topography strongly depends on the tunneling conditions. For $V_B < 0$, the adsorbates appear as *sombreros*, meaning round protrusions surrounded by a circular depression. As V_B increases, the height of the *sombrero's* apex tends to decrease until it disappears, leaving only a depression in the topography. The *sombrero*-to-depression transition occurs at a positive bias voltage value that depends on the applied tunneling current.

These results are consistent with DFT studies [28], which predict the hollow adsorption site on this surface to be energetically the most favorable one for F adatoms. In addition, the ATs are also in good agreement with the theory except for small differences, which are expected within the approximations of the computations.

On the Ag(110) surface, adsorbates are detected with three different apparent topographies. Type-A adsorbates appear as depressions for the whole range of V_B studied, with a weak dependence on the bias voltage; type-B adsorbates exhibit a *sombrero*-to-depression transition as a function of V_B ; finally, type-C ones appear as round depressions surrounded by a bright halo, with its appearance only weakly affected by V_B .

Due to different experimental conditions, the spatial resolution was decreased, and the split-image method appeared less conclusive than for the case of fluorine in the (100) surface. The following tentative assignments were found: type-A adsorbates appear located at the short-bridge site, type-B at the hollow site, and type-C at the top site of the Ag(110) surface. The relative abundance of these three species is found to be 60% for type-A, 35% for type-B, and only 5% for type-C.

Computation of adsorption energies and simulations of the AT of fluorine in different high-symmetry locations partially agreed with these findings. The population ratios for adsorbates of various types are compatible with equilibrium Boltzmann factors at the room temperature of the exposure, with differences in energies of the order of $\lesssim 60$ meV in agreement with the DFT predictions.

Comparison of experimental profiles with ones obtained from simulated ATs partially verifies the experimental assignment for AT(A) and AT(B) to the short bridge and hollow site, with some important differences: i) The short bridge/AT(A) shows the deepest AT for negative bias, both in experiment and theory but shows the sombrero shape only in the theory. Its energy is the most stable one in DFT, compatible with the largest abundance in the experiment. ii) The hollow site/AT(B) is the third most stable location in DFT, but the second most abundant site in the experiment. It shows sombrero features in the experiments and not in the theory. iii) The long bridge, which is the second most stable location following DFT, was not found in the experiment.

AT(C) was found in the top position, which is the lesser favorable in DFT. Furthermore, the observed height of the AT is not compatible with what is expected for a fluorine in the top position. This suggests that AT(C) may originate in an adsorbate/site combination different from the F in the highly symmetric sites studied in DFT. The AT has remarkable similarities with the theoretical one corresponding to a fluorine adatom on a vacancy site of the surface. In particular, the volcano shape is reproduced. The similarities increase when lateral resolution effects are taken into account.

In general, the simulations underestimated the lateral size of the wells and overestimated the depth. This issue was attributed to the various simplifications of the Tersoff-Hamann approximation. Furthermore, lateral resolution effects, inherent to the tip shape, can play an important role in these problems. We hope that the present results will stimulate more theoretical and experimental work to shed light on the AT assignments for the (110) surface.

On both surfaces, a low density (<0.07 nm $^{-2}$) of individual adsorbates was observed for the exposure times of the experiment (less than 3 h). For Ag(100), coverages were found in the range of $\theta = 0.001 - 0.002$ ML, while for Ag(110) $\theta = 0.003 - 0.006$ ML. Surprisingly, it was discovered that the initial values of the sticking coefficients of monoatomic F on both surfaces is anomalously low ($S_0 \sim 10^{-5}$ for Ag(100) and $S_0 \sim 10^{-4}$ for Ag(110)). These values are subject to uncertainties as, for example, the initial pressure estimated in 10^{-8} Torr can decrease down to 20% during the exposure. However, such variations do not change the order of magnitude, which is sufficient for the discussion. The present results are unique as previous experiments have dealt with molecular gases. This provides important clues to understand the difference. We have discussed some possibilities to explain the anomalously small sticking coefficient. However, no satisfactory explanation exists for this very interesting result. Further theoretical and experimental investigations are needed to resolve this puzzle.

It is worth mentioning that this work reports the first STM investigation of the early stages

of fluorination of a transition metal, specifically Ag. In this context, and considering the recent interest in AgF_2 as a possible high- T_c superconductor [21], the rich dataset shown here is a valuable addition to current knowledge and will bolster additional studies on this topic.

Chapter 5

Fluorine overlayers studied by scanning tunneling microscopy

5.1 Introduction

In the previous Chapter, we studied the early stages of silver fluorination on the Ag(100) and Ag(110) surfaces, focusing on low coverages where interaction among fluorine adatoms can be neglected. Here, we extend this study for the same surfaces but for the regime where the interactions are important and new phases can emerge. We utilized the same technique, namely, a low-temperature UHV scanning tunneling microscope (LT-STM).

The two-dimensional (2D) phase diagram of adsorbates on surfaces exhibits a variety of phases. Some of these phases are analogous to the phases of atoms or molecules in three-dimensional space. Thus, adsorbed species can exist on surfaces in the form of 2D gases, liquids, or solids, with distinct structural phases emerging as a function of both temperature and surface coverage.

Many experimental techniques, including scattering and diffraction methods, have been employed to investigate phase transitions in such 2D systems [74]. Among these, scanning tunneling microscopy stands out for its ability to provide real-space imaging with atomic resolution. The main advantage of this method is that it is possible to track positions of individual adatoms and their spatial distribution [113]. STM allows direct visualization of ordered patterns and surface reconstructions.

It is interesting to compare STM with other techniques which in general give information in reciprocal space. For example, Low Energy Electron Diffraction (LEED) [114], which is widely used in this field, provides complementary information. LEED directly yields insights into surface symmetry and the size of ordered domains, typically in the 1–100 nm range, which are not always accessible by STM. Thus, while STM excels in detecting local variations, step edges, and point defects, LEED is more powerful in capturing long-range order and average structural properties.

Another important distinction concerns the timescale of the measurements. LEED patterns are recorded within seconds, effectively giving instantaneous snapshots of surface order on that time scale. STM images, by contrast, require sequential scanning and are acquired over minutes. As a consequence, STM is more suitable for tracking at most very slow dynamics of adsorbates, but it struggles to resolve processes on the scale of seconds.

Despite these limitations, STM remains uniquely suited for visualizing local equilibrium struc-

tures in real space. However, reactions at surfaces often occur at very high speeds, which makes it experimentally challenging to achieve sufficient temporal resolution, and in most cases, it is not possible at all. As a result, the acquired data typically represent snapshots between the initial and final states of the system. In the best-case scenario, one can observe average values of correlation functions between adsorbates over a period of time [115], but more commonly, only a few STM images are available before and after the transition. Therefore, it becomes impossible to reconstruct the full sequence of intermediate states through which the system evolves during a surface reaction. Because of these problems, in this chapter, we concentrate on equilibrium configurations, which are instead accessible to STM.

From a more theoretical perspective, when adsorbates are distributed randomly over available adsorption sites at low coverages (i.e., significantly less than one monolayer), the system is referred to as a *lattice gas*. As coverage increases, more complex behavior emerges. In particular, the adsorbates may self-organize into islands that eventually coalesce into a complete monolayer with internal order and high symmetry, characteristic of a 2D solid or crystalline phase. Between these two regimes, one can observe intermediate states in which adsorbates form dense, disordered clusters lacking long-range order, often referred to as 2D liquid-like droplets or amorphous islands. The transitions between these phases represent true 2D analogs of classical phase transitions, such as condensation from gas to liquid. In general, all these structures (both amorphous and ordered) are called overlayer structures (or simply overlayers). The self-organization of adatoms into these structures stems from their mutual interactions and represents a complicated physical problem, which calls for the introduction of new concepts [116, 117], such as *indirect interactions* between adsorbates mediated by the substrate.

Models used to describe such systems are generally referred to as *lattice gas models*, wherein the surface is treated as a periodic array of adsorption sites separated by energy barriers low enough to permit adatom diffusion. While the positions of adatoms are assumed to be random, short-range correlations with neighboring sites are taken into account. The simplest such model is the *non-interacting lattice gas*, which is based on two key assumptions: (1) only a single type of adsorption site exists, and (2) the adsorption energy is independent of the occupation of neighboring sites. Though this model is solved analytically using a mean-field approach, it fails to capture the essential physics of phase transitions in adsorbate systems.

An alternative mean-field theoretical framework is the *two-dimensional Van der Waals gas model*. In this approach, surface potential corrugation and site-to-site hopping are neglected; adsorbates are treated as a free gas constrained to two dimensions by surface bonding. The model emphasizes lateral interactions between adsorbates while effectively neglecting the variations in the adsorbate-substrate potential energy. This approximation is often valid for physisorbed systems [118], where the interaction with the surface is weak, or when the scale of the phenomena of interest is much larger than the surface lattice constant scale. Neglecting the lattice discretization is also valid at elevated temperatures when adatoms exhibit high mobility.

5.1.1 Van der Waals equation of state

We start by recalling the van der Waals equation of state for the ordinary three-dimensional liquid-gas transition. The phenomenological equation was suggested by J.D. van der Waals (vdW) more than 100 years ago and can be seen as an interpolation formula that qualitatively describes this

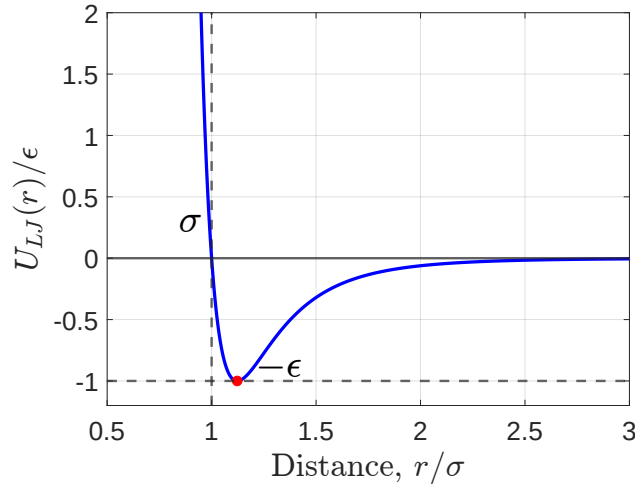


Figure 5.1: Lennard-Jones (12,6) potential. It crosses the x-axis at σ and has a minimum $U_0 = -\epsilon$

process [119]. It can be written in as

$$\left(P + \frac{N^2 a}{V^2}\right)(V - Nb) = NT. \quad (5.1)$$

Here, V is the volume of the system, P is the pressure, T is the temperature, and N is the number of atoms in the considered volume. The same concepts apply to molecules, but for brevity, in the following we mention only atoms. a, b are vdW constants. Their physical meaning is clear from the equation. b is of the order of the volume of an atom; therefore, Nb is the excluded volume, and $V - Nb$ is the volume that atoms effectively have to occupy. There is an additive correction to the pressure that has the following meaning: in the presence of long-range attractive interactions, atoms will be subject to an external pressure plus the pressure due to the interaction with other atoms, $N^2 a/V^2$. Therefore, a parametrizes long-range attractive interactions.

The equation can be derived with several assumptions starting from the free energy expression F for a dilute non-ideal gas. F can be written as a sum of the free energy of an ideal gas F_{id} and some corrections as shown in [120]:

$$F = F_{id} + \frac{N^2 T B(T)}{V} = -NT \left(1 + \ln \frac{V}{N}\right) + \frac{N^2 T B(T)}{V} \quad (5.2)$$

As can be seen, the deviation in comparison with the ideal gas arises because of

$$B(T) = \frac{1}{2} \int \left(1 - e^{-\frac{U(r)}{T}}\right) dV \quad (5.3)$$

which depends on the pair interaction potential $U(r)$ between atoms. A typical example of $U(r)$ is the Lennard-Jones (12,6) potential, which defines a strong repulsion at short distances and weak attraction at long distances

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]. \quad (5.4)$$

The Lennard Jones potential written in this form has a minima $U(r_{min}) = U_0 = -\epsilon$ at $r_{min} = 2^{1/6}\sigma$, and crosses the x -axis at $r_c = 2r_0 = \sigma$ (Fig. 5.1). It is important to note that the discussion is not limited to this form and is valid for other forms of the potential with a short-range repulsive

part and a long-range attractive part. As interaction potential $U(r)$ depends only on the distance between atoms we can rewrite $dV = 4\pi r^2 dr$ and divide the integral in $B(T)$ into two parts

$$B(T) = 2\pi \int_0^{r_c} (1 - e^{-U(r)/T}) r^2 dr + 2\pi \int_{r_c}^{\infty} (1 - e^{-U(r)/T}) r^2 dr \quad (5.5)$$

Here, we consider atoms as hard spheres with radius r_0 . In other words, two atoms can't approach each other at a distance less than $r_c = 2r_0$, because afterward, the interaction potential increases steeply. Therefore, in the first integral we can neglect the exponential term ($e^{-U(r)/T} \ll 1$). This yields for the first integral the positive constant:

$$b = 2\pi \frac{r_c^3}{3}. \quad (5.6)$$

The second integral we assume is dominated by the long range weak attractive tail (i.e. for $r > r_c$, $\frac{U(r)}{T} \leq \frac{U_0}{T} \ll 1$). Notice that the r^2 factor from the differential of volume weights strongly the long-range part. If the temperature is not too low $e^{-U(r)/T}$ can be expanded in degrees of $U(r)$ and after leaving only first member we get

$$\frac{2\pi}{T} \int_{r_c}^{\infty} U(r) r^2 dr = -\frac{2a}{T} \quad (5.7)$$

where, for strong enough attraction, a is a positive constant. Finally, for $B(T)$ we have

$$B(T) = b - \frac{a}{T} \quad (5.8)$$

Putting this form of $B(T)$ into Eq. (5.2) we obtain free energy for vdW gas

$$F_{vdw} = Nf(T) - NT(1 - \ln N) - NT(\ln V - \frac{Nb}{V}) - \frac{N^2a}{V} \quad (5.9)$$

We consider $Nb \ll V$, which means that the volume occupied by atoms is much smaller than the volume of the gas. Therefore

$$\ln(V - Nb) = \ln V + \ln(1 - \frac{Nb}{V}) \approx \ln V - \frac{Nb}{V}. \quad (5.10)$$

The free energy of vdW gas with this approximation becomes

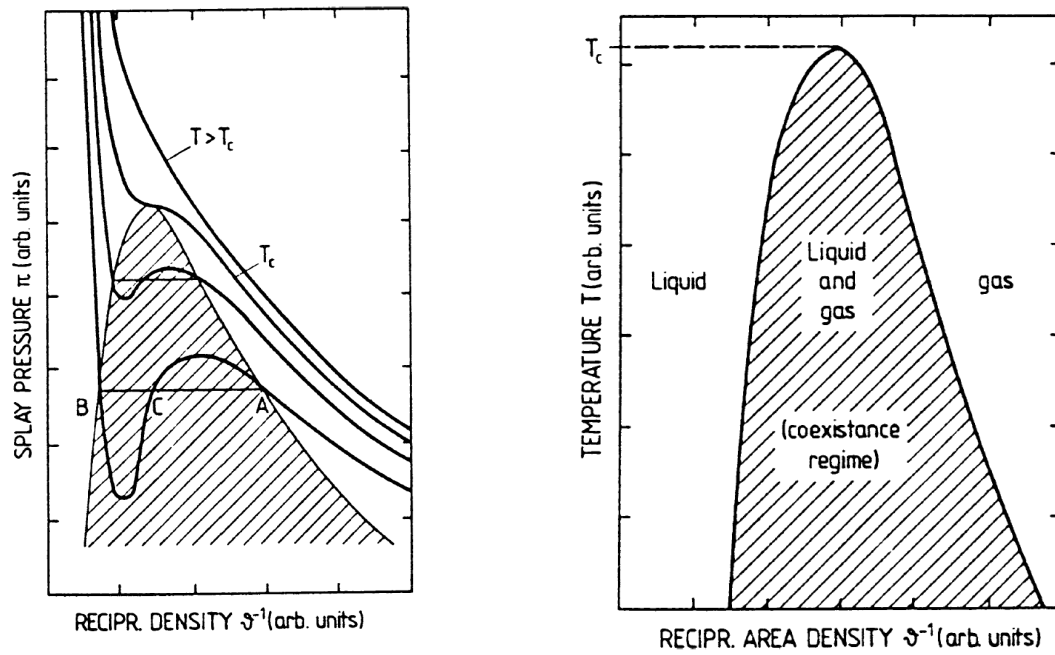
$$F = Nf(T) - NT(1 + \ln \frac{V - Nb}{N}) - \frac{N^2a}{V} \quad (5.11)$$

From these equations, one can derive the equation of state ($P = -\partial F / \partial V|_{T,N}$) as,

$$P = \frac{NT}{V - Nb} - \frac{N^2a}{V} \quad (5.12)$$

or in the form discovered by Van der Waals

$$\left(P + \frac{N^2a}{V^2}\right)(V - Nb) = NT \quad (5.13)$$



(a) Qualitative phase diagram depicting coexistence of liquid-like and gas-like structures on the surface. For temperatures above T_c , only the gas phase appears. For temperatures below T_c , both phases coexist in the range of reciprocal densities corresponding to the points A and B.

(b) Qualitative 2D phase diagram (substrate temperature versus reciprocal area density) for phase coexistence of adsorbate structures. The coexistence curve is plotted, with the shaded region indicating the area where both phases coexist. For temperatures higher than T_c , only the gas phase exists.

Figure 5.2: Phase transition in Van der Waals gas model (qualitatively). Image is from [121].

These expressions derived in the 3D case can be converted into the 2D case, replacing volume V by area A and 3D pressure P with splay pressure p acting on the unit of length. Additionally, vdW constants a, b should be replaced by their 2D counterparts a', b' . In this case, the integral for $B(T)$ has the form

$$B(T) = \pi \int_0^{2r_0} (1 - e^{-U(r)/T}) r dr + \pi \int_{2r_0}^{\infty} (1 - e^{-U(r)/T}) r dr \quad (5.14)$$

The difference lies in that we integrate not over the volume $dV = 4\pi r^2 dr$ as before, but over the area $dA = 2\pi r dr$. With the same assumptions as before, we obtain for 2D vdW parameters a', b' ,

$$\begin{aligned} b' &= \frac{\pi}{2} r_c^2 \\ a' &= -\pi \int_{r_c}^{+\infty} U(r) r dr \end{aligned} \quad (5.15)$$

With the new definitions, the equation becomes

$$\left(p + \frac{N^2 a'}{A^2} \right) (A - N b') = N T \quad (5.16)$$

However, in this chapter, we always deal with 2D case; therefore, we omit "prime" symbols, so a, b parameters are always computed following Eq. (5.15), and pressure p refers to the 2D case.

We introduce the 2D density $n = \frac{N}{A}$, and work in a system of units where $k_b = 1$. The VdW equation is rewritten as

$$(p + a n^2)(1 - n b) = n T \quad (5.17)$$

Fig. 5.2, panel (a) shows qualitative isotherms in coordinates (p, n^{-1}) (2D pressure and reciprocal density) for 2D vdW gas. For high temperatures T the pressure decays monotonously with an increase of reciprocal density. However, for temperatures below some critical value T_c , trying to find the density that corresponds to a given splay pressure yields three solutions; for example, points B, C, and A have the same splay pressure. The critical point can be found when the density n is equal to the critical density n_c . At this point, all 3 roots of the equation, which is solved with n as a variable, coincide, and it becomes a full cube

$$(n - n_c)^3 = n^3 - 3n_c n^2 + 3n_c^2 n - n_c^3 \quad (5.18)$$

At a critical point, vdW equation of state reads

$$(p_c + a n_c^2)(1 - n_c b) = n_c T_c \quad (5.19)$$

Compare (5.18) and (5.19) we get coordinates for critical point (n_c, p_c, T_c) :

$$n_c = \frac{1}{3b} \quad (5.20)$$

$$p_c = \frac{a}{27b^2} \quad (5.21)$$

$$T_c = \frac{8a}{27b} \quad (5.22)$$

The vdW equation can be rewritten in the reduced variables

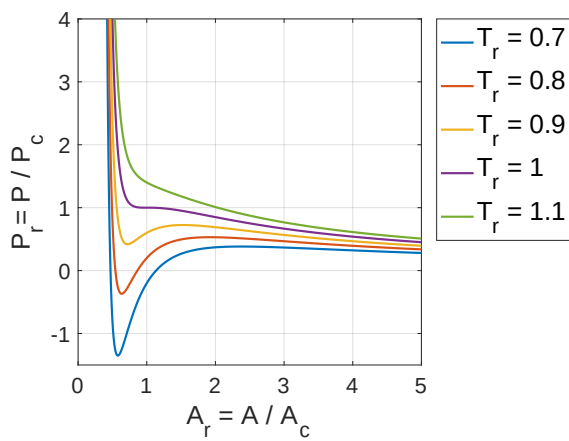
$$\begin{aligned} P_r &= \frac{p}{p_c}, \\ A_r &= \frac{A}{A_c}, \\ T_r &= \frac{T}{T_c}, \end{aligned} \quad (5.23)$$

In these new variables, the equation has the same shape for all vdW gases

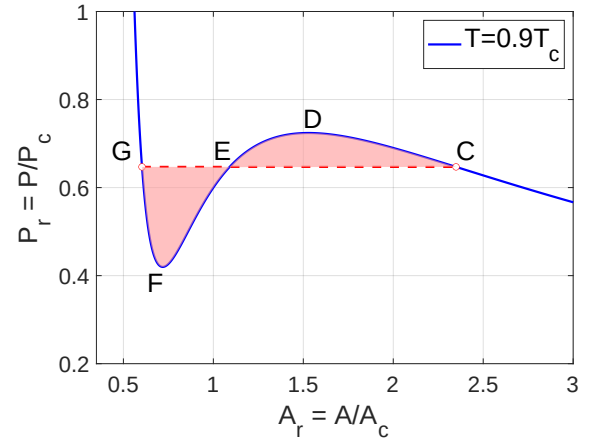
$$\left(P_r + \frac{3}{A_r^2}\right) \left(A_r - \frac{1}{3}\right) = \frac{8}{3}T_r \quad (5.24)$$

So each isotherm has an equation

$$P_r = \frac{8T_r}{3A_r - 1} - \frac{3}{A_r^2} \quad (5.25)$$



(a) VdW isotherms in reduced variables for various temperatures. For $T_r \geq 1$, there is no phase coexistence regime in the system, while for $T_r < 1$ there is a range of areas where both phases coexist, which is shown in detail in panel (b)



(b) Maxwell construction applied to VdW isotherm with $T_r = 0.9$. Horizontal line GEC refers to the equilibrium pressure of phase coexistence $P_x = 0.647$. Areas bordered by points GFE and EDC are equal (filled with red color)

Figure 5.3: Van der Waals isotherms in reduced variables and application of Maxwell construction to one isotherm

Phase transition in two-dimensional Van der Waals gas model

VdW equation of state is, probably, the simplest model that can describe the gas-liquid phase transition. Fig. 5.3 panel (a) shows the isotherms in reduced coordinates ($P_r, A_r \equiv n_c/n$) (2D pressure and area) plotted for various reduced temperature T_r . The isotherm for $T_r = 0.9$ is shown in panel (b). They are similar to $p(n^{-1})$ isotherms shown in Fig. 5.2 panel (a).

Below the critical point, the isotherms have local maxima and local minima within certain intervals (the interval is marked by points B and A in Fig. 5.2(a) and G-C in Fig. 5.3 (b)). In the latter, maxima and minima are marked D and F, respectively. These curves assume that the density is uniform. However, between F and D, an increase in the area occupied by the 2D gas leads to an increase in pressure. This corresponds to a negative compressibility, and it is an unstable situation. One can show that density fluctuations of the uniform state tend to amplify. Actually,

in all the segment G-C, an inhomogeneous state has lower free energy than the uniform gas. This inhomogeneous state consists of a fraction of the system with the high-density phase (point G) and another fraction with the low-density phase (point C). The two phases are at equilibrium, which means that they have the same splay pressure given by the horizontal red dashed line ($P_r = 0.647$). Points G and C are determined by Maxwell's construction, which states that the two red shaded areas should be equal ($\text{area}(\text{GFE}) = \text{area}(\text{EDC})$). Thus, within this range of densities, two phases - liquid and gaseous coexist simultaneously in equilibrium, and the splay pressure as a function of the average coverage ($\theta \propto n \propto 1/A_r$) remains constant. In principle, metastability is possible between points G and F and between C and D, but this requires very peculiar conditions that are not likely to be met in the two-dimensional experiments. Therefore, for equilibrium at temperature T , we expect phase separation between a threshold density $n_g^*(T)$ corresponding to point G and a second threshold density $n_l^*(T)$ corresponding to point C.

Two important points are worth noting, which will become useful for the analysis of the experimental data: i) In the phase separation regime, the area fraction of the high-density phase increases linearly with the average density. ii) The local density of the phase-separated regions remains locked at their values at the extreme of the phase separation interval, $n_g^*(T)$ and $n_l^*(T)$ (points G and C).

Another way to illustrate phase transitions is to plot a graph in the plane of temperature T versus reciprocal density n^{-1} (Fig. 5.2, panel (b)). The area inside the coexistence curve corresponds to the case when both liquid and gas phases are present in the system. Below T_c this area separates the liquid phase and the gas phase (which exist at small and large n^{-1} correspondingly). The apex of the coexistence curve defines the critical point, with coordinates (p_c, n_c^{-1}, T_c) .

Using Maxwell's construction, the vdW equation has already been solved numerically for all reduced temperatures T_r , and the coordinates of points G and C, which refer to $n_l^*(T)$ and $n_g^*(T)$, are well-known [Tab. B.1 in Appendix is from [122]].

5.1.2 Pair correlation function

In our experiments, samples were cooled below a temperature T_0 , at which point diffusion became very slow and the system became arrested. T_0 is deemed as the last temperature at which the system was in thermodynamic equilibrium, and it is assumed that no significant change occurs below T_0 . Therefore, we will assume the images obtained at the measurement temperature $T < T_0$ are snapshots, i.e. frozen configurations of the equilibrium system at T_0 . We would like to obtain information from the images to infer the properties of the interaction among the adsorbates. In Sec. 5.2.4 we estimate T_0 .

The 2D pattern of Fluorine adatoms can be considered a planar point pattern (PPP) [3]. With this approach, we neglect the spatial sizes of F-adatoms and consider them as points, distributed on the 2D plane of the substrate. Therefore, all the statistical machinery developed for analyses of PPP can be applied to 2D gas of adsorbates.

The interaction energy of one frozen configuration can be written as,

$$E_I = \frac{1}{2} \sum_{ij} U(\mathbf{r}_i - \mathbf{r}_j) \quad (5.26)$$

where $\mathbf{r}_i$ is the position of the i -th adsorbate on the surface.

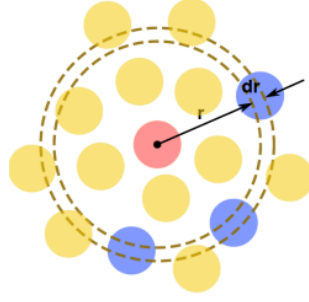


Figure 5.4: Number of particles in the shell dr at the distance r from the tagged particle. Image is from Wikipedia

We can write the interaction energy in terms of a two-particle density

$$E_I = \frac{1}{2} \int d^2\mathbf{r}_a d^2\mathbf{r}_b U(\mathbf{r}_a - \mathbf{r}_b) n^{(2)}(\mathbf{r}_a, \mathbf{r}_b)$$

with

$$n^{(2)}(\mathbf{r}_a, \mathbf{r}_b) = \sum_{ij} \delta(\mathbf{r}_a - \mathbf{r}_i) \delta(\mathbf{r}_b - \mathbf{r}_j).$$

We can make the change of variables, $\mathbf{R} = (\mathbf{r}_a + \mathbf{r}_b)/2$ and $\mathbf{r} = (\mathbf{r}_b - \mathbf{r}_a)$. Equation Eq. (5.26) can be written as,

$$E_I = \frac{1}{2} \int d^2\mathbf{r} d^2\mathbf{R} U(\mathbf{r}) n^{(2)}(\mathbf{R}, \mathbf{r})$$

We can define the area average of $n^{(2)}(\mathbf{R}, \mathbf{r})$,

$$\langle n^{(2)}(\mathbf{r}) \rangle = \frac{1}{A} \int d^2\mathbf{R} n^{(2)}(\mathbf{R}, \mathbf{r})$$

Then the interaction energy per unit area reads,

$$E_I/A = \frac{1}{2} \int d^2\mathbf{r} U(\mathbf{r}) \langle n^{(2)}(\mathbf{r}) \rangle.$$

Up to here, there are no approximations. However, if the system is isotropic, we can expect the average two-particle density to be isotropic. In this case, we can put it in terms of a radial distribution function,

$$\langle n^{(2)}(\mathbf{r}) \rangle = n^2 g(r)$$

which serves as a definition of $g(r)$, also known as the pair correlation function (PCF).

For an ideal gas, there are no correlations and $\langle n^{(2)}(\mathbf{r}) \rangle = n^2$. Therefore $g(r) = 1$. Deviation from one has the meaning of deviation from the ideal gas to the true particle distribution function.

The following expression

$$\frac{\langle n^{(2)}(\mathbf{r}) \rangle}{n} = n g(r) \tag{5.27}$$

has a meaning of conditional probability density that a particle will be found at $\mathbf{r}$ given that another is at the origin. Indeed, the conditional probability distribution for variable y given a specific value of x , can be defined as $\frac{P(x,y)}{p(x)}$, where x and y are random variables with a joint distribution $P(x, y)$

and $p(x)$ is a probability distribution for x (in our case $p(\mathbf{r}) = n$) and $P(\mathbf{r}_a, \mathbf{r}_b) = \langle n^{(2)}(\mathbf{r}_a, \mathbf{r}_b) \rangle$, where the last average is over statistically independent configurations. In other words, $ng(r)$ can be defined as the average density of particles at $\mathbf{r}$ given that a chosen particle is at the origin. In the case of 2D, $dN(r) = ng(r)2\pi r dr$ gives the average number of particles in a ring of thickness dr at a distance r away from the origin (Fig. 5.4). If we assume that the $g(r)$ of our frozen configuration represents the equilibrium distribution at T_0 we can obtain information on the interaction between the particles. One can show [123] that for dilute gas, the pair correlation function is related to $U(r)$ as

$$g(r) = e^{-\frac{U(r)}{T_0}} \quad (5.28)$$

which connects the pair interaction potential with PCF.

5.1.3 Fry plot as a tool for visualization of correlations in the system

There is a straightforward graphical method for studying correlation and interpoint distances in PPP, called Fry or Patterson plot. It was initially developed in crystallography and later reinvented in geophysics [124–127].

To draw a Fry plot, we choose one point, select it as the origin, and calculate relative displacements from this reference point to every other point in the dataset. These vector displacements are found by subtracting the reference point's coordinates (x_r, y_r) from each point's coordinate (x_i, y_i) : $\Delta x = x_i - x_r$ and $\Delta y = y_i - y_r$. This procedure should be applied to the whole dataset, treating each point as the origin once. Finally, we draw a scatter plot of calculated displacements $(\Delta x, \Delta y)$.

The Fry plot offers a complementary and intuitive means of visualizing $\langle n^{(2)}(\mathbf{r}) \rangle$ before performing any angular average. Unlike the PCF, which provides a radial, statistical average over all particle pairs, the Fry plot is a direct spatial visualization technique that highlights anisotropies. Therefore, Fry plots provide qualitative insights into the local ordering and symmetry of the adatom configurations that may not be immediately evident from the radial PCF alone. They are especially useful in systems where anisotropic interactions are suspected or where the data may not be sufficient to produce a reliable PCF due to limited statistics.

5.2 Results

5.2.1 Phase separation in the 2D system of F-adatoms on Ag

As discussed in Chapter 4, experiments with fluorination times ≤ 3 hours for Ag(100) and ≤ 1 hour for Ag(110) surfaces resulted exclusively in the appearance of isolated F-adatoms uniformly distributed on the surface. To explore the effects of prolonged exposure, we conducted additional experiments with extended fluorination times of up to 15 hours for the Ag(100) surface and 3 hours for Ag(110). These longer treatments yielded markedly different STM images, revealing the formation of two-dimensional island-like structures composed of F-adatoms.

All the STM images were processed in *Gwyddion* software [96] and are presented without application of correction factors for STM piezo (which are 1.12 in X and Y, 0.867 in Z). Images with independent adatoms (following 1.9 and 3 hours experiments performed on Ag(100) and 45 min on Ag(110)) are available in free access [128].

We didn't focus on a precise study of topography in this chapter; the attention was drawn primarily to the phenomenological description of the phase separation phenomenon in the system and the growth of overlayer structures. Another goal is to demonstrate the capabilities of the fluorination apparatus presented in Chapter 3.

5.2.2 Ag(100) surface

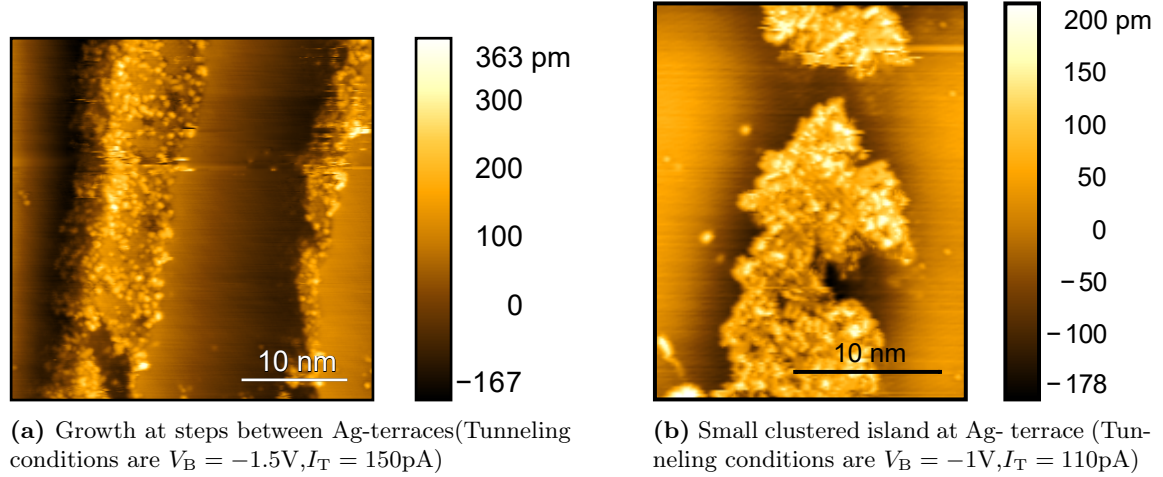


Figure 5.5: Ag(100) surface after a 4-hour of fluorination (Dose=238 L). Overlayer structures cover less than 5% of the terrace area. Growth happens preferentially at Ag-steps.

We noticed that for the 4-hour experiment (dose 238L) on Ag(100) the growth of overlayer structures starts at Ag-step edges, accompanied by small island-like structures found at terraces (Fig. 5.5). Less than 5% of the flat surface is covered by amorphous overlayer structures at this fluorination time.

For the next experiment done in the set (5.5h time, dose 450L), we noticed that already more than 80% of the flat Ag terraces were covered by amorphous overlayer structures of F-adatoms as shown in Fig. 5.6. However, in the areas that are not covered by a dense mass of F-adatoms, we still found separate F-adatoms (Figs. 5.6b, 5.8). We interpret this as phase separation in the system. We associate the dense phase with a "2D liquid"-like phase (panel b in 5.8) and the low-density regions characterized by uniformly distributed F-adatoms, with a dilute "2D F-gas" (panel c). Of course, these names refer to what we presume where the equilibrium phases at the temperature T_0 . At the temperature of the STM scan, the atoms are frozen; therefore, a more appropriate name for the liquid phase is amorphous or glass. We will use the terms amorphous and/or liquid to refer to the same disordered pattern. Following Fig. 5.8 panel a, there is a well-resolved phase boundary between the amorphous 2D liquid-like structure, which occupies the bottom part of the image, and the 2D gas above. The counterpart in 3D of this image is a liquid that stays in equilibrium with its vapor inside a reservoir. The difference is only that in our case, instead of a reservoir of fixed volume, in 2D we have a fixed area where F adatoms are confined.

The amorphous region is characterized by bright spots distributed over a region with a lower apparent height than the gas region. Such a lower-height background (darker in the image in Fig. 5.8) may represent a uniform underlayer of a fluorinated phase.

Figure 5.7 shows STM topographies and height profiles of amorphous F regions obtained after

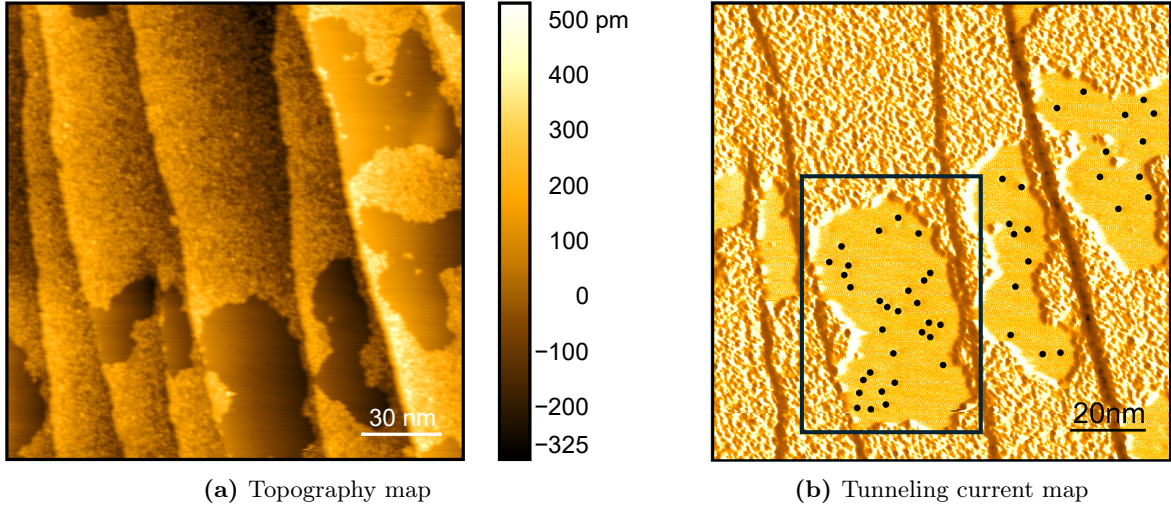


Figure 5.6: Ag(100) surface after 5.5 hours of fluorination (Dose=450 L). (Panel a) Large field of view. Approximately 80% of the surface is covered by an amorphous 2D-liquid-like F structure. (Panel b) The image illustrates the coexistence of 2D gas and liquid phases. F-adatoms are located on the pristine Ag-surface inside "bubbles", formed by a layer of the liquid phase, and are indicated by black dots. One of these "bubbles" is shown by a rectangle with 40 adatoms inside. STM measurement was done at 10K, when both phases are essentially frozen and immobile. (Tunneling conditions, $V_B = -1V$, $I_T = 80pA$)

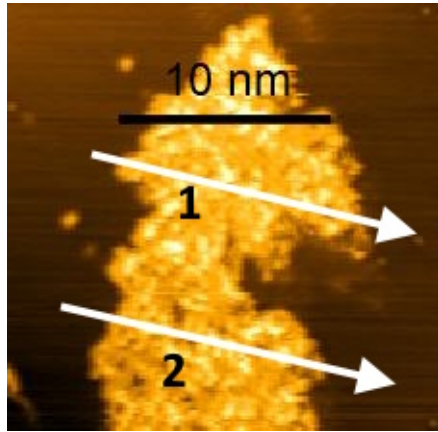
fluorination times of 4, 5.5, and 15 hours. Remarkably, the thickness of the amorphous layer is consistently $\leq 2 \text{ \AA}$ for all disordered structures observed on Ag(100) in this chapter. Thus, we do not film thickness growth; instead, the system forms the same disordered phase by extending the coverage area, whose thickness is independent of fluorination time within the investigated range.

There are several possible scenarios for the structure of the amorphous phase, as well as potential underlying structures. For example, oxides often show missing row reconstructions [129]. It is possible that a uniform fluoride has formed, and the bright spots are excess Ag atoms expelled from the surface. In this case, the darker background region would have an apparent lower height because of the lower conductance of the fluoride with respect to pure Ag, and not because of topographical reasons. Another possibility is that F-adatoms within this phase form dimers and chains (1D structures), so each bright spot corresponds to several adsorbates situated at short distances. For other halogens like Cl and Br on Ag(111) [77, 82], the first structure that forms on the surface with the increase in the coverage is a 1D chain of adatoms, which we didn't discover in the current experiments. However, some scattered segments can be seen in Fig. 5.8.

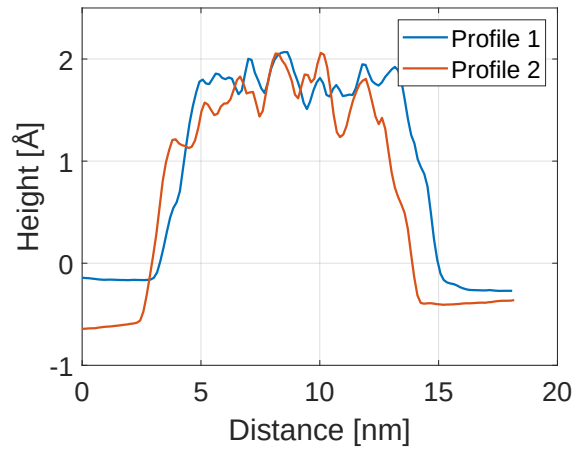
We attempted to estimate the density in the amorphous regions using the sticking coefficient and the dose. A natural question is: How does the sticking coefficient S depend on the coverage? The simplest model assumes that at the regime of small coverages, each adsorbed adatom inhibits one site and the sticking coefficient decays linearly,

$$S(\theta) \approx S_0(1 - \theta). \quad (5.29)$$

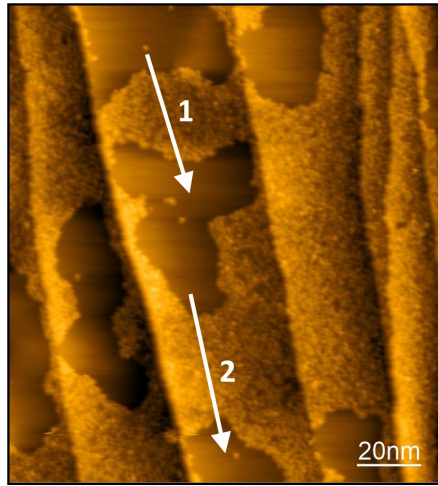
Based on that, we can estimate that at small coverages $\leq 10^{-1} \text{ ML}$, it can be assumed nearly constant. The sticking coefficient at low coverages was estimated in the previous Chapter and reported in Tab. 4.2. Using these values, we estimated the average coverage at higher doses. Tab. 5.1 shows values of coverage/density of adsorbates computed following these assumptions. For longer



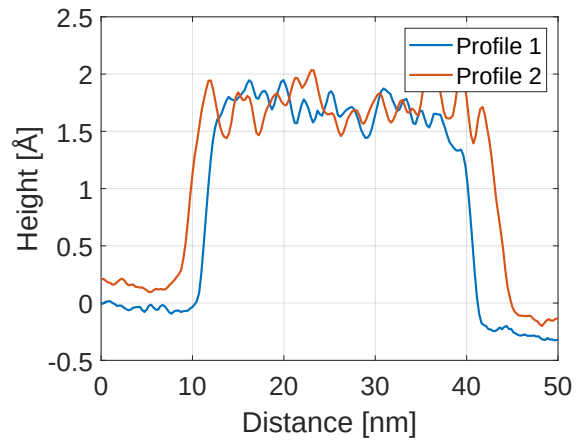
(a) 4 hour reaction with Dose=238L. Tunneling conditions, $V_B = -1V, I_T = 110pA$



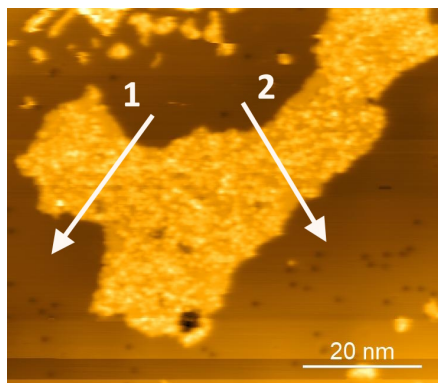
(b) Apparent height profiles corresponding to directions 1,2 as indicated in panel (a)



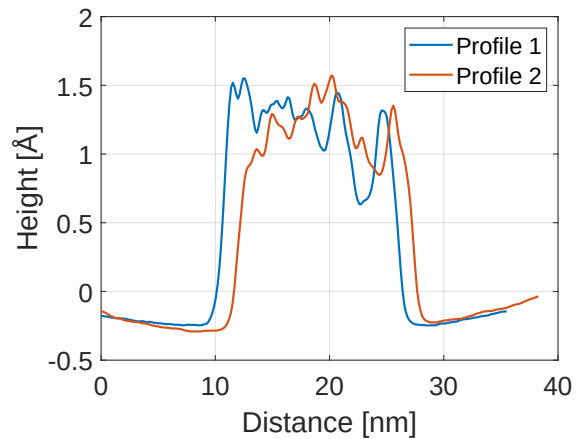
(c) 5.5 hour reaction with Dose=450L. Tunneling conditions, $V_B = -1V, I_T = 80pA$



(d) Apparent height profiles corresponding to directions 1,2 as indicated in panel (c)



(e) 15 hour reaction with dose=810L. Tunneling conditions, $V_B = 1V, I_T = 35pA$



(f) Apparent height profiles corresponding to directions 1,2 as indicated in panel (e)

Figure 5.7: Apparent topographies of Ag(100) surfaces (left column) and corresponding apparent height profiles (right column) following marked directions after several fluorination reactions. Panels show data after 4 hours (a,b), 5.5 hours (c,d), and 15 hours (e,f) of fluorination. Linear background was subtracted. Tunneling conditions are indicated in the caption of each AT image.

Time (h)	Dose (L)	Average density ($\times 10^{-2} \text{ nm}^{-2}$)	Average coverage ($\times 10^{-3} \text{ ML}$)	Liquid area fraction %
1.9	70	1.1	0.7	Only 2D gas phase
3	120	2.0	1.3	
4	238	10 (10)	25 (6.5)	$\leq 5\%$
5.5	450	160 (19)	100 (11.8)	$\approx 80\%$
15	810	- (37)	- (23.5)	$\leq 80\%$

Table 5.1: Experiments with various fluorination times for Ag(100). In the uniform gas phase, the average coverage is estimated by counting adatoms. For 4 and 5.5 hours experiments, the average density estimates are obtained with very rough assumptions of the local density in the liquid regions. Quantities in parenthesis are estimates based on the assumption of a sticking coefficient independent of coverage ($S = S_0 = 6 \times 10^{-5}$) and should not be considered accurate in the phase-separated region. In the case of the 15-hour experiments, noise in the data prevented the evaluation of the area fraction of the liquid phase. Dose is computed in Langmuir ($1 \text{ L} = 10^{-6} \text{ torr} \cdot \text{s} = 1.33 \times 10^{-6} \text{ mbar} \cdot \text{s}$).

fluorination time, it predicts average densities and coverages in the range of 10^{-2} nm^{-2} and $10^{-3} - 10^{-2} \text{ ML}$ correspondingly. However, the density of the liquid phase n_l^* , which covers most of the surface, is much larger than 10^{-2} nm^{-2} (it is clear from Fig. 5.8, panel b). Therefore, the average coverage observed in the experiment is much larger than the one we estimated with the low-density sticking coefficient.

We can explain this contradiction assuming a much larger sticking coefficient $S' \gg S_0$, in the amorphous overlayer structures and/or around the interface regions. In this scenario, the growth rate would increase once certain areas of the surface become covered by overlayer structures.

Fig. 5.6b shows steps between Ag-terraces where we observe coexistence between liquid and gas phases. Dilute 2D gas of F-adatoms is located on a pristine Ag-surface and forms "bubbles", being bordered by the liquid phase.

We counted all F-adatoms (they are marked by black spots) inside each of these "bubbles" (where it is possible, following the quality of STM scans) and after measuring corresponding areas, we estimated the equilibrium density of 2D gas n_g . It provides us with the local $n_g^*(T_0) \approx 2 \times 10^{-2} \text{ nm}^{-2}$. The notation emphasizes that in a simple liquid-gas phase separation scenario, the density of the gas phase in the coexistence region at a given T_0 coincides with the threshold global density at which phase separation starts, $n_g^*(T_0)$. Notice that this density coincides with the uniform density of the 3-hour experiment, indicating that this experiment is close to the threshold to trigger phase separation.

While it is possible to compute the density of F-gas simply by counting the number of adatoms over the unit area, it is difficult to proceed in the same way for a liquid-like phase. Indeed, individual F adatoms are not distinguishable in this case. We can count bright spots in the amorphous regions, but, as discussed, it is not at all clear that they correspond to F adatoms.

Overall, from the images (Fig. 5.8 panels b and c) it is clear that the difference in densities between the liquid n_f and gas n_g phases is at least two orders of magnitude. Indeed, the assumption of a single order of magnitude will lead to distinguishable adatoms. This will be clear below, where we show images of the Ag(110) surface with an order of magnitude larger density of the gas phase. Therefore, we take as a lower bound $n_l^*(T_0) = 100n_g^*(T_0)$.

Assuming such fluid phase density, we can crudely estimate average coverages for all experiments reported in Tab. 5.1. For 5.5-hour experiment, taking into account the estimated local density

of liquid as $n_l \approx 2 \text{ nm}^{-2}$ and a surface fractional coverage of 80% we have the average density, $\langle n \rangle = 1.6 \text{ nm}^{-2}$, which correspond to $\theta' = 0.1 \text{ ML}$, instead of previously estimated $\theta \approx 0.01 \text{ ML}$, made with assumption of constant sticking coefficient equal S_0 . The same argument can be used to estimate an effective sticking coefficient S' at intermediate coverages, which results in being 20 times larger than S_0 .

The same approach provides us with an estimate of $\theta \approx 0.025 \text{ ML}$ for a 4-hour experiment. For the 15-hour experiment, low quality of experimental data makes it impossible to perform any quantitative analyses except estimate of average coverage.

Overall, based on these corrections, we can conclude that the growth of F-overlayer structures on Ag(100) starts at coverages $\theta \propto 0.01 \text{ ML}$ at Ag-steps, continues at $\theta \propto 0.1 \text{ ML}$ with the emergence of an amorphous liquid-like phase. Even at larger doses (up to 800L) under the same experimental conditions, we have only observed the formation of an amorphous overlayer F-structure, which, however, didn't cover the whole Ag-surface.

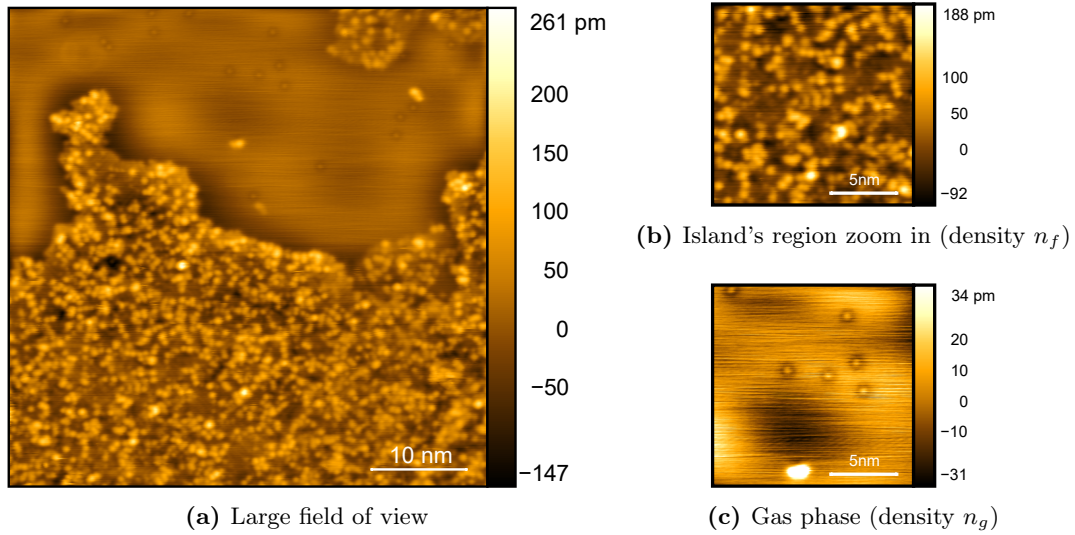


Figure 5.8: 2D Liquid - 2D gas coexistence on Ag(100) after 5.5 hours of fluorination (Dose=450 L) (Tunneling conditions are $V_B = -0.5 \text{ V}$, $I_T = 50 \text{ pA}$)

We recall to the reader that the initial sticking coefficient for F on Ag surfaces is very small ($S_0 \leq 10^{-4}$). This is probably related to the lack of defects on the surface. Indeed, island formation tends to happen first in steps as shown in Fig. 5.5a. Therefore, it is reasonable to assume that the interfaces and/or disordered regions increase the sticking coefficient.

For experiments with 15 hours of fluorination time, the surface looked very similar to the 5.5-hour experiment, despite the almost two times larger applied dose (810L and 450L, respectively). We attribute this to variations in the composition of the gas in the chamber or different partial pressures, which may also have an effect on the growth rate. For example, small variations of HF concentration (which has on average a partial pressure one order less than Fluorine during synthesis as evidenced by Fig. 4.5) may have an important impact on the final coverage. Precise estimates of F-density in the amorphous regions and dependence of sticking coefficient from coverage and gas composition in the chamber still remain an open problem.

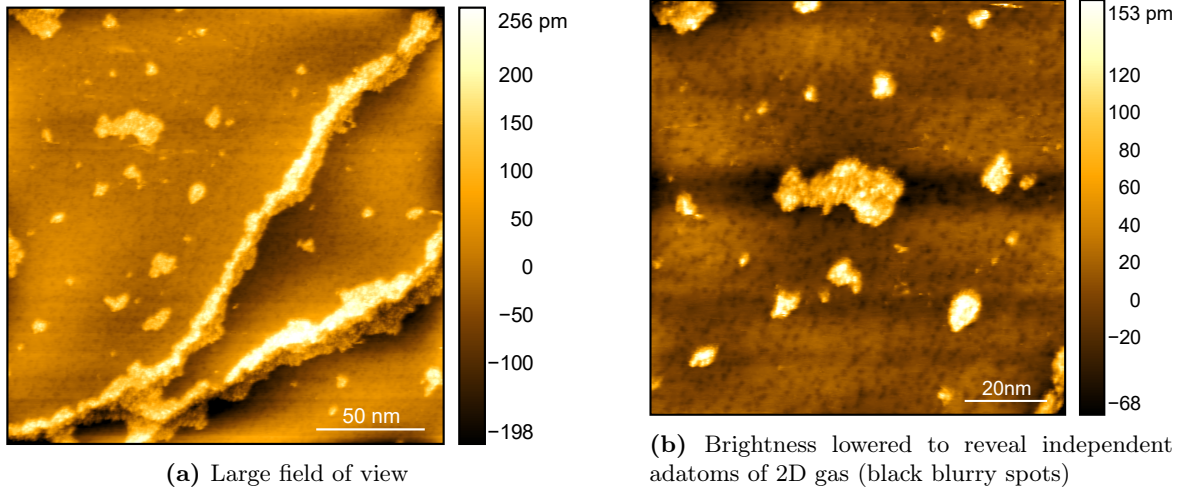


Figure 5.9: Ag(110) surface after 3 hours of fluorination (Dose=80 L). Less than 10% of Ag-terraces are covered by island-like F-structures. Growth happens mostly near Ag-steps. (Tunneling conditions are $V_B = -1.250\text{V}$, $I_T = 50\text{pA}$)

Time (h)	Dose (L)	Average density ($\times 10^{-2} \text{ nm}^{-2}$)	Average coverage ($\times 10^{-3} \text{ ML}$)	Liquid area fraction %
0.75	20L	≤ 7.5	≤ 5	Only 2D gas phase
3	80L	$\leq 75^*$	$\leq 47.5^*$	$\leq 10\%$

Table 5.2: Experiments with various fluorination times for Ag(110) surface. Quantities marked by * are estimates based on the assumption that the sticking coefficient is independent of coverage ($S = S_0 = 1.5 \times 10^{-4}$). Dose is computed in Langmuir ($1 \text{ L} = 10^{-6} \text{ torr} \cdot \text{s} = 1.33 \times 10^{-6} \text{ mbar} \cdot \text{s}$)

5.2.3 Ag(110) surface

Due to time constraints, it was possible to perform only two experiments for the Ag(110) surface: a 45 min with a dose of 20L and a 3-hour experiment with an estimated dose of 81L as shown in Tab. 5.2. Data for the 45 min was already reported in Tab. 4.2. From this table, we obtain that the initial sticking coefficient in this case is approximately $S_0 = 4 \times 10^{-4}$ (average value).

After 45 min of fluorination (Dose=20L) in some regions of the sample, the density of F-adsorbates reached $n = 7.4 \times 10^{-2} \text{ nm}^{-2}$ without any evidence of clustering. In contrast, after 3 hours (Dose=80), it was observed that phase separation arises (Fig. 5.9). At this value of dose, the growth of overlayer structures starts at Ag-steps, while only a small area of flat terraces is covered by island-like structures ($\leq 10\%$). Overall, the situation is very similar to the 4-hour experiment on Ag(100) surface (Fig. 5.5) with a very important difference: the density of the 2D gas $n_g^*(T_0)$ phase is much larger than for the Ag(100) surface.

Additionally, Fig. 5.10 presents the apparent topography of an amorphous F-overlayer island together with two corresponding height profiles. A comparison with Fig. 5.7, obtained for Ag(100), indicates that the apparent thickness of the amorphous phase does not differ significantly between the two surfaces.

We estimated the density of 2D gas of adsorbates on Ag(110) in the same way as for Ag(100), choosing a small window in the large scan area and computing F-adatoms manually within this window, as it is shown in Fig. 5.11. For Ag(100) after 5.5 hours experiment (Dose 450 L), almost 80% of Ag-terraces are covered by an amorphous overlayer structure, so adsorbates representing

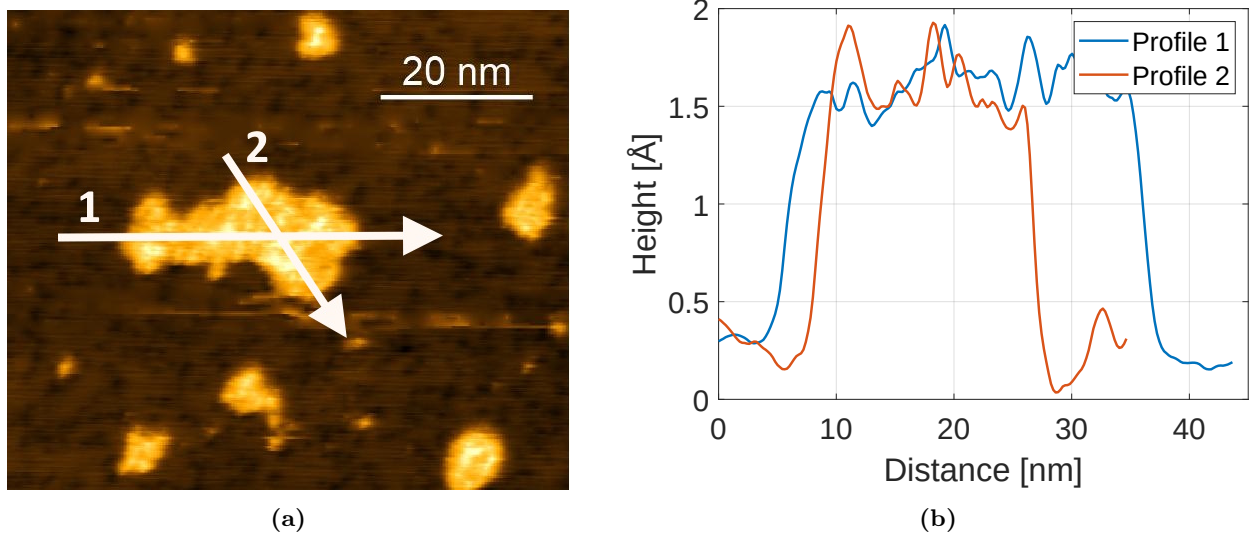
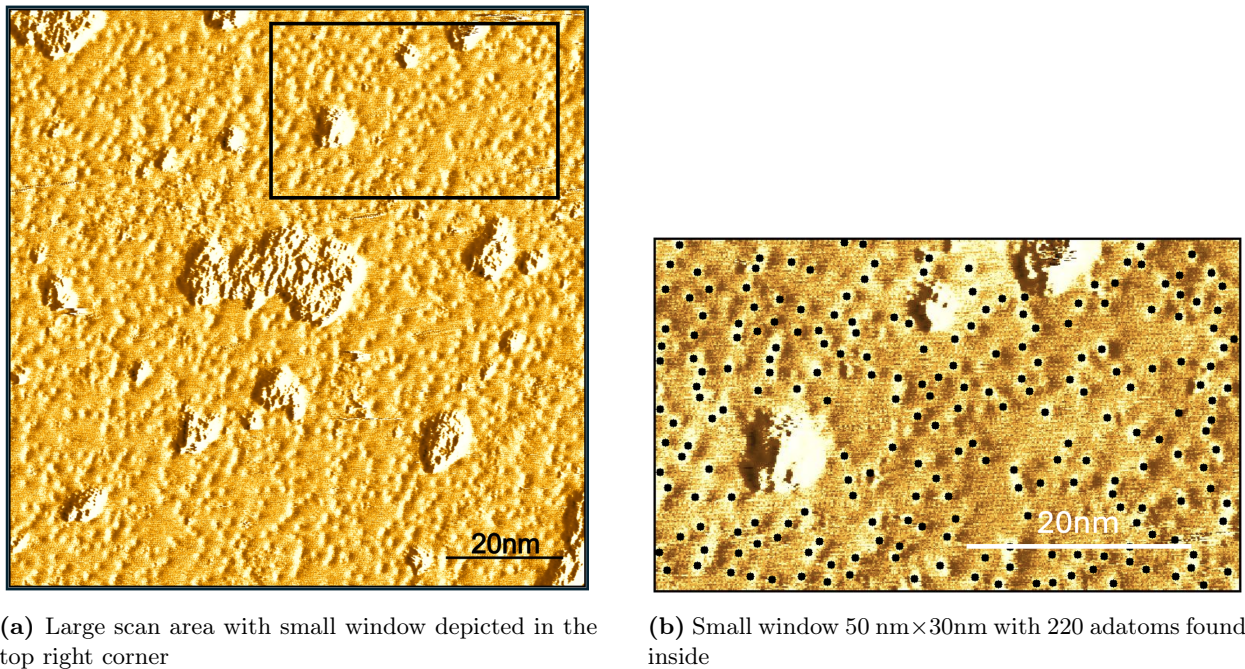


Figure 5.10: (panel a) Apparent topography of Ag(110) surface after 45 min of fluorination (Dose=20 L) (panel b) Apparent height profiles for corresponding directions as indicated in panel (a). Linear background was subtracted. (Tunneling conditions, $V_B = -1.25\text{V}$, $I_T = 50\text{pA}$)

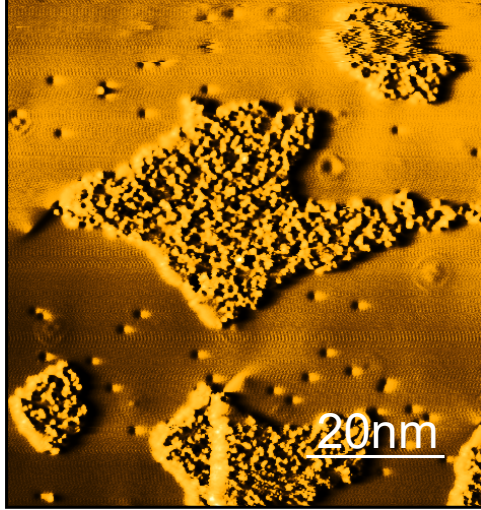


(a) Large scan area with small window depicted in the top right corner

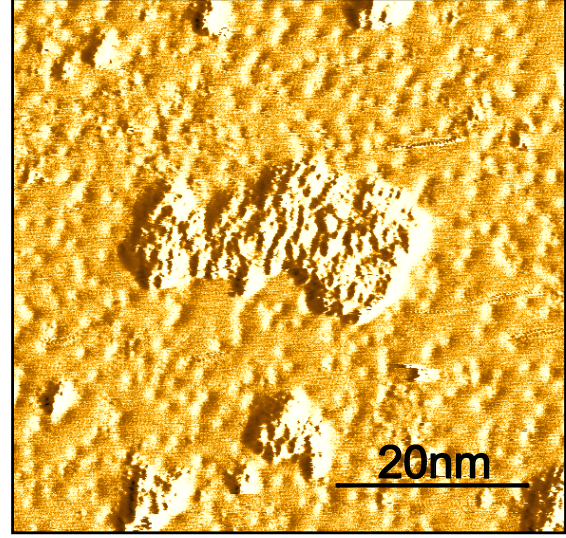
(b) Small window 50 nm x 30 nm with 220 adatoms found inside

Figure 5.11: Density estimation of 2D gas of F-adatoms on Ag(110). Tunneling current maps. (Tunneling conditions: $V_B = -1.25\text{V}$, $I_T = 50\text{pA}$).

2D gas are located on the pristine Ag-surface and bordered by this liquid phase (Fig. 5.6b). For Ag(110), after a 3-hour experiment (Dose 81 L), only a small part of the Ag surface is covered by island-like structures ($\leq 10\%$), so we observe quite dense 2D gas surrounding these small clustered areas. Counting adatoms over the unit area, we estimate the average density of the gas on this surface as $n_g \approx 2 \times 10^{-1} \text{ nm}^{-2}$, thus one order larger than the density of 2D gas on Ag(100) surface. Fig. 5.12 serves as a good illustration of this difference, showing a similar field of view with



(a) Low-density 2D gas of F-adatoms in equilibrium with amorphous islands on Ag(100) (15 hours, 810L; Tunneling conditions: $V_B = 1.0\text{V}$, $I_T = 350\text{pA}$)



(b) High-density 2D gas of F-adatoms in equilibrium with amorphous islands on Ag(110) (3 hours, 81L; Tunneling conditions: $V_B = -1.25\text{V}$, $I_T = 50\text{pA}$)

Figure 5.12: Tunneling current maps of phase separation on Ag (100) (panel a) and Ag(110) (panel b) to qualitatively illustrate differences between Ag surfaces. Difference in Apparent Topographies (AT) of adsorbates between panels a and b caused by various V_B ($V_B > 0$ for panel a, while $V_B < 0$ for panel b, the question of AT is studied in details in Chapter 4)

a similar area fraction of the high-density phase but very different densities of the gas phase in the two surfaces. Panel (a) corresponds to a 15-hour experiment on Ag(100) (dose 810L), while panel (b) corresponds to 3 hours of fluorination of Ag(110) (dose 80L). The fact that the critical density for phase separation is larger in the Ag(110) surface clearly indicates a smaller tendency to phase separation. As we shall see, this is confirmed by the analysis of the correlation functions at low densities.

Phase separation on Ag(110) occurs at lower fluorination time which we attribute to the larger value of initial sticking coefficient S_0 as it was estimated earlier ($S_0(100) \approx 10^{-5}$ while $S_0(110) \approx 10^{-4}$). Therefore, lower values of doses are needed to reach the threshold density $n_g^*(T_0)$, despite this density is larger than for the Ag(100) surface.

5.2.4 Hopping rate and estimate of T_0

We can use the DFT results of Chapter 4 to estimate the surface diffusion constant. From the diffusion constant, we can propose a criterion to determine T_0 .

It is important to emphasize that all synthesis experiments described in this chapter were done at room temperature (300K), while STM measurements were held at 10K. The relaxation of the temperature took significant time (usually a few hours) after the sample had been transferred from

the fluorination chamber to the STM chamber. Therefore, we can consider that temperature was decreasing slowly, and the system can equilibrate for any temperature $T > T_0$.

As it is shown below and in Ref. [28] DFT predicts that F-adatoms are quite mobile and make frequent thermal hopping at room temperature, while at $T = 10$ K they are essentially frozen. The latter could be experimentally tested by performing several scans in the same field of view. It was observed that the positions of F-adatoms remained the same.

Furthermore, the fact that we see phase separation is good evidence that the system can equilibrate at room temperature. Although in principle, preferential sticking on interfaces without diffusion can also produce fluorine-rich and fluorine-poor regions, such dynamical processes usually generate dendritic growth that we do not observe. Furthermore, for different experiments with different area fractions of the islands, we find approximately the same density in the gas regions. This is only compatible with an equilibrium phase separation scenario, which implies that the freezing temperature T_0 is lower than room temperature. In the following, we provide approximate estimates of T_0 .

The diffusion of the F on the surface happens due to Brownian motion as it has already discussed in Chapter 4. At finite temperatures, fluorines are scattered by lattice vibrations. To jump from one hollow site to another, the adatom should climb to the bridge site, which determines the activation barrier. For both studied Ag-surfaces DFT predicts the lowest diffusion barrier $\Delta E_{ad} = 140$ meV corresponding to 1600 K. Although this is larger than room temperature we can estimate a jump hopping rate as $\Gamma = \nu \exp(-\Delta E_{ad}/k_B T) = 10^{10}$ jumps/sec where, as an order of magnitude, we estimated $\nu = 15$ THz by a typical Ag-F stretching phonon frequency [17] in AgF_2 . This indicates that at room temperature, there is substantial diffusion and the system can equilibrate at least at the length scale of the STM experiment. At 53 K the jumps become of the order of one per second, and, at the typical temperature of the STM experiment (10 K), the adatoms are essentially frozen. Therefore we can arbitrarily define T_0 by the condition that the jumps are 1 per second giving $T_0 \approx 50$ K.

5.2.5 Estimation of Van der Waals parameters from experiments

At large scales with respect to the underlying silver lattice constant, we can neglect the lattice discretization and treat the system in the continuum. In this limit, the Van der Waals model provides a simple framework to describe phase separation between a fluorine-rich and a fluorine-poor region. Clearly, in the high-density phase, the effect of the lattice can be important, especially if there is some underlying ordered phase exists. In the following, for simplicity, we will ignore these effects and treat the high-density amorphous phase as a frozen liquid.

Eq. (5.28) provides a direct relationship between experimental PCF and pair interaction potential. Once the interaction potential is determined, Eq. (5.15) can be applied to extract the corresponding vdW parameters. These parameters, in turn, enable an estimation of the critical point and the range of densities for phase separation. This analysis can serve as a guide for future experimental efforts and can provide valuable insight into the underlying physical interactions between adsorbates.

The PCFs for F-adatoms were computed directly from the images of the lowest density using the `spatstat` package implemented in the R environment [3, 130]. Ripley's border correction [131] was applied to mitigate boundary effects that would otherwise lead to decay of the PCF at large

distances.

The standard deviation σ was used as a measure of statistical uncertainty throughout our analysis. In general, σ depends on the distance r (as implemented in `spatstat`); however, we adopted the maximum value of σ across the entire range of distances as an upper bound. The number of adatoms within the analyzed windows on the Ag(110) surface is several times greater than on the Ag(100) surface, resulting in a smaller upper bound for σ . For all datasets on Ag(110), we found $\sigma(110) \leq 0.1$, while for Ag(100), $\sigma(100) \leq 0.2$.

Ag(100) surface

We first proceed with Ag(100) surface due to the larger available experimental data. From experiments with very low coverage ($\theta \approx 0.001$ ML) a few STM images were chosen and processed. The idea of this simple computation is shown in Fig. 5.13. First, the positions of all the F-adatoms were detected within a scan, and then each image was divided into trapezoidal windows to exclude the Ag-step area. PCFs were computed in each window separately and, finally, averaged, which led to a more accurate estimate. The resulting averaged PCF is shown in Fig. 5.14(a) and has several characteristic features.

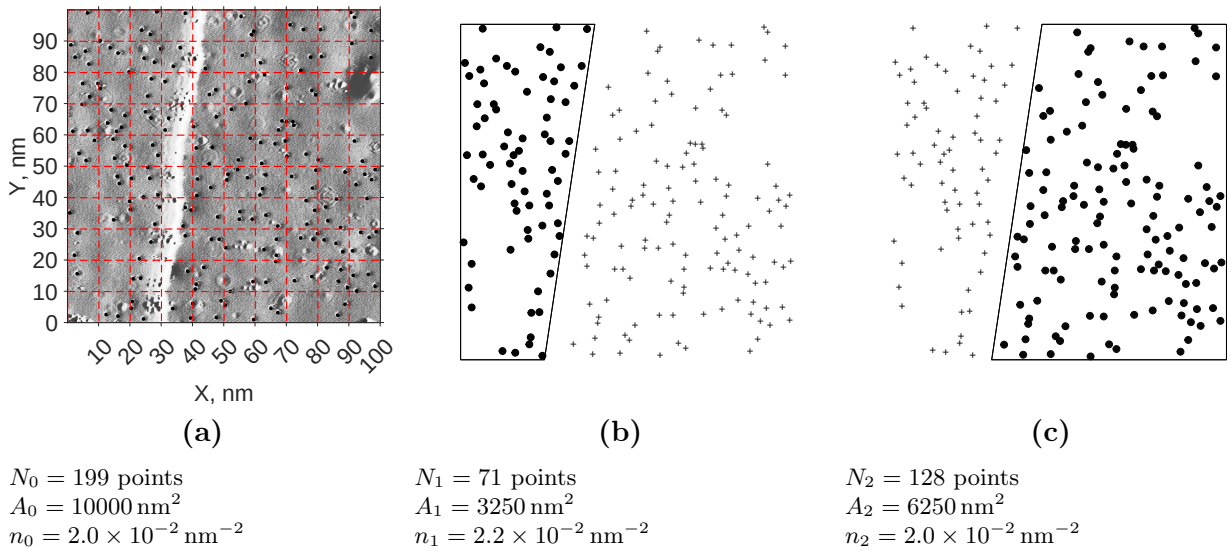
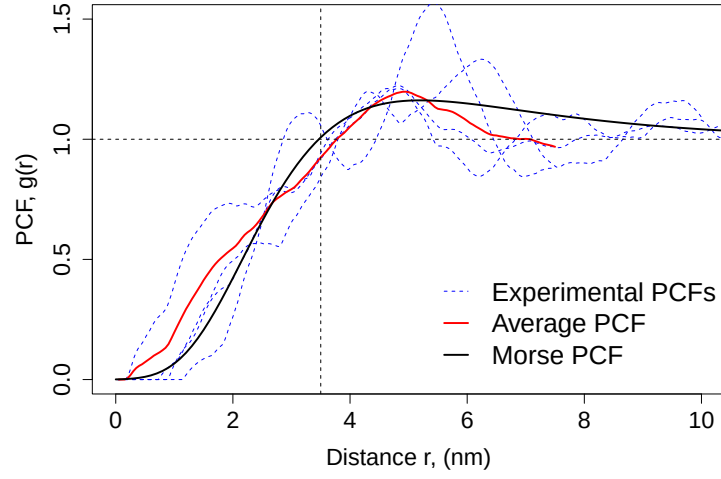


Figure 5.13: Transformation of F-adatoms on Ag(100) into planar point pattern. Panel (a): STM scan image 100nm×100nm. Panel (b): Choice of the left terrace. Panel (c): choice of right terrace. Black spots represent F-adatoms, while pale crosses are particles excluded from evaluation for the correspondent trapezoidal window

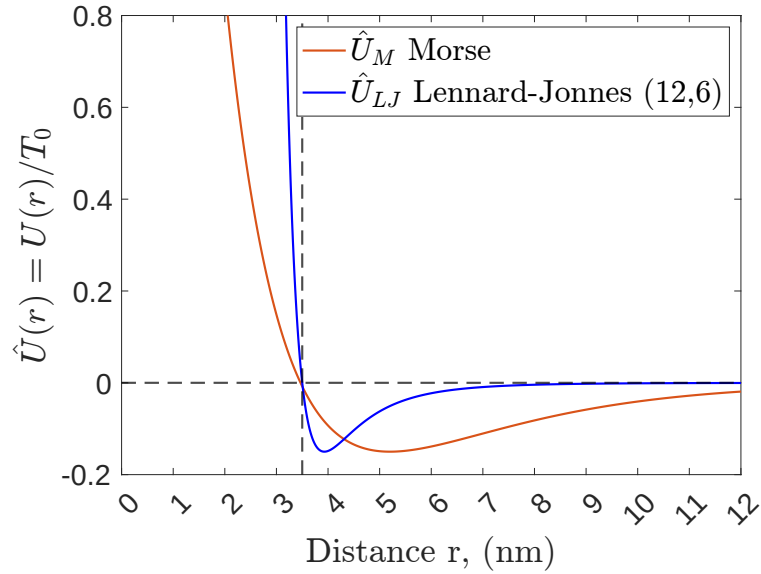
Firstly, at small distances $g(r) < 1$, indicating repulsion between adsorbates. For $4\text{nm} < r < 7\text{nm}$, $g(r) > 1$, which suggests an attraction at this interval of distances. Afterward, $g(r)$, slowly oscillates and approaches 1. The availability of the $g(r)$ is restricted by the quite narrow size of the polygonal windows used in the computation.

We found that for a given experimental PCF $g(r)$ shown in Fig. 5.14 panel (a), the PCF can be fitted with Eq. (5.28) using a Morse Potential $U(r)$

$$\hat{U}_M(r) = U(r)/T_0 = D_0 \left[(1 - e^{-a_0(r-r_0)})^2 - 1 \right] \quad (5.30)$$



(a) Experimental PCF for several images (blue dashed lines), averaged PCF (bold red line), approximation by PCF computed from Morse potential (bold black line). Dashed vertical line corresponds to application an criterion $g(r) = 1$, which provides us with $r = 3.5\text{nm}$



(b) Potentials $\hat{U}(r)$. (Red line) Morse potential computed from averaged experimental PCF ($D_0 = 0.15$, $a_0 = 0.4$, $r_0 = 5.2\text{nm}$). (Blue lene) Lennard Jones (12,6) potential ($\epsilon = 0.15$, $\sigma = 3.5\text{nm}$). Dashed vertical line corresponds to application an criterion $U(r) = 0$, which provides us with $r = 3.5\text{nm}$

Figure 5.14: Fitting of experimental PCF by Morse potential

Fitting parameters are specified in the caption of Fig. 5.14(b).

The potential $U_M(r)$ and PCF $g(r)$ are connected as

$$g(r) = e^{-\frac{U(r)}{T_0}} = e^{-\hat{U}(r)}. \quad (5.31)$$

where we defined $\hat{U}(r)$ as the potential in units of T_0 . Here we assume that PCF measured at low temperatures is a snapshot of the equilibrium PCF at T_0 .

$\hat{U}_M(r)$ is shown in Fig. 5.14 panel (b). The PCF computed from Morse potential (red curve in Fig. 5.14 a) reproduces the data well within the experimental uncertainties.

To compute the parameters a, b in vdW gas model, we need to estimate the critical radius r_c , which defines the excluded volume in vdW theory. This is an interparticle distance below which particles have a small probability of finding each other. For rapidly growing potentials, r_c is estimated as the point where $U(r) = 0$. Plotting the $g(r)$ for the Leonard Jones potential, one can check that $g(r) \ll 1$ for r slightly below r_c determined this way. This is not the case for our potential because it has a very soft form of repulsion. We therefore adopt a different criterion to determine r_c . We chose a small threshold value of g^* and assume that r_c corresponds to $g(r_c) = g^*$. The value of g^* is arbitrary but allows for the comparison of the tendencies of different surfaces and provides an order of estimate of T_c . In the following, we conventionally adopt $g^* = 0.2$. Because of the rapid change of $g(r)$ with distance, our criteria practically do not change the estimates of the critical parameters of the LJ potential compared with the traditional criteria ($U = 0$ implying $g(r_c) = 1$). A better criterion for a soft repulsion would be to take a temperature-dependent b parameter, as in the theory by Barker and Henderson[132, 133]. Here, since we search for a very rough estimate, we stick to the above approximation.

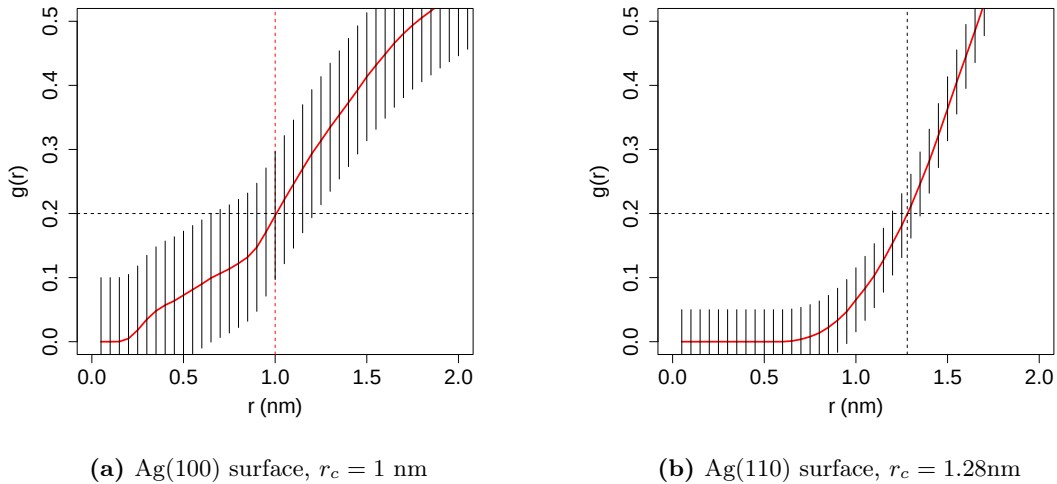


Figure 5.15: Application of the same criteria for cutoff $g(r) = 0.2$ of averaged PCFs on various Ag-surfaces. (panel a) Ag(100), $r_c = 1$ nm (panel b) Ag(110), $r_c = 1.28$ nm. Error bars given by the upper boundary of the standard deviation ($\sigma(100) = 0.1$, $\sigma(110) = 0.05$) are shown for each curve.

Applying the criterion $g(r_c) = 0.2$ to the Ag(100) surface, we obtain $r_c = 1$ nm, as shown in Fig. 5.15 panel (a). Using $\sigma = 0.1$ as a measure of errors, we have $0.65 \text{ nm} < r_c < 1.22 \text{ nm}$ (error bars are shown on the graph).

To compute the attractive a coefficient, we introduce $\hat{a} = \frac{a}{T_0}$ in analogy with $\hat{U}(r)$. Hence, $\hat{a}$ is

computed following

$$\hat{a} = -\pi \int_{r_m}^{\infty} \hat{U}(r) r dr. \quad (5.32)$$

We restrict the integral to the attractive part of the potential. Therefore, the lower limit of integration is defined by $U(r_m) = 0$ or equivalently $g(r_m) = 1$. From the experimental data in Fig. 5.14 we find $r_m = 3.5$ nm. This is shown by the vertical dashed line in the figure. Notice that we are using different values for the critical radius $r_c = 1$ nm and the cutoff radius $r_m = 3.5$ nm to estimate b and a respectively. This is necessary because of the very soft potential.

Using $r_m = 3.5$ nm we find $\hat{a} = 17.0$ and finally for critical parameters

$$n_c(T_c) = \frac{2}{3\pi r_c^2} \quad (5.33)$$

$$\hat{T}_c = \frac{T_c}{T_0} = \frac{8\hat{a}}{27b} \quad (5.34)$$

$$\hat{p}_c = \frac{p_c}{T_0} = \frac{\hat{a}}{27b^2} \quad (5.35)$$

which leads to $T_c/T_0 \approx 3.2$. Knowing T_0 allows us to determine the temperature T_c below which phase separation occurs. For example, if we assume that $T_0 = 53$ K when the hopping rate decays to the order of one per second, as it was computed in the section 5.2.4, we get $T_c \approx 170$ K. The choice of a smaller T_0 only decreases the value of T_c . However, with the aforementioned errors, the interval of estimated T_c is quite broad. In the following, we will use only $T_c/T_0 = 3.2$ as a reference estimated value.

Keeping in mind that synthesis was done at room temperature (300 K) while STM measurement was held at low temperatures (10 K), the found $T_c \approx 170$ K suggests that a liquid phase was formed only after transfer of the sample from the reaction chamber to the probe chamber, during relaxation of the temperature in the system. Unfortunately, we didn't vary the temperatures of synthesis and STM measurement during experiments, but this result points out an interesting direction for future experimental efforts in order to construct a simple phase diagram for F on Ag(100).

Ag(110) surface

The PCFs for F-adatoms on the Ag(110) surface were evaluated using the same methodology as for the Ag(100) surface, based on STM images obtained after a 3-hour fluorination experiment (Dose=20L) (Tab. 5.2). The average adsorbate density in these images is higher than that observed for Ag(100), ranging from 3.6×10^{-2} nm⁻² to 7.4×10^{-2} nm⁻², depending on the region of the surface (Fig. 5.16 and Fig. 5.17, panel (a)).

Fig. 5.18 (panel a) presents the corresponding PCFs obtained from several images with various densities (namely 3.6, 4.0, 4.2 and 7.4×10^{-2} nm⁻²), along with their average (shown as the red curve). The resulting PCF for this surface has several differences from the PCF computed for Ag(100) (Fig. 5.14). Firstly, within an error interval at any distance $g(r) \leq 1$, showing that there is no measurable attraction between adsorbates. There is a small peak at $r > 7$ nm which will be discussed later. Error intervals for Ag(110) are smaller than for Ag(100) due to better statistics given by a larger number of adatoms in the analyzed windows. For an average curve, we estimate $\sigma = 0.05$ as an upper boundary of standard deviation for this surface.

Fig. 5.18 (panel b) shows a comparison between averaged PCFs computed for both surfaces. It

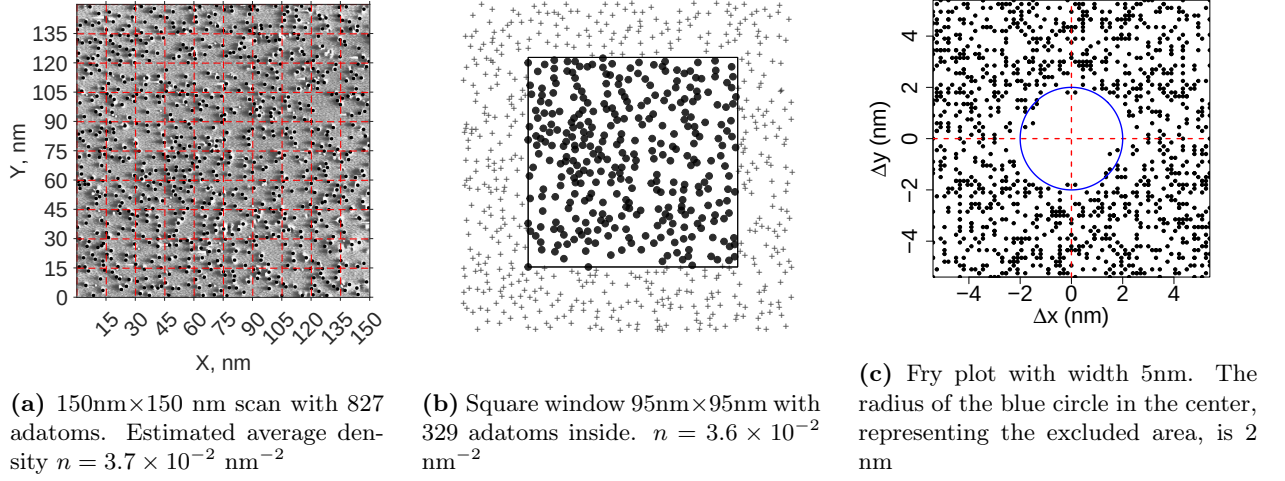


Figure 5.16: Processing STM scan for Ag(110), smaller density region of the surface (Tunneling conditions: $V_B = -1.5\text{V}$, $I_T = 60\text{pA}$)

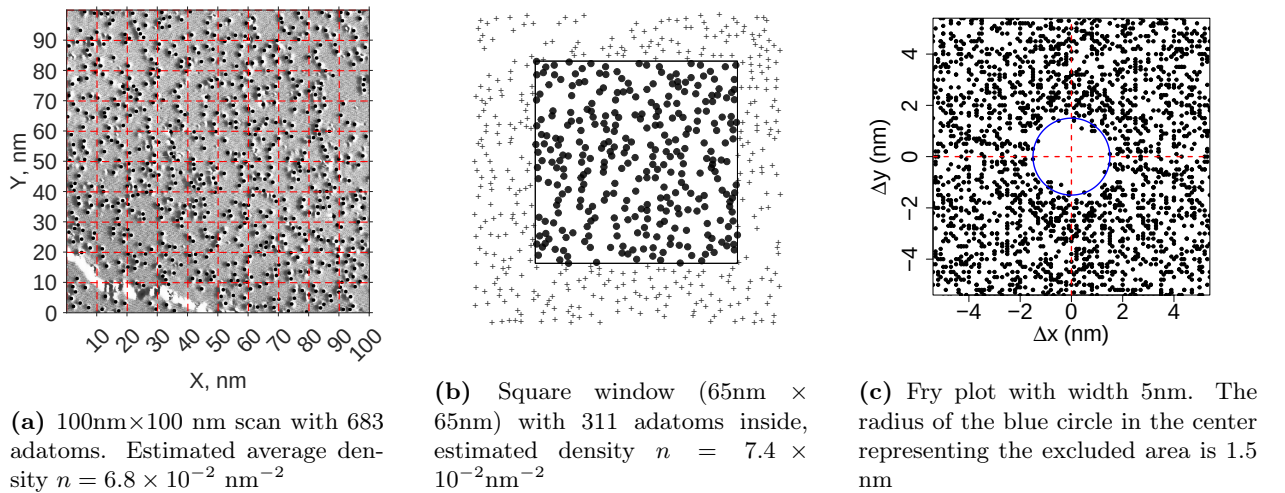
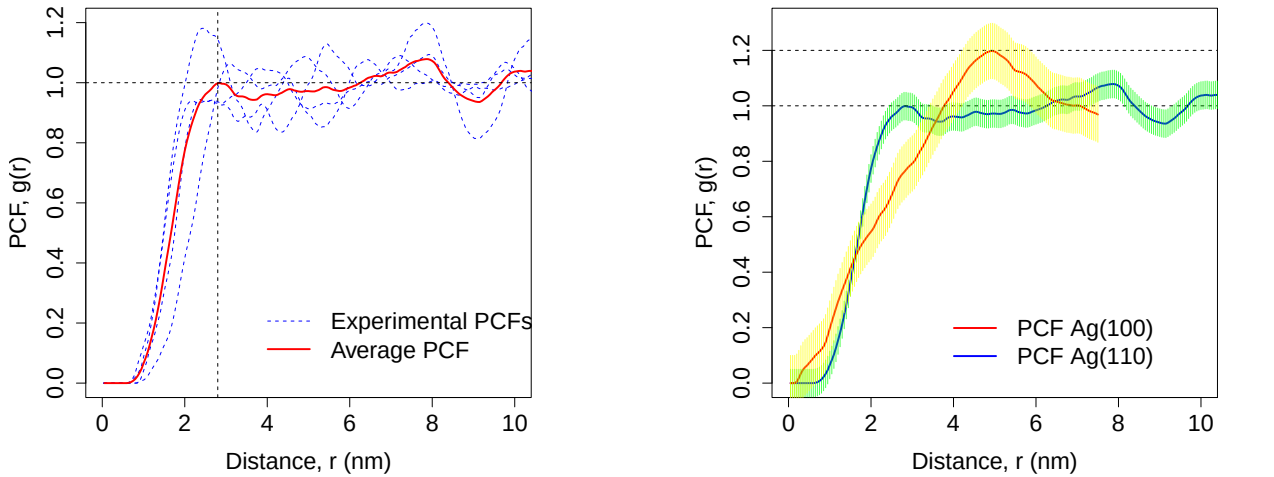


Figure 5.17: Processing STM scan for Ag(110), higher density region of the surface (Tunneling conditions: $V_B = -1.5\text{V}$, $I_T = 60\text{pA}$)

is clear that while PCF for Ag(100) surface has a visible peak between 4nm and 6nm, the PCF for Ag(110) at this interval of distances $g(r) = 1$ within the interval of errors. There could be some small peak there, but with the current experimental data, we can't resolve it.

With the same definition of critical radius, namely $g(r) = 0.2$ we get $r_c = 1.28\text{nm}$. It provides us with the critical density in 2D vdW gas model $n_c(T_c) = 13 \times 10^{-2}\text{nm}^{-2}$ (Fig. 5.15 panel b). Nevertheless, from Fig. 5.18 panel b it is clear that both surfaces have very similar critical radii r_c . The interval of errors is given by standard deviation and truncation of $g(r)$ at any small value less than 0.5, leads to the very close estimates of r_c . Actually, this will still be true for any $g^* < 0.5$.



(a) Ag(110) surface. Experimental PCFs computed for several densities (ranging from 3.6 to $7.4 \times 10^{-2}\text{nm}^{-2}$) (dashed blue curves). Averaged interpolated PCF (bold red curve). The dashed vertical line shows the cutoff radius $r_m = 2.7\text{ nm}$ ($g(r_m) = 1$).

(b) Comparison between averaged PCFs for Ag(100) and Ag(110) surfaces. Error intervals are shown by yellow and green vertical arrows, given by $\pm\sigma$ ($\sigma(100) = 0.1$, $\sigma(110) = 0.05$)

Figure 5.18: Experimental PCFs for Ag(110) surface (panel a). Comparison between PCFs for Ag(100) and Ag(110) surfaces (panel b)

The critical radius manifests qualitatively as an exclusion region in the Fly plots. Fig. 5.16 (panel c) and Fig. 5.17 (panel c) show Fry plots for two analyzed samples. Notice, however, that the region of zero density depends on the density of the sample, so this criterion can not be used to determine r_c .

After a careful analysis of all available experimental data, we did not find any evidence of anisotropy in the size of the exclusion area. In certain regions of the sample, the exclusion area appeared elliptical; however, when averaging over all data, the results indicate only a strong repulsion between adsorbates without a clear angular dependence. In our view, further experimental work is required to clarify this issue.

Similar effect of repulsion between adatoms at macroscopic distances has already been observed for the adsorption of oxygen on the Ag-surface in [86, 134] when the excluded area was estimated as a circle with radius 0.8nm . However, in the case of oxygen, the adatoms were formed after dissociation of O_2 molecule during adsorption with the following hot transient motion, which is different from adsorption of monoatomic fluorine (this phenomenon was already discussed in Chapter 4). The brief description and essence of hot transient motion phenomenon can be found in Appendix A.

Because the attraction is much smaller, we can not make quantitative estimates for all the vdW parameters on the Ag(110) surface. However, the fact that the possible attraction is very small Ag(100) implies that the critical temperature will be small. Therefore, we expect that T_c/T_0 to be much smaller than for the Ag(100) surface. This is consistent with a larger density in the gas phase, as indeed observed.

Alternative estimate of the Van der Waals critical temperature

The vdW phase diagram predicts that n_g^* and n_l^* should coincide at the critical point and should diverge as the temperature is lowered. Therefore, we can compare $n_l^*(T_0)/n_g^*(T_0)$ with the prediction of the vdW model (Tab. B.1) and obtain an alternative estimate of T_c/T_0 .

As we mentioned already, it is not possible to count the fluorine atoms in the amorphous phase. However, for Ag(100) surface we provided the lower bound estimate $n_l^*(T_0)/n_g^*(T_0) \approx 100$. From Tab. B.1 (which contains results of numerical solutions of vdW equation of state), we obtain that this corresponds to $T_c/T_0 = 2$. This is smaller than the previous estimate from the correlation function $T_c/T_0 = 3.2$ but is reasonable given that $n_l^*(T_0)/n_g^*(T_0) \approx 100$ is a lower bound estimate. As an upper bound, we can assume that the liquid phase has a local coverage $\theta_l = 1$, which leads to $n_l^*(T_0)/n_g^*(T_0) \approx 770$ and $T_c/T_0 = 2.6$. We see that our estimate from the correlation functions $T_c/T_0 = 3.2$ is above the bound but still compatible with it, given the large errors in the parameters. Increasing the arbitrary criteria used to determine b leads to a smaller T_c/T_0 within the bound. Our intention here was to obtain order-of-magnitude estimates and show the methodology. We leave more accurate estimates for future work.

Assuming that for the Ag(110) surface the liquid density in the coexistence region $n_l^*(T_0)$ is similar as for the Ag(100) surface and $n_g^*(T_0)$ is an order of magnitude larger than our lower bound, i.e. $n_l^*(T_0)/n_g^*(T_0) \approx 10$ we obtain $T_c/T_0 = 1.3$ which is consistent with the smaller attraction adsorbate-adsorbate interaction revealed by the pair correlation function.

5.2.6 Possible origin of the interaction potential

From a theoretical perspective, a long-range interaction between adsorbates can arise due to the coupling of their wave functions mediated by the electronic states of the metal substrate. First models describing interactions of two chemisorbed on metal surface adatoms were built by Grimley [135] and T.Einstein [136] and later by Kohn in [137]. In latter it was shown that the interaction energy depends on distance as

$$U_{int} \propto \frac{\cos(2k_F r)}{r^2}. \quad (5.36)$$

where k_F represents surface Fermi vector. This potential exhibits an oscillatory character due to Friedel oscillations [117, 138] and decay as r^{-2} at large separations instead of r^{-5} for bulk states. Therefore, the interaction remain non-negligible even at distances of several nanometers. It is tempting to attribute our findings to this kind of *indirect interactions* between adsorbates. The attractive peak observed in the PCF appears around 5 nm, as shown in Fig. 5.14 which is difficult to attribute to a direct overlap of F orbitals.

At shorter distances ($r \leq 1$ nm), the interaction potential becomes more complex, and *dipole-dipole repulsion* between adsorbates must be considered. As discussed in Chapter 4, there is significant charge transfer from the Ag substrate to the F-adatoms, which induces a dipole moment since

the two dipoles are parallel such interaction will be repulsive and may explain the soft rise in the potential that we found.

While a detailed analysis of long-range interactions lies beyond the scope of this experimental chapter, it is noteworthy that similar features in PCFs have been observed in colloidal systems with screening medium. Indeed, ions in the surrounding medium tend to screen charged colloidal particles, leading to a potential attractive part of which decays as $\propto \frac{e^{-kr}}{r}$. Notably, in [139] such a screened attractive interaction was found in colloidal particles confined between two plates. Remarkably, the PCFs computed for our F-adatom system on the Ag surface (see Figs. 5.14 and 5.18) resemble those measured in colloidal systems. In the latter case, experimental data are of higher quality, allowing the pair interaction potential to be fitted with elementary functions—showing measurable deviations from the classic DLVO [Derjaguin–Landau–Verwey–Overbeek] theory [140]. Unfortunately, such a precise analytical description is not achievable for our system within the present data set but a more accurate determination of pair correlation functions is certainly an interesting direction for the future.

5.3 Discussion and Conclusion

Summarizing, in this chapter, we demonstrated that amorphous fluorine overlayer structures can be grown on highly symmetric silver surfaces, specifically Ag(100) and Ag(110). For small average coverage, the adatoms distribute uniformly, while above a critical average coverage, the system phases separate into fluorine-poor and fluorine-rich regions.

Even after a 15-hour fluorination experiment on Ag(100), the amorphous F-overlayer did not fully cover the surface, with a fractional coverage of less than 80%, nearly identical to that observed after 5.5 hours. Measurements of the apparent thickness of amorphous overlayers, carried out across all studied reaction times (from 4 to 15 hours), consistently revealed the presence of the same stabilized amorphous phase. Although exact quantitative estimates of thickness and density are not provided here (due to the limitations of raw STM data and the conductance-dependent nature of apparent thickness), the persistence of this stabilized phase highlights the need for further investigation.

To interpret the observed phase separation behavior, we introduced a minimal theoretical framework, namely the two-dimensional van der Waals gas model, which captures the essential features of phase coexistence. From this model, we estimated the critical parameters of the system. For the Ag(100) surface, we obtained that phase separation appears below a critical temperature $T_c \approx 2T_0 \sim 3T_0 \approx 100 \sim 150$ K. These estimates are very approximate and should be taken as an order of magnitude. In any case, we showed the methodology that can be used to improve the estimates systematically.

We speculated that the effective interaction between fluorine adatoms was due to a balance between repulsive dipole-dipole interactions and Friedel-oscillation-mediated attraction arising from perturbations in the local electron density. More experimental and theoretical work is needed to confirm this hypothesis.

A key open question concerns the balance between order and disorder in the fluorination process. While the experiments presented here consistently yielded an amorphous phase, it is possible that under suitable conditions, long-range ordered structures could also form. The composition of

residual gases in the reaction chamber is likely to play a decisive role in determining the final overlayer morphology. This balance is delicate, and more elaborate experimental studies are required to clarify the conditions under which ordered phases might be stabilized. In particular, we cannot exclude the possibility that even at identical reaction times, variations in chamber environment (which we called "Fluorine-rich" atmosphere) could lead to different structural outcomes. Addressing this issue represents an important direction for future investigations.

Further experimental studies are required, also, to clarify the observed phase separation phenomena. Notably, all synthesis procedures reported here were performed at room temperature (300K), with STM characterization conducted at cryogenic temperatures (10K). It would be particularly interesting to investigate the resulting structures when synthesis is carried out at lower temperatures. Alternatively, a temperature-stepping approach—where STM measurements are conducted sequentially from cryogenic temperatures to progressively higher values, up to the limit where thermal fluctuations and surface diffusion hinder reliable STM imaging—could provide valuable insights into equilibration processes and kinetic effects.

Another promising direction is to conduct experiments with fine control over the adatom density. This is experimentally feasible due to the extremely low initial sticking coefficient of fluorine on silver (on the order of $10^{-5} - 10^{-4}$), which allows for precise dosing and the controlled introduction of individual adatoms. Such experiments would enable the systematic exploration of the system's phase behavior and may ultimately allow the construction of a density-temperature (n, T) phase diagram for the F/Ag system.

In addition to experimental work, the Van der Waals description can be improved by implementing corrections for soft potentials[132, 133]. Furthermore, Monte Carlo simulations may also offer a valuable tool for estimating key thermodynamic properties, such as the order-disorder transition temperature. Developing a more comprehensive theoretical model of the indirect interactions between F-adatoms could further illuminate the formation of various ordered phases. These theoretical predictions could be tested by complementary techniques such as XPS, providing a pathway toward a deeper understanding of the system's phase behavior and electronic structure.

Chapter 6

Resonant Inelastic X-ray Scattering for silver fluorides: comparison with cuprates

6.1 Introduction

This chapter represents a transition from the synthesis- and surface-focused investigations of earlier chapters to the application of advanced spectroscopic methods for probing the electronic structure of silver fluoride compounds. In Chapters 3–5, we described the development of ultrahigh vacuum systems and growth strategies aimed at synthesizing a two-dimensional form of AgF_2 , motivated by its predicted similarity to cuprate superconductors. While these efforts are ongoing, the fabrication of stable, atomically thin AgF_2 remains a significant challenge. These efforts can receive a strong stimulus if the similarity between bulk AgF_2 and cuprates can be substantiated and confirmed with more extensive investigations. With this aim, here we present resonant inelastic X-ray scattering (RIXS) measurements performed on bulk crystalline AgF_2 and AgFBF_4 —two structurally distinct but electronically intriguing silver fluoride systems.

Although the main focus here is on bulk materials, the data presented provide a crucial baseline for interpreting future RIXS spectra from thin-film or monolayer AgF_2 , once successfully synthesized. A comparative study between the 2D and 3D cases would offer valuable insight into the role of dimensionality in shaping the low-energy excitation spectrum, with implications for understanding the emergence of high-temperature superconductivity in fluorinated silver compounds.

As discussed in Sec. 2.3.2, Ref. [46] presented the RIXS spectra of AgF_2 at the fluorine K edge (682 eV, soft X-rays). The spectra are dominated by charge transfer excitations above 3 eV, but also dd excitations around 2 eV are clearly visible due to cross-talking between the transition metal and the ligand. Moreover, a tail of the elastic peak around 200 meV has been assigned to bimagnon excitations. Interestingly, the spectrum of AgF_2 holds several analogies to that of La_2CuO_4 measured at the O K edge. This is a very encouraging result to attempt doping and search for superconductivity in AgF_2 . Because the RIXS was performed on the F K edge and on a powder sample, polarization information was not available. Therefore, the assignment of the symmetry of the different dd excitations could be done only indirectly by comparing the energy with DFT computations.

Besides the interest as high- T_c superconductors silver fluorides are interesting because of the possibility to host exotic magnetic phases[141–147]. In this regard, a particularly intriguing system is AgFBF_4 [Fig. 2.5(c)]. Initially thought to be a metal because of its temperature-independent susceptibility[148] it is now believed to be an excellent realization of the one-dimensional Heisenberg model[143, 144] with a superexchange interaction $J \approx 300$ meV. Ironically, this model can be mapped to a one-dimensional “metallic” system, but in which the fermionic excitations are not electrons but neutral spinon excitations[149].

According to DFT computations[143, 144], the strong superexchange in AgFBF_4 is due to partially filled $d_{3z^2-r^2}$ orbitals oriented along the c -axis hybridizing with ligand p_z orbitals. Up to now, one of the best realizations of the one-dimensional Heisenberg model is Sr_2CuO_3 whose spinon spectra observable in optics, can be perfectly fitted with this model[150] with $J = 246$ meV. The spectrum has a logarithmic singularity at $\omega_s = J\pi/2 = 386$ meV. This can be observed in RIXS[151], and the value of J coincides with the theoretical fit of the optical experiments. In the case of AgFBF_4 , which we studied here, the DFT predicted J would imply a Van Hove singularity in the RIXS spectra (due to powder average) at $\omega_s=470$ meV.

For insulating cuprates, the determination of dd excitations[49, 152], and the full characterization of the single and multimagnon spectra[153–156] was made by Cu L_3 RIXS. This is because at the L_3 edge (930 eV), those excitations are accessed directly and not indirectly as at the ligand K edge. In $3d$ transition metals, these $2p \rightarrow 3d$ resonances are particularly intense, providing ideal conditions for RIXS spectroscopy.

Even though AgF_2 is not a new material, advanced spectroscopy studies are scarce, due to its instability and the lack of single crystals. To have a complete comparison of the electronic structure of the AgF_2 and cuprates, it is highly desirable to perform RIXS at the X-ray edge of the metal. Unfortunately, the Ag L_3 RIXS is at 3350 eV (tender X-rays), and the high-resolution detectors and lines developed for $3d$ electrons (soft X-rays) are useless.

In order to perform a RIXS measurement at the Ag L_3 edge, we used the ID26 TEXS beamline (ESRF, Grenoble) [157]. Although this beamline is dedicated mainly to high-energy-resolution fluorescence detection and does not have the resolution of present-day experiments at dedicated RIXS beamlines, we show here that RIXS measurements at the Ag L_3 edge are feasible, and clear conclusions about the electronic similarity between silver fluorides and cuprates can be drawn.

We present silver L_3 XAS ($2p \rightarrow 4d$) of AgF_2 and AgFBF_4 (d^9) of both powder and small single crystal samples obtained with a new technique [158]. We compare the spectra with that of silver d^{10} (AgF , Ag_2O) systems. The near-edge spectra of the d^9 materials show a strong predge excitonic line, which suggests a fertile ground for RIXS. Indeed, a rich RIXS spectrum was obtained at the Ag L_3 edge for AgF_2 and AgFBF_4 while the AgF and Ag_2O show essentially only fluorescence signals.

For the present RIXS study, it was essential the collaboration with G. Ghiringhelli, P. Glatzel, and M. Moretti Sala. The samples were prepared and provided by W. Grochala and collaborators. DFT computations were performed by A. Gomez Pueyo. A work is on preparation [159].

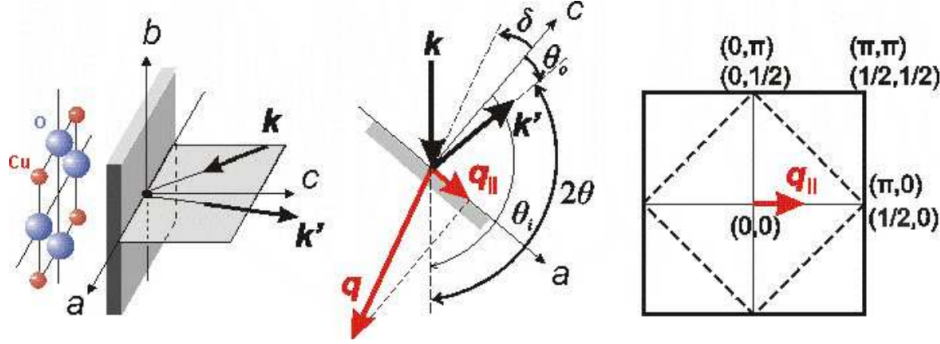


Figure 6.1: Sketch of the experimental layout for the RIXS in cuprates in the case of an oriented crystalline sample. See the text for details. The images are from [160]

6.2 Brief introduction to RIXS

6.2.1 Experimental details

A more detailed review of RIXS can be found in [161, 162] and in [163]. Here, we provide a brief introduction to the main aspects of this technique, which has achieved tremendous progress over the last several decades.

Firstly, RIXS is a "photon in-photon out" spectroscopic technique suitable for the study of elementary excitations in solids. Following the experiment, energy, momentum, and polarization of the scattered photon can be measured, which differ from those values for the incident photons. It leads to the situation when, after interaction, the system remains in a state different from the ground state. After measuring the energy and momentum of incident $[\hbar\omega_k, \mathbf{k}]$ and scattered $[\hbar\omega_{k'}, \mathbf{k}']$ photons, considering corresponding conservation laws, one can impose

$$E_{loss} = \hbar\omega_{k'} - \hbar\omega_k \quad (6.1)$$

$$\mathbf{q} = \mathbf{k}' - \mathbf{k} \quad (6.2)$$

where E_{loss} refers to the energy of excitation remaining in the sample, while $\mathbf{q}$ is the transferred momentum, which is determined by experimental geometry. Furthermore, a conservation law of total angular momentum should be added to this list. It concerns the polarization states of the ingoing ϵ and outgoing ϵ' photons. This set of parameters (energy, momentum, and polarization) provides a good deal of knowledge about the available excitations in the system.

As an example, fig. 6.1 shows the sketch of the typical experimental layout for RIXS measurement of cuprates, in the case of oriented crystals. Due to the quasi-2D nature of these compounds, all the interesting physics takes place in CuO_2 planes; therefore, the important quantity to measure is the projection of the transferred momentum $\mathbf{q}$ onto the sample ab -plane, $\mathbf{q}_{||}$. Following experimental geometry, the two X-rays belong to the scattering plane. In the general case, the polarization of the incoming (outgoing) photon can be decomposed into components parallel(π) and perpendicular(σ) to the scattering plane. The angle between $\mathbf{k}'$ and $\mathbf{k}$ is the scattering angle 2θ , which is fixed during the experiment. The incident angle θ_i can be changed by rotation of the sample holder, while the outgoing beam is always collected at θ_0 . Overall, they define δ , the angle between the sample c -axis and the transferred momentum $\mathbf{q}$. Rotating the sample over the axis

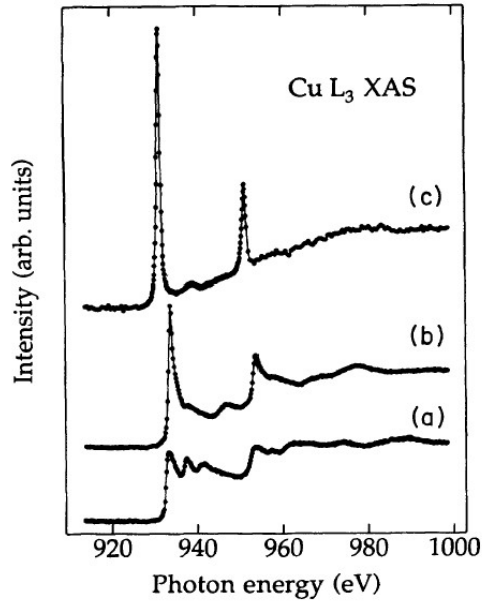


Figure 6.2: Cu $L_{2,3}$ edge X-ray absorption (XAS) spectra of (a) copper metal, (b) Cu_2O (Cu^{1+}), and (c) CuO (Cu^{2+}). The image is from [164]

perpendicular to the scattering plane allows changing δ and consequently $q_{\parallel}$, allowing measurement of dispersing excitations. Following this way it is possible to scan all the square 2D Brillouin Zone of cuprates (shown on the right in Fig. 6.1 (a)). In our experiments below, we are dealing with polycrystalline samples or randomly oriented samples. Therefore, any theoretical result for a given crystal orientation should be averaged over all possible crystal orientations. Likewise, the outgoing polarization is not measured and therefore should be averaged.

RIXS is a spectroscopy that exploits the resonance condition: the incident photon energy is tuned to an absorption edge of the element of interest in the studied compound. This resonance dramatically enhances the scattering cross-section compared to non-resonant inelastic X-ray scattering and many other spectroscopic techniques.

Fig. 6.2 illustrates Cu $L_{2,3}$ X-ray absorption spectra for three compounds with different Cu oxidation states ((a) copper metal, (b) Cu_2O (Cu^{1+}), and (c) CuO (Cu^{2+})). By choosing the appropriate absorption edge, it is possible to selectively probe specific atomic species, oxidation states, and coordination environments. The only requirement is that the energy separation between neighboring edges must exceed the experimental energy resolution.

Despite its strengths, RIXS is intrinsically photon-hungry and therefore requires synchrotron radiation sources of very high brilliance, such as those provided by the latest-generation facilities. The core of any RIXS setup is the spectrometer, which selects a given scattering angle, collects the outgoing radiation, and disperses it for energy analysis.

One of the most advanced instruments developed for this purpose is the *European RIXS* (ERIXS) spectrometer [165] at the ESRF beamline ID32 (Grenoble, France). ERIXS was specifically designed for high-resolution experiments at the Cu L_3 edge and introduced several major innovations compared with previous instruments. It achieves a combined energy resolution of about 35 meV at the Cu L_3 edge, which, at the time of its commissioning (2015, upgraded in 2020), surpassed all other available soft X-ray spectrometers worldwide. This unprecedented resolution has enabled

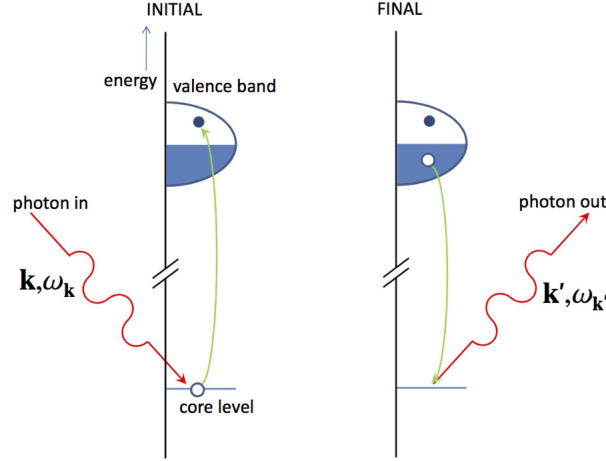


Figure 6.3: In RIXS process, the incoming x-rays excite an electron from a deep-lying core level into the empty valence. An electron from the occupied states under the emission of an x-ray then fills the empty core state. This RIXS process creates a valence excitation with momentum $\hbar\mathbf{k}' - \hbar\mathbf{k}$ and energy $\hbar\omega_{\mathbf{k}} - \hbar\omega_{\mathbf{k}'}$. The image is from [161]

detailed studies of low-energy collective excitations such as magnons, bimagnons, and phonons in cuprates. Unfortunately, the range of incident energies in this spectrometer is too low to access the Ag L_3 edge. Therefore, the results below are obtained in a different beamline with much less resolution than in cuprates.

6.2.2 Scattering process and cross section

The excitations probed by RIXS involve the charge, spin, orbital, and lattice degrees of freedom of the system, while always conserving the total charge (Fig. 6.4 panel (a)). Historically, the development of this technique has coincided with studies of superconductivity in cuprates; however, it doesn't have any limitations for other transitional metal oxides. In this chapter, we focus primarily on dd - and pd -excitations (the latter corresponding to charge-transfer processes), while also providing a brief discussion of magnetic excitations such as magnons accessible through RIXS.

Using cuprates again as an application example, in the CuO_2 plane, the Cu^{2+} ion has the configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9$, with a partially filled $3d$ shell typical of transition metals. The K -edge transition ($1s \rightarrow 4p$) occurs around 9000 eV, placing it in the hard x-ray regime. The $L_{2,3}$ edge ($2p \rightarrow 3d$) appears near 900 eV, while the $M_{2,3}$ edge ($3p \rightarrow 3d$) is located around 80 eV, both in the soft x-ray regime. Similarly, at the oxygen K edge ($1s \rightarrow 2p$), excitations can be induced at about 500 eV.

Absorption of such a photon brings the system into a highly excited intermediate state containing a deep core hole (Fig. 6.3). This state is unstable and has a very short lifetime, on the order of 1–2 fs, after which the system decays. One decay channel is Auger emission, in which the core hole is filled and another electron is ejected; this process, however, does not contribute to RIXS. Instead, RIXS originates from radiative decay, where the core hole is filled by an electron while a photon is simultaneously emitted.

The RIXS cross section can be expressed using the Kramers-Heisenberg generalized formula [160, 161]. It can be derived starting from the Hamiltonian for a system with N electrons interacting with the electromagnetic field, perturbatively taking into account photon-electron interaction and

using the Fermi Golden Rule. In the dipole approximation, it leads to

$$\frac{d^2\sigma}{d\hbar\omega d\Omega} \propto \omega_k \omega_{k'}^3 \sum_f \left| \sum_n \frac{\langle f | \hat{\epsilon}^* \cdot \hat{\mathbf{r}} | n \rangle \langle n | \hat{\epsilon}' \cdot \hat{\mathbf{r}} | g \rangle}{E_g + \hbar\omega_k - E_n + i\Gamma_n} \right|^2 \delta(E_g - E_f + \hbar\omega). \quad (6.3)$$

Here $|g\rangle = |g, \mathbf{k}, \hat{\epsilon}\rangle$ is the ground state of the system plus incident photon (with corresponding energy E_g), $|n\rangle$ is the intermediate state with energy E_n and lifetime broadening Γ_n , while $|f\rangle = |f, \mathbf{k}', \hat{\epsilon}'\rangle$ is the final state of the system plus scattered photon (with corresponding energy E_f). The energy transfer (energy loss) to the system $E_{\text{loss}} = E_f - E_g = \hbar(\omega_{\mathbf{k}'} - \omega_{\mathbf{k}}) = \hbar\omega$. Polarizations of incoming (outcoming) photons $\hat{\epsilon}(\hat{\epsilon}')$ and position of electrons $\hat{\mathbf{r}}$ are written in terms of operators. It is important to emphasize that in the general case, summation through the manifold of all intermediate states should be done before taking the square of the modulus in Eq. (6.3).

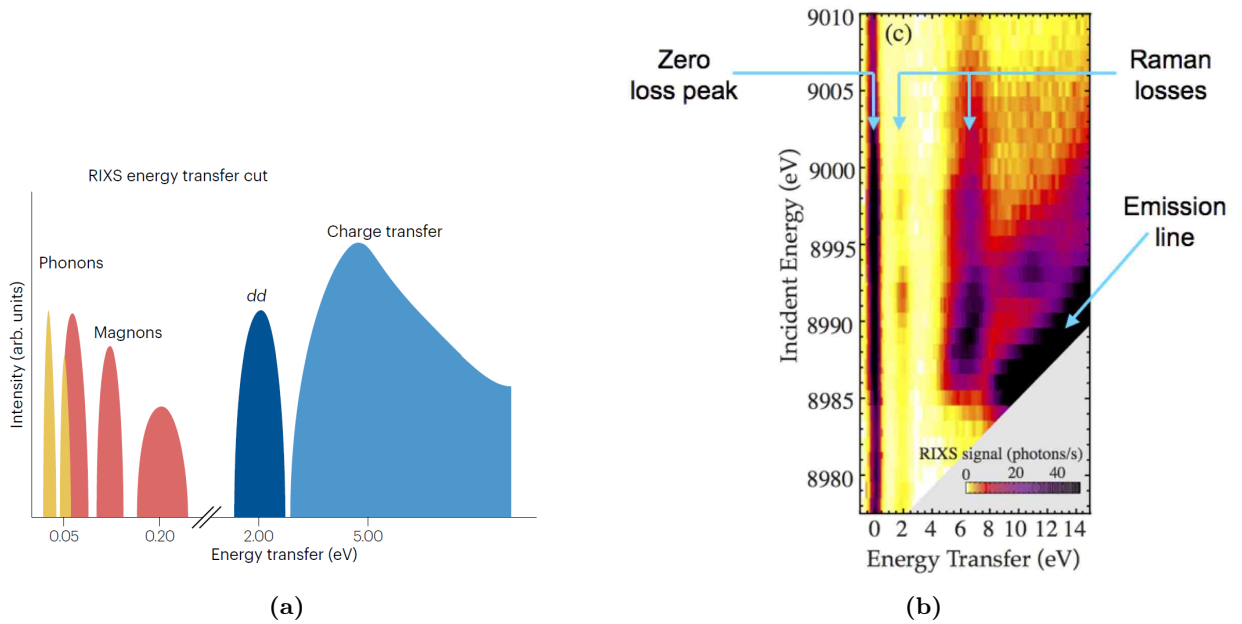


Figure 6.4: (a) Different elementary excitations in condensed matter systems and their approximate energy scales in strongly correlated electron materials such as transition-metal oxides. Image is from [162]. (b) Two classes of inelastic energy-loss features in the RIXS spectrum of CuB_2O_4 . The RIXS intensity is represented on a color scale versus transferred energy (energy loss) $\hbar\omega$ and incident energy $\hbar\omega_{\mathbf{k}}$. The zero-loss line is the vertical line at zero transferred energy. Raman-like features appear as horizontal lines at constant $\hbar\omega$, resonating at specific incident energies (e.g., the $\hbar\omega = 2$ eV loss feature at $\hbar\omega_{\mathbf{k}} = 8992$ eV). Fluorescence features appear as diagonal lines, since the emitted photon energy $\hbar\omega_{\mathbf{k}'}$ is approximately constant. Image is from [166].

The used dipole approximation is appropriate only when $\mathbf{k} \cdot \mathbf{r} \approx \frac{2\pi r}{\lambda} \ll 1$, with $r \sim 1$ Å. It is easy to show that Cu L_3 edge (soft X-rays) as well as Ag L_3 edge (tender X-rays) satisfy this condition while for hard X-ray photons quadrupole transitions also should be taken into account.

In RIXS, the role of intermediate states is fundamental. The presence of a core-excited state between two dipole transitions enables processes that would otherwise be forbidden in direct dipole scattering. A notable example is the observation of dd -excitations explained in detail in Section 6.2.3. Furthermore, the polarization dependence of both absorption and emission processes provides valuable information on the symmetry properties of the underlying excitations.

The δ -function in Eq. 6.3 enforces energy conservation, ensuring that the energy loss of the

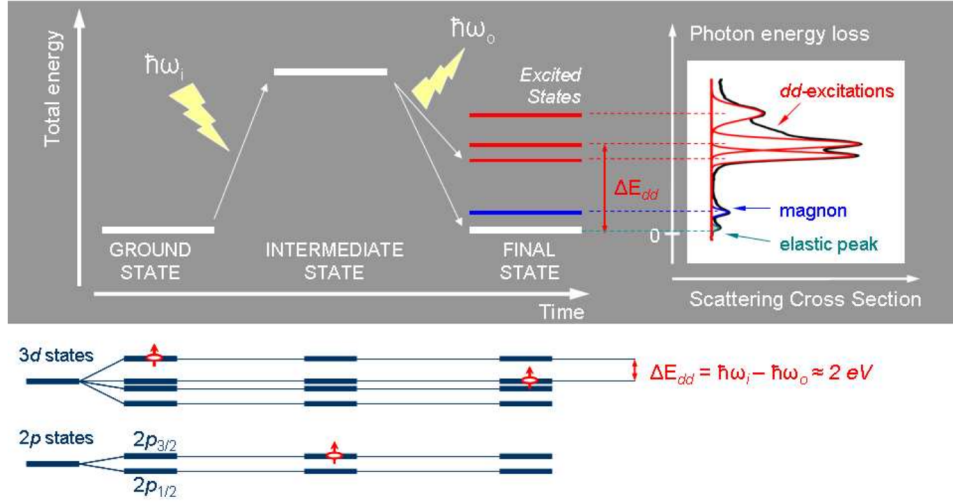


Figure 6.5: Total energy scheme of copper at the various stages of a Cu L_3 RIXS process and associated typical RIXS spectrum of a cuprate. The Cu $3d^9$ hole (open red circle) makes two dipole allowed transitions making possible a dipole forbidden dd -excitation of energy ΔE_{dd} . The image is from [160]

scattered photon corresponds precisely to the excitation energy of the system. As a result, well-defined excitations manifest as spectral peaks at constant energy loss. These Raman-like features can be clearly distinguished from fluorescence peaks, which appear at a fixed emitted photon energy determined by the atomic species, independent of the incident photon energy. Since fluorescence corresponds to radiative decays that no longer retain information about the intermediate state, it generally provides less insight compared to Raman-like features, which are the focus of this work.

In most cases, RIXS results are conveniently represented as two-dimensional intensity maps, with the incident photon energy plotted on one axis and the energy loss defined as $E_{\text{loss}} = \hbar\omega_{k'} - \hbar\omega_k = \hbar\omega$ on the other. In this representation, Raman-like excitations appear as horizontal (or vertical, depending on the chosen convention) lines at constant E_{loss} resonating at particular incident energy, whereas fluorescence features give rise to diagonal streaks, as shown in panel (b) of Fig. 6.4. This distinction provides a simple criterion to separate Raman-like and fluorescence contributions, and will be particularly important for the interpretation of silver fluoride spectra presented later in this thesis.

6.2.3 Probing dd excitations in cuprates by RIXS

In cuprates, high-resolution RIXS has established itself as a powerful method to detect both ligand field (dd) and magnetic excitations, as demonstrated experimentally and theoretically in recent years [49, 153, 167, 168].

At the Cu L_3 edge, the process follows the scheme shown in Fig. 6.5: copper ions in the CuO₂ planes are typically in a $3d^9$ configuration with a single hole in the d shell. The relevant electronic process is

$$2p_{3/2}^4 3d^9 \rightarrow 2p_{3/2}^3 3d^{10} \rightarrow 2p_{3/2}^4 3d^{9*},$$

Where asterisks denote the final state containing dd excitations. Following this scheme, resonant absorption promotes the hole into the $2p_{3/2}$ core level, creating a highly excited intermediate state with a core hole. Because of the large $2p$ spin-orbit splitting (≈ 20 eV), interference effects with the

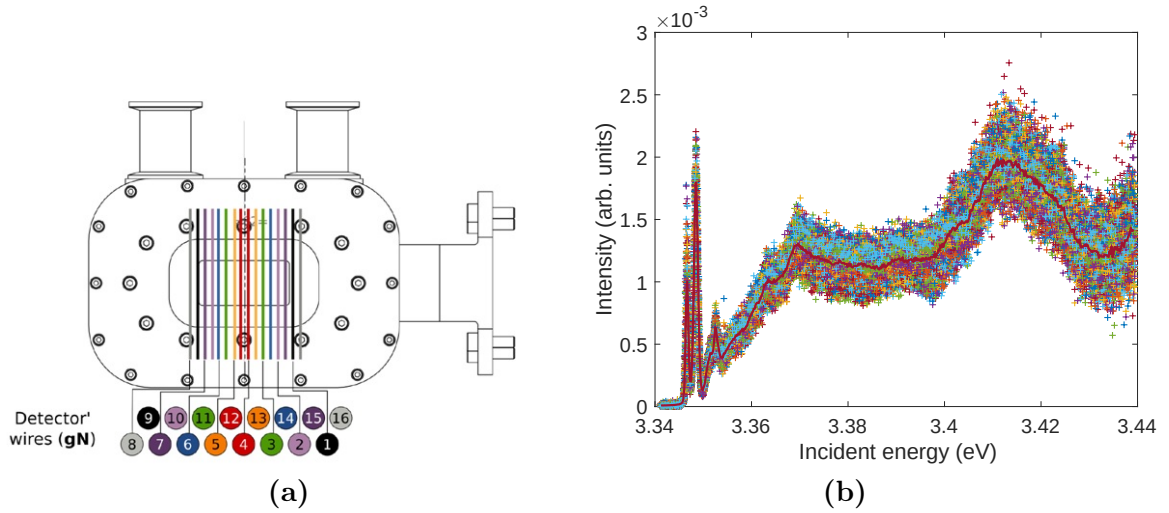


Figure 6.6: (a) Scheme of the 16-wire TEXTS detector used at the ID26 beamline of ESRF. Each wire is marked with a different color and corresponds to an independent channel in the dataset. Image is from [157]. (b) Averaging XAS signal between available channels for pellet AgFBF_4 . Signals from various channels are shown as colored markers. The bold purple curve represents the averaged signal used in the computation afterwards.

$2p_{1/2}$ states can be neglected. The subsequent decay emits a photon and restores the hole to the d shell.

In layered cuprates, a hole has almost $d_{x^2-y^2}$ ground state and therefore the dd excitations can be described as the transfer of the this hole from the $d_{x^2-y^2}$ orbital to the $d_{3z^2-r^2}$, d_{xy} , d_{yz} or d_{xz} orbitals. Also the case of $d_{x^2-y^2}$ final state can be viewed as a dd excitation, giving rise to an elastic scattering

If the final d -orbital differs from the initial one, the system ends in an excited state, giving rise to a dd excitation with typical energies of about 2 eV. While such transitions are dipole-forbidden ($\Delta l = 0$), they become accessible in RIXS because the two-step process consists of dipole-allowed transitions ($d \rightarrow p$ and $p \rightarrow d$). In the experimental part of this chapter, the RIXS spectra of La_2CuO_4 are used as a benchmark for comparison with the newly acquired spectra of AgF_2 and AgFBF_4 .

6.3 Methods

6.3.1 Samples

We measured pellets and small crystals of AgF_2 and AgFBF_4 . For the single crystal samples, the size was around 500 microns $\times$ 500 microns, and no attempt was made to orient the sample. Because the samples are very sensitive to moisture, it was necessary to mount them in a specially designed cell with an inert atmosphere and a Be window. This avoided degradation in the low vacuum (10^{-5} mbar) of the TEXTS instrument. For comparison, we also measured RIXS spectra of pellets Ag_2O and AgF .

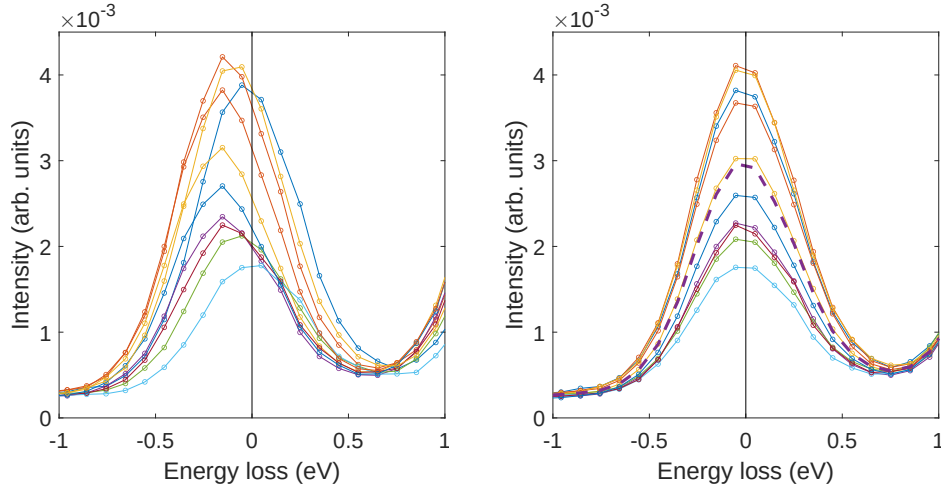


Figure 6.7: Alignment of signals from various channels of TEXS detector for AgF_2 pellet RIXS (incident energy 3.3485 keV) (a) Initial signals: each curve represents a separate channel (b) Signals after alignment: all the curves are centered at 0 energy loss after introducing small shifts and interpolation. The bold purple curve represents the averaged signal used afterward for computation of RIXS intensities.

6.3.2 Experimental

The measurements were done at beamline ID26 of ESRF – The European Synchrotron (Grenoble, France) using the Tender X-ray Emission Spectrometer (TEXS) [157]. The spectrometer consists of 11 cylindrically bent Johansson Si(220) crystal analyzers arranged in a non-dispersive Rowland circle geometry and a sixteen-wire detector. The energy resolution of the spectrometer is approximately 0.4 eV, comparable to the bandwidth of the cryogenically cooled double Si(111) crystal monochromator. All measurements were performed at $T = 15$ K.

We used high-energy resolution fluorescence detection (HERFD) for XAS and RIXS. This technique [169] consists of measuring the X-ray absorption spectrum of the incident photons by monitoring the intensity of a fluorescence line, in our case $L\beta_{2,15}$, using a narrow energy resolution. The $L\beta_{2,15}$ line corresponds to the decay $4d \rightarrow 2p_{3/2}$. Naturally, only the part of the spectra with energy larger than the $L\beta_{2,15}$ line can be measured.

In the displayed XAS spectra below, we removed the data in the region of the elastic line i.e., the line at the incoming photon energy, which was tuned to the $L\beta_{2,15}$ energy (≈ 3.346 keV)[170, 171]. For RIXS, the measurement is similar, but the detection energy is detuned from the emission line and scanned around and below the incoming photon energy, so both fluorescence and inelastic signals are detected.

It should be noted that the fluorescence line used for detection is in the same energy region as the outgoing RIXS photons. Normally, the fluorescence line used for detection is far from the X-ray absorption resonance edge. Here, this unusual configuration was chosen for technical reasons and proved efficient for the experiment, but does not allow for a clear identification of white lines as explained below. All the measurements were done with the incoming polarization in the scattering plane (π polarization), and the angle between the incident and the outgoing momentum is nearly 90° .

The TEXS detector (principal scheme is shown in Fig. 6.6 panel a) provides the signal from each wire separately. It was noticed that several external wires from each side of the detector had almost zero signal, so they were discarded from all reported spectra. Additionally, channels within one

dataset have a discrepancy between each other (of the order of 0.5 eV), thus presenting calibration differences. Therefore, in the XAS spectra before averaging, we fitted the narrowest structure in the spectrum (like a white line) with a Gaussian and introduced a small energy shift so that all spectra have the said line at the measured average energy. Afterward, the signal between all the channels was averaged, which can be considered as a reduction of the noise (Fig. 6.6 panel b). In the case of RIXS spectra, we used the quasielastic line for the same purpose, centering it at zero energy as it shown in Fig. 6.7.

Because of the limitation in resolution, the quasielastic line likely has significant inelastic contributions (for example, from magnetic excitations and phonons). Thus, the energy of our “elastic” feature has a systematic positive error and which implies an underestimation of the reported energy of excitations (of the order of the energy resolution) as discussed below.

Several scans were performed for each sample to check for possible degradation during measurement. In the absence of significant changes, the reported spectra are the average over such scans.

The 0.4 eV resolution is much lower than state-of-the-art RIXS lines for soft X-rays usually used for cuprates. Still, as we shall see, the main structures could be identified and compared to typical spectra in cuprates.

6.4 Results

6.4.1 X-ray absorption spectroscopy

The experimental results were compared with DFT computations of the X-ray absorption spectra and the DOS. The former were obtained in the so-called supercell core hole (SCH) approximation. This relies on the fact that the core hole has a very small bandwidth, and therefore it can be considered localized in a given atom. The computation is an optical absorption computation in the presence of such a localized core hole in a supercell. Because the localized core hole acts as a local impurity, states can be split off the conduction band, providing in-gap states in the case of an insulator. Transitions to these final states simulate excitonic effects, while transitions to the valence band simulate the edge.

In Ag the L_3 edge is due to transitions from the core $2p_{3/2}$ states to $4d$ or $5s$ unoccupied states. Typically, the transition to empty d states leads to pre-edge peaks in X-ray absorption (the excitonic effects mentioned above), commonly referred to as “white lines” due to their appearance in old photographic detection.

Figure 6.8 shows the experimental XAS spectra from the present work for powder samples (full lines) and from previous measurements [172] by Miyamoto et al. (dot-dashed lines). The Ag_2O and AgF spectra are in good agreement with Ref. [172], although our measurements show sharper features and more detail, probably because of the different techniques used. Black lines are the theoretical computations in the SCH approximation.

Although the spin-orbit interaction, which splits the L_2 and L_3 edges by 172 eV is not considered in the calculations, the energy of the theoretical edge is surprisingly close to the experiment for the L_3 edge. A shift of 2 eV was enough to align the theoretical data to the experiments, except for Ag, where the shift was -2 eV, and AgF_2 , where the shift was 5.5 eV. Another important aspect

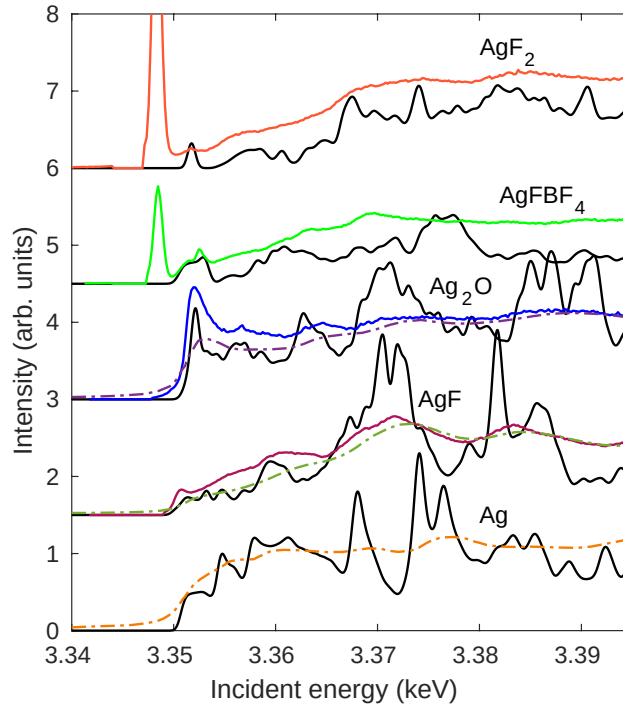


Figure 6.8: Ag L_3 experimental absorption spectra of the compounds studied and silver (color lines). The curves are normalized to 1 at the highest measured energy and plotted with a vertical shift of 1.5 [arb. unit]. We show data from the present work (full lines) and Ref. [172] (dot-dashed lines). We also show the SCH results in the non-magnetic DFT solution (black). The intensity of the DFT data was adjusted to ease the comparison with the experiment. Furthermore, to match the experiment, it was necessary to shift the theoretical spectra by 2 eV to higher energy, except for AgF_2 (+5.5 eV shift) and Ag (-2 eV shift).

neglected by the theory is lifetime effects, which will broaden narrow peaks in the theory. Despite those shortcomings, the theory reproduces several features of the data.

Ag

The experiment shows no white line consistent with its $4d^{10}5s$ configuration of pure Ag. The theory describes the overall edge shape quite well (Fig. 6.8) and shows some peaks at 3.368 keV, 3.374 keV, and 3.377 keV that correspond to broad structures in the experiment. Naively, one would expect the edge to have a dominant $5s$ character, but the DOS analysis (Fig. 6.9) shows that there are significant $5p$ and $4d$ contributions due to strong hybridization. In general, the theoretical XAS spectra reflects main structures in the DOS except for the strong s peak at high energy.

$4d^{10}$ compounds

The AgF Miyamoto data in Fig. 6.8 (dot-dashed lines) show no evident pre-edge peak, although a weak structure at 3.352 keV was interpreted as a peak. We do observe a weak excitonic resonance at the edge of the absorption, which can be seen as a precursor of the white line. We interpret this as due to the mixing of the nominally d^{10} ground state with the d^9s^1 state mediated by the fluorine p orbitals. Similar preedge peaks have been observed[164] in Cu_2O with a $3d^{10}$ ground state and in other Ag $4d^{10}$ compounds[172].

The SCH computation shows a gradual increase in intensity from the edge and intense structures at high energy (3.36 keV, 3.37 keV, and 3.382 keV), which also corresponds to broad structures in

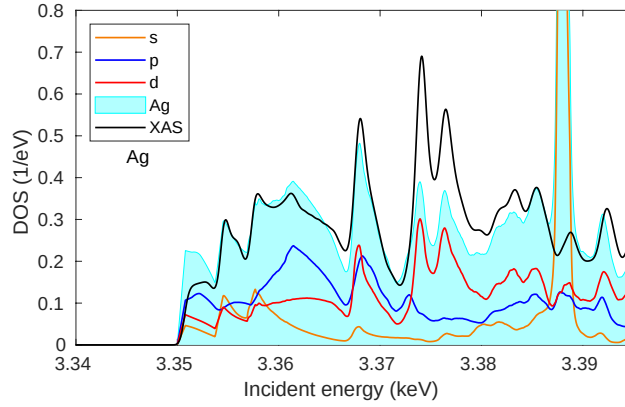


Figure 6.9: Ag symmetry projected (orange, blue, red) DOS and total silver DOS (green), and total DOS (cyan shadowing) compared to the computation of the XAS in the SCH method shown in Fig. 6.8 (black, intensity in arbitrary units). To simulate the edge, we show only the unoccupied part of the DOS, and the Fermi energy has been shifted to match the main features of the SCH computation.

the experiment. We attribute the very weak excitonic resonance to the small density of states at the edge, which has mainly $5s$ character (Fig. 6.10).

For Ag_2O the resonance becomes much more pronounced, although it is not separated from the continuum. Also, in this case, the resonance is sharper than results from Ref. [172] (c.f. Fig. 6.8). In contrast to AgF , the DOS of Ag_2O (Fig. 6.10) shows a steep rise at the edge region, which explains the strong excitonic resonance both in the theory and in the experiment. Compared to AgF , the DOS analysis shows a weaker s contribution and more weight of other symmetries due to stronger hybridization. The difference in the DOS reflects the fact that ligand $2p$ orbitals are located at a higher energy with respect to Ag $4d$ orbitals compared to the fluoride compound, which is the main motivation to replace O by F mentioned in the introduction.

$4d^9$ compounds

In the case of AgF_2 and AgFBF_4 , one expects white lines to appear due to the promotion of an electron to the open d shell. Strong features appear at 3.348 keV in Fig. 6.8 resembling white lines. However, these features are not white lines but are due to the overlap of the very intense dd RIXS features with the fluorescence line as described below.

More insight can be gained comparing with the theory computations which predicts a weak white line for AgF_2 . Aligning the theory spectra to the main features of the experiment, the theoretical white line agrees with a weak experimental feature which we identify with the white line. Interestingly, the overall match of the high energy features is similarly good as for the previous compounds.

Also in the case of AgFBF_4 the leading peak is a RIXS dd excitation. Then there is a broad preedge peak at 3.352 keV which resembles a similar theoretical feature. The matching of the theoretical and experimental high-energy features is less obvious in this case.

It is interesting to compare the unoccupied DOS with the SCH computation in the d^9 compounds. The leading peak of the unoccupied DOS resembles a strong white line. Indeed, because $4d$ are narrow and only $1/10$ of the $4d$ DOS is unoccupied, one obtains an intense narrow feature. As expected, this is almost purely $4d$ -character.

The reason why this feature is much weaker or absent in the SCH is that the core hole acts as a

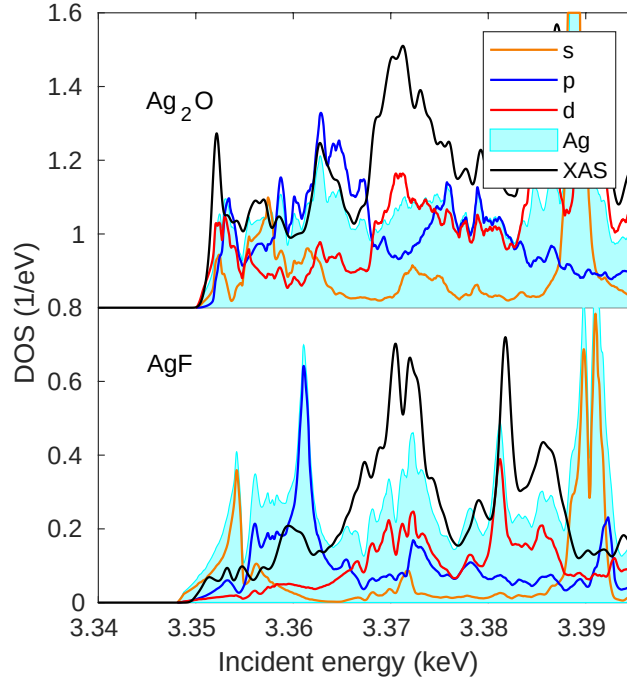


Figure 6.10: Same as Fig. 6.9 for d^{10} compounds. The Ag_2O data has been shifted by 0.8 eV^{-1} .

positively charged impurity. Relaxing the charge, metallic electrons fill the “impurity” state, which therefore becomes Pauli blocked as a possible final state in agreement with the experiment. In the DOS computation, this screening is not present, explaining the appearance of an intense feature.

It is interesting that excitonic shifts are surprisingly small. Aligning main features, the position of the white line in the SCH (in the presence of the core hole) coincides with the DFT computation of the DOS without core hole. This is again due to screening effects. Bound states below the Fermi level are automatically filled in the SCH computation and the white line is actually formed by scattering unoccupied states of the $4d$ band.

Repeating the computation in the insulating antiferromagnetic state using DFT+ U (Fig. 6.12), a small white line appears for AgFBF_4 and the white line of AgF_2 splits into two with small excitonic shifts. Clearly these effects are due to decreased screening in the insulating state but because of the small charge-transfer gap the changes are not dramatic.

Coming back to AgFBF_4 , because of the symmetry of the structure [Fig. 2.5(c)], the theoretical spectra for the x and y polarizations are identical and different from the z polarization. We find that the overall form of the absorption has a weak dependence on polarization (not shown) except for the broad preedge feature, which is 10 times more intense for the electric field oriented perpendicular to the chain (x, y) than along the chain direction (z).

For AgF_2 , the theoretical white line intensity shows some anisotropy (50% changes in the intensity, not shown). A similar feature as the broad white line of AgFBF_4 is present in AgF_2 shown at 3.357 keV in Fig. 6.8, and shows also a nearly 10 times anisotropy in intensity but with the stronger feature when the electric field is along the z -direction (c -axis in Fig. 2.5). This inversion of the anisotropy is consistent with the nature of the ground-state hole found in DFT, which is $d_{3z^2-r^2}$ for AgFBF_4 and $d_{x^2-y^2}$ for AgF_2 . These anisotropic effects can be the subject of a future study in oriented single crystals.

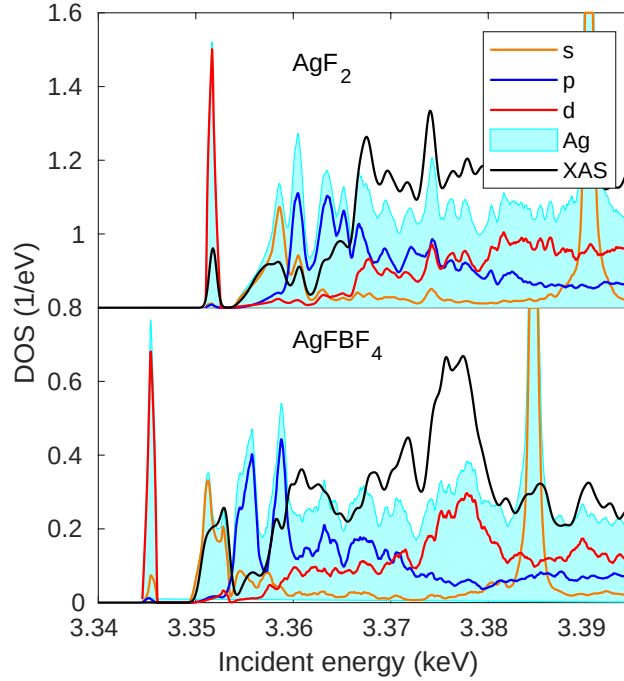


Figure 6.11: Same as Fig. 6.9 for d^9 compounds. The AgF_2 data has been shifted by 0.8 eV^{-1} .

6.4.2 Resonant Inelastic X-ray Scattering

Fig. 6.13 (panels (a) and (b)) shows the false color map of the RIXS/fluorescence spectra of AgF and AgF_2 . The dispersive features correspond to fluorescence, while the non-dispersive ones are the RIXS spectra. AgF_2 shows a strong feature at 2 eV of energy loss corresponding to dd transition and a faint structure in the 4-8 energy loss range corresponding to charge transfer excitations (notice the log intensity scale). These assignments are based on previous computations and measurements at the fluorine K-edge [46] as discussed in more detail below. In contrast, for AgF , these features are not present; only the elastic line and the dispersive fluorescence feature are visible. This behavior is consistent with the closed-shell nature of AgF in contrast to the open $4d$ shell of AgF_2 . Ag_2O (AgFBF_4) exhibits a map similar to AgF (AgF_2) consistent with the d^{10} (d^9) nature and are shown in panels (c) and (d) of the same figure.

The black dashed line in panels (b) AgF_2 and (d) AgFBF_4 corresponds to the scan done at constant outgoing photon energy in the XAS experiments. Clearly, such a scan intercepts a strong dd process which is not related to fluorescence. This leads to the strong leading peak at 3.349 KeV in Figs. 6.8 and 6.12. Because such peaks are not related to an absorption process, they were not taken into account in the analysis of the d^9 compounds in Figs. 6.8 and 6.12.

During the RIXS measurements, we found some evidence of radiation damage for crystalline samples. After the first attempt for both crystalline AgF_2 and AgFBF_4 , it was noticed that RIXS maps were more similar to full shell analogs ($\text{AgF}/\text{Ag}_2\text{O}$) than to powder samples of the same compounds. Additional measurement allowed to obtain RIXS maps for AgF_2 crystalline sample (Fig. 6.14, panel (a), the step of the map in incident energy is 0.2 eV instead of 0.001 eV as for other shown maps). Panel (b) of the same Fig. shows a cut of the map at 3.35 keV, which has the same shape as for AgF_2 powder sample shown in panel (b) of Fig. 6.13. Notice that this problem did not arise for the powder samples for which we based most of our analysis.

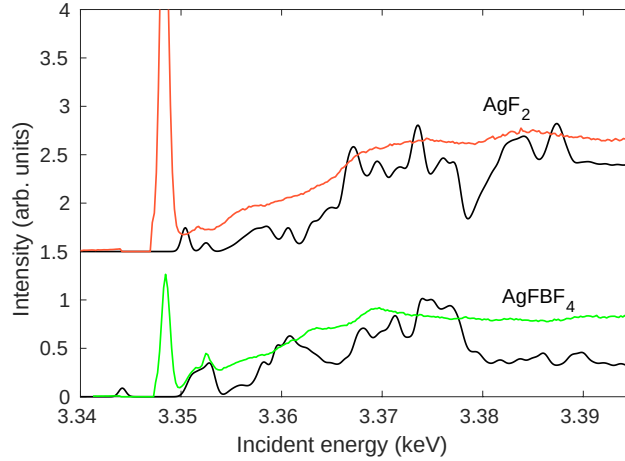


Figure 6.12: For the d^9 compounds, we show the comparison with DFT+ U computations assuming a magnetic ground state. To match the white line, the shift of the theoretical spectra is the same as in Fig. 6.8.

For AgF_2 in Fig. 6.13 (b), the maximum RIXS intensity is obtained for an incident photon energy of 3.349 keV. Therefore, in the following, we concentrate on the spectra at this incident energy.

In Fig. 6.15 panel (a), we show the RIXS spectra corresponding to a photon energy of 3.349 keV. The inset shows the CT part of the spectrum for different photon energies, confirming that it does not disperse and therefore it is not a fluorescence feature. A similar conclusion is obtained from single-crystal data [Fig. 6.14 panel (c)].

The vertical lines in Fig. 6.15 panel (a) are the results of the exact diagonalization computations from Ref. [39, 46] showing the position of one-hole states in a AgF_6 cluster. We write the one-hole states as,

$$\begin{aligned} |\psi_d(\nu)\sigma\rangle &= \alpha_\nu |d^9, \nu\sigma\rangle + \beta_\nu |d^{10}\underline{L}, \nu\sigma\rangle \\ |\psi_p(\nu)\sigma\rangle &= -\beta_\nu |d^9, \nu\sigma\rangle + \alpha_\nu |d^{10}\underline{L}, \nu\sigma\rangle \end{aligned} \quad (6.4)$$

where $\nu = x^2 - y^2, 3z^2 - r^2, xy, yz, zx$ and σ denotes the spin. The notation indicates the ionic configuration: $|d^{10}\underline{L}, \nu\sigma\rangle$ denotes a d^{10} state with a hole in a linear combination of ligand p orbitals that transforms like one of the d orbitals [46, 50]. α_ν, β_ν are real coefficients and without loss of generality we take $\alpha_\nu^2 > \beta_\nu^2$ so $|\psi_d(\nu)\sigma\rangle$ ($|\psi_p(\nu)\sigma\rangle$) has prevalent d^9 ($d^{10}\underline{L}$) character. Each pair $(|\psi_d(\nu)\sigma\rangle, |\psi_p(\nu)\sigma\rangle)$ represents a bonding-antibonding combination for one hole states in D_{4h} symmetry. This is not an exact symmetry in AgF_2 , but it can be assumed within the AgF_6 cluster to a good approximation. The ionic levels and the bonding-antibonding levels are also shown in Figure 6.19 (a). This will be discussed in more detail below in connection with the computation of matrix elements.

The ground state has approximate $d_{x^2-y^2}$ symmetry and is represented by the vertical line at zero energy in Fig. 6.15 panel (a). The excited states near 2 eV correspond to the states with the hole in orbitals of prevalent Ag d character and different symmetry, as indicated by the labels. Transitions between the ground state and these states are classified as dd transitions. The excited states between 4 eV and 6 eV have a prevalent hole ligand character, so transitions from the ground state to these states correspond to charge-transfer transitions. Comparison of the cluster computation with the

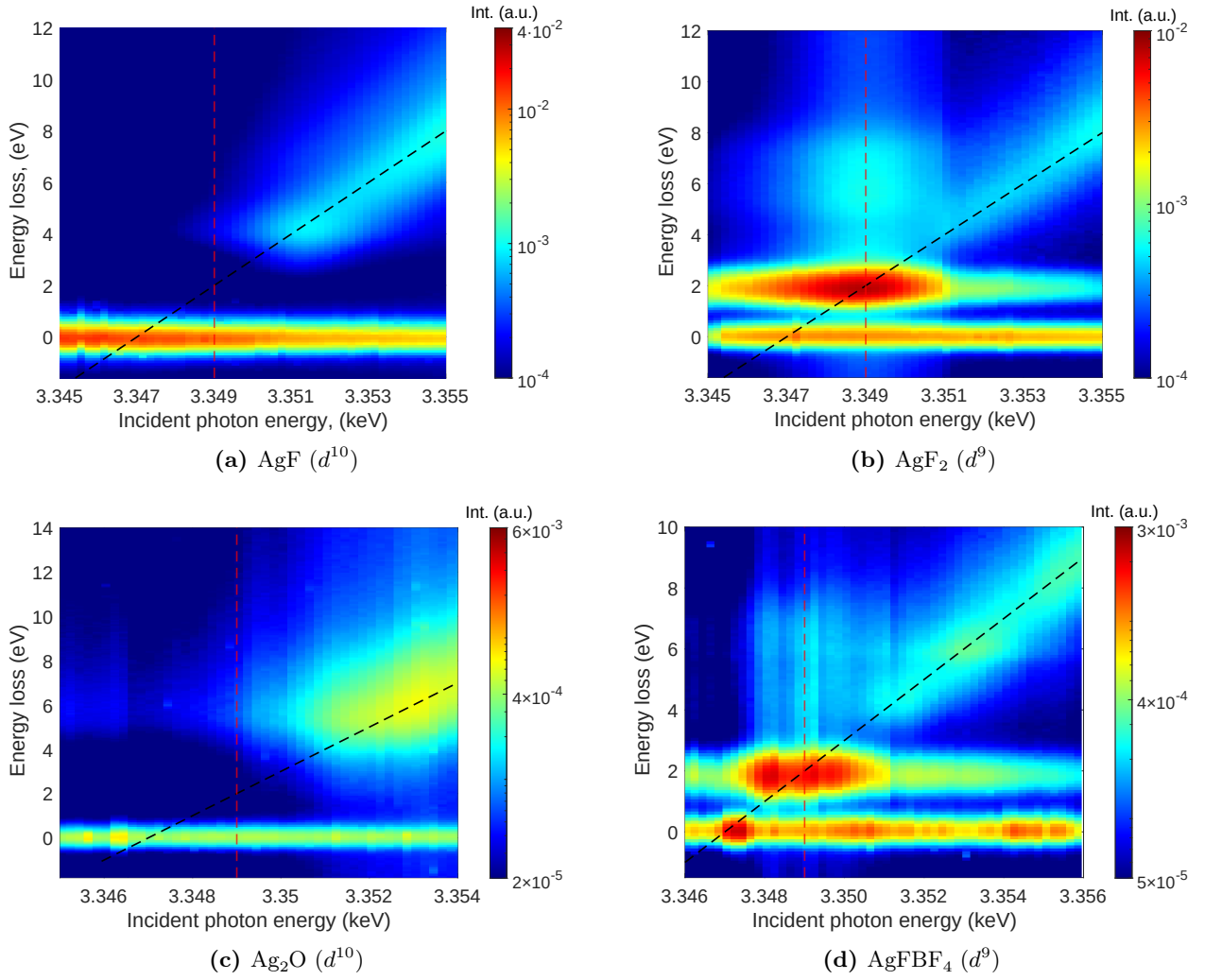


Figure 6.13: RIXS/fluorescence intensity maps for all measured d^{10} and d^9 powder samples in log-scale. Vertical red dashed lines indicate cuts of the maps at incident energy 3.349 keV (for AgF₂ it is shown in Fig. 6.15 panel (a)). The black-dashed line is the fluorescence scan used for the absorption measurement. Notice the overlap with the strong dd RIXS excitation at panels b and d

spectra confirms the peak at 2 eV as the dd excitations and the broad feature at high energy as the CT part.

Fig. 6.15 panel (b) shows the RIXS spectrum for AgFBF₄. The spectrum is practically identical to that of AgF₂ with similar dd and CT features. Also, here we have checked that the CT feature shows no sign of dispersion (not shown), so that fluorescence contamination can be excluded. A cluster computation has not been performed in this case, but the experimental results point to similar hybridizations and charge transfer energies as for AgF₂, Fig. 6.15 (a).

6.4.3 Observability of spin-flip process

It was suggested long ago that spin-flip processes may be excited in RIXS[173] because of the strong spin-orbit interaction in the transition metal core-hole. It was later shown [168] that in the case of a d^9 system with a $d_{x^2-y^2}$ hole state (as in parent cuprates and AgF₂), for the spin-flip process to be allowed requires that the magnetic moment lies in the basal plane. This is the case in cuprates and also in AgF₂ according to early neutron scattering experiments[174].

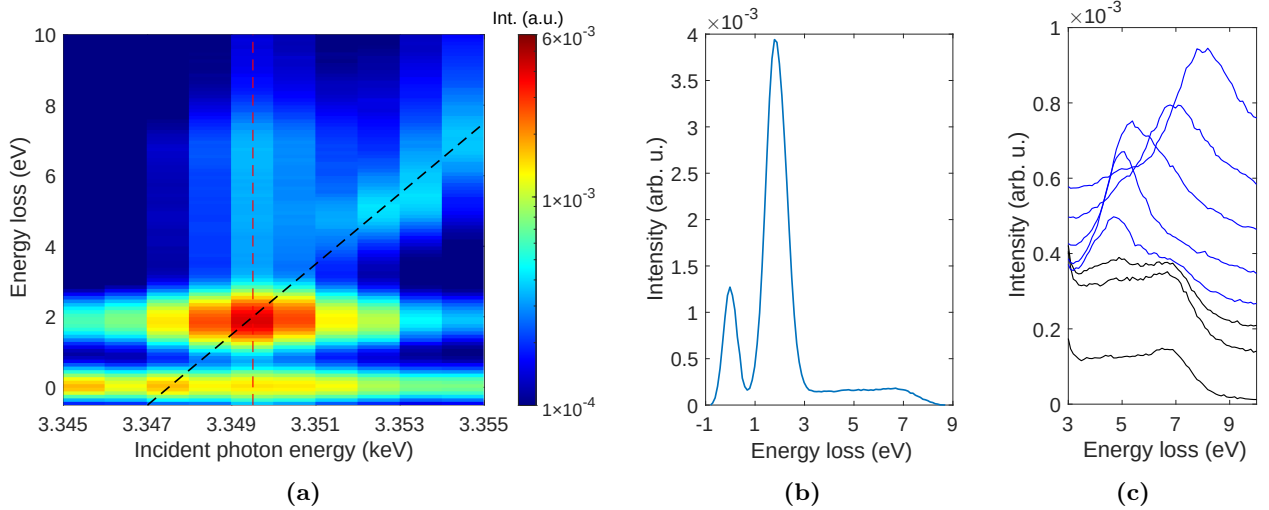


Figure 6.14: (a) RIXS intensity map for AgF_2 single crystal sample in log scale (b) vertical cut of the map at 3.349 keV indicated by red dashed vertical line on the map (c) black curves correspond to CT curves in the range [3.3480;3.3510] while blue curves are the fluorescent part in the range [3.3520;3.3560]. The vertical shift between curves in both cases equal to 0.00002 arb.u. The linear background was subtracted.

The transitions that make the spin flip possible are the following:

$$|x^2 - y^2 \uparrow_x\rangle \xrightarrow{x E_x} |x \uparrow_x\rangle \xrightarrow{S_z L_z} |y \downarrow_x\rangle \xrightarrow{y E_y} |x^2 - y^2 \downarrow_x\rangle. \quad (6.5)$$

Here $|x^2 - y^2 \uparrow_x\rangle$ represents the $|d^9, x^2 - y^2 \uparrow_x\rangle$ state (for brevity we omit the ionic configurations) with the hole spin pointing in the x direction, $x E_x$ represents an electric dipole transition with the photon electric field in the x direction, $|x \uparrow_x\rangle$ represents the d^{10} state with a core hole in a p_x state, $S_z L_z$ is the spin-orbit coupling with the term $S_z(x\partial_y - y\partial_x)$, which flips both the direction of the spin and the p orbital. The remaining terms follow an analogous notation. The two dipole transitions correspond to the incoming and the outgoing photon electric field, and the chain of transitions illustrates the well-known fact that the two polarizations should be crossed for the spin-flip transition to be allowed[168].

For the case of AgFBF_4 an important difference according to DFT[143, 144, 146] is that the ground state has prevalently $d_{3z^2-r^2}$ character with the z axis oriented along the chain, different from parent cuprates and also one-dimensional cuprates as Sr_2CuO_3 . Long-range order has not been reported, consistent with a spin liquid ground state. We can still expect antiferromagnetic quasi-long-range order to develop with the magnetic moment predominantly in one spatial direction. Adding spin-orbit coupling, we find that at the DFT level, the spin is in the $x - y$ plane. In this case, the chain of transitions that can lead to a spin-flip process reads

$$|3z^2 - r^2 \uparrow_x\rangle \xrightarrow{z E_z} |z \uparrow_x\rangle \xrightarrow{S_y L_y} |x \downarrow_x\rangle \xrightarrow{x E_x} |3z^2 - r^2 \downarrow_x\rangle. \quad (6.6)$$

This shows that the process is allowed with one polarization in the chain direction and the other polarization perpendicular to it.

Unfortunately, the quasielastic line is too broad in both compounds to disentangle these excitations, but the present considerations set the stage for future, higher-resolution measurements.

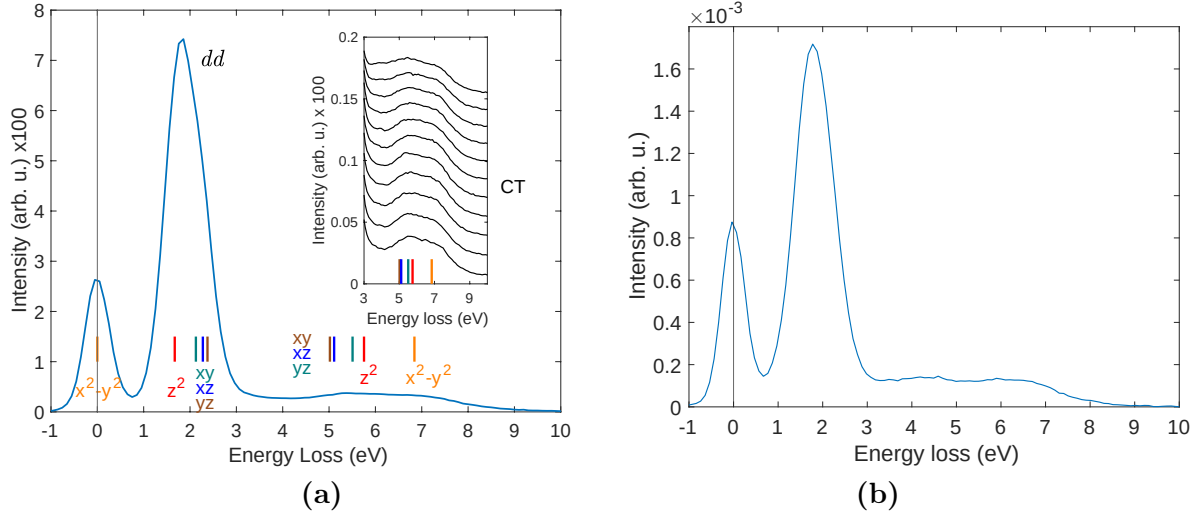


Figure 6.15: (a) Ag L_3 RIXS spectrum of powder AgF_2 sample (blue curve) - measured at 3.349 keV incident energy. A linear background was subtracted. Colored vertical lines represent bonding and antibonding states for hybridized orbitals between d^9 and $d^{10}L$ configurations following cluster computation done in [46] with the colors identifying the symmetry of the states ($z^2 \equiv 3z^2 - r^2$). The inset shows the CT part of the spectrum for different incoming photon energies. The lower curve is for an incoming photon energy of 3.3491 keV, and the following curves correspond to steps of 0.2 eV successively shifted by 0.015 (a.u.) (b) RIXS spectra for powder AgFBF_4 sample measured with 3.349 keV incident photon energy. A linear background was subtracted.

6.4.4 The electronic structure of AgF_2 vs La_2CuO_4 according to RIXS.

Having available data in the Cu L_3 and O K edge in La_2CuO_4 [175] and analogous data for the Ag L_3 (this work) and the F K edge [46] we can now make a detailed comparison of the electronic structure of the two compounds.

Fig. 6.16 shows the RIXS spectra in the metal and the ligand edge for La_2CuO_4 (a) and for AgF_2 (b). Despite the much lower resolution of the present Ag L_3 data, the similarity of the spectra in the two materials is striking.

Fig. 6.17 shows a comparison of the data in the L_3 edge of both compounds, normalizing to have equal intensity for the CT band. Due to the difference in resolution, the dd -excitation appears much

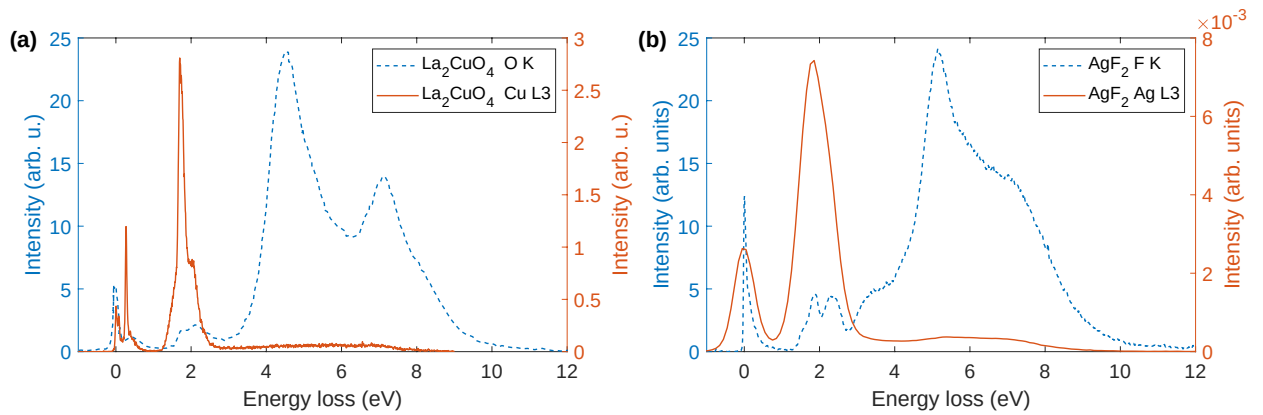


Figure 6.16: Comparison between RIXS spectra for AgF_2 (a) and La_2CuO_4 (b) measured at both edges (K,L). The AgF_2 Ag L_3 data is the present measurement. The other curves are based on reference data from [46, 49]

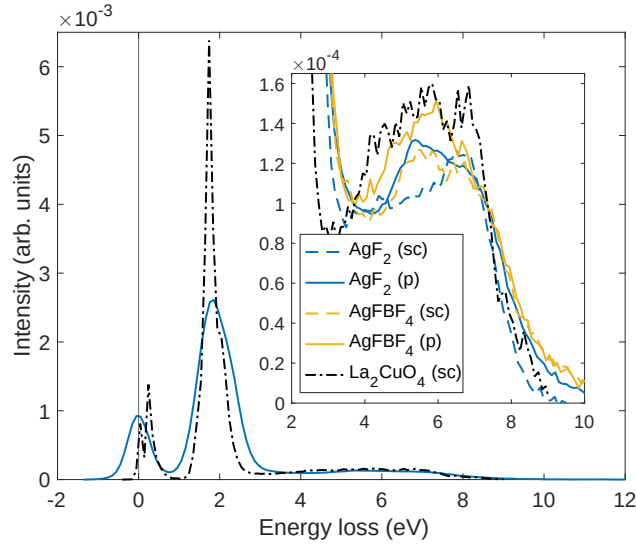


Figure 6.17: RIXS Ag L_3 spectrum for AgF_2 powder sample (full line) compared with Cu L_3 spectra of La_2CuO_4 (dotted-dashed line). The inset shows a zoom of the CT part for AgF_2 and AgFBF_4 for powder (p) and single crystal (sc) samples compared with La_2CuO_4 . Graphs are normalized so that the total $dd+CT$ area coincides, the curve for La_2CuO_4 was smoothed with step 0.2 eV

broadened in AgF_2 [$\text{FWHM}(\text{AgF}_2)=0.98$ eV versus $\text{FWHM}(\text{La}_2\text{CuO}_4)=0.19$ eV]. The inset shows the surprising similarity of the CT band in AgF_2 samples, AgFBF_4 , and La_2CuO_4 . This clearly indicates that electronic parameters in these materials are very similar, apart from the following caveat. The main panel shows that the quasielastic peak of AgF_2 has probably magnetic and phonon excitations, which are visible in high-resolution experiments in La_2CuO_4 but can not be separated in the present low-resolution experiments. From this comparison, it is clear that the zero of energy determined for AgF_2 , in reality, corresponds to an average between magnetic excitations and the truly elastic line. Therefore, all spectra should be shifted by some systematic error of the order of the difference between a broadened version of the cuprate data and our elastic peak ~ 0.3 eV. In other words, we estimate that all excitation energy reported for the Ag L_3 edge should be increased by about that amount. However, since the relative weight between elastic and inelastic signals is not known, and there is no systematic way to estimate this effect, we do not attempt such correction. Notice that the excitations at the F K edge measured at high resolution and shown in Fig. 6.16(b) appear systematically at higher energy with respect to the analogous features in the Ag L_3 edge, which we attribute to this effect.

To quantify the similarity in relative intensities of different features, we fitted all the spectra with Gaussians as shown in Fig. 6.18. The same procedure was applied to other available experimental datasets for powder and crystal samples of AgF_2 and AgFBF_4 (not shown).

Integral intensities were computed by integrating the fitting functions representing each peak. Relative weights of the peaks to the whole $dd+CT$ area are shown in Tab. 6.1. The quasielastic spectral weight was found to be too sensitive to the experimental conditions and is not reported in the table.

Computed values of dd/CT ratios measured at L_3 edges show remarkable similarity between Ag-compounds and reference La_2CuO_4 data.

The physical content of the relative spectral weight can be understood in the following way. The RIXS cross-section is given by the Kramers-Heisenberg equation[176]. The Ag L_3 core state

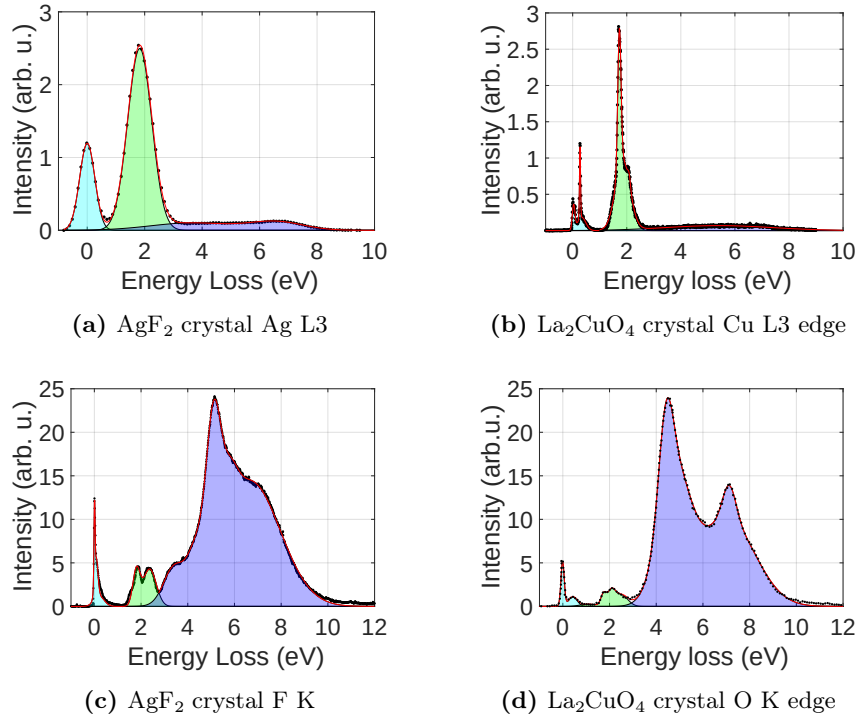


Figure 6.18: Fits of elastic, dd and CT peaks of RIXS spectra measured at metal and ligand edges of AgF_2 and La_2CuO_4 . Correspondent areas on the graphs are marked by various colors (light blue for elastic peak, green for dd excitations, and violet for CT). Panel (a) represents the results of the current experiment (Ag L3 edge), while panels (b),(c), (d) are based on the previously measured data. Correspondent compounds and edges are written in the subcaption of each figure

is quite broad ($\text{FWHM}[177]=2.4$ eV), which implies a quite short lifetime. To leading order in the ultra-short hole lifetime approximation[178–181] we can neglect the state dependence of the energy denominators. Then the total spectral weight of dd excitations (including elastic and spin flip) is proportional to the sum of the matrix elements of Ref. [49],

$$I(dd) = \sum_{\nu\sigma} \int d\Omega' \times |\langle \psi(x^2 - y^2) \downarrow | (\hat{\epsilon} \cdot \hat{r}) P_{3/2}(\hat{\epsilon}' \cdot \hat{r}) | \psi_d(\nu) \sigma \rangle|^2 \quad (6.7)$$

with the projector onto the core hole $j = 3/2$ manifold $P_{3/2} \equiv \sum_m |p_{3/2,m}\rangle \langle p_{3/2,m}|$ and the dipole operator for incoming and outgoing photons written in terms of their polarization vectors, ϵ, ϵ' .

Table 6.1: Comparison of RIXS integral intensities for dd and CT peaks for powder and single crystal samples from this work and integrated spectra from F K edge data of AgF_2 [46] and Cu L_3 and O K RIXS of La_2CuO_4 [49].

Edge	Compound	Sample	dd (%)	CT (%)
L_3	AgF_2	powder	79	21
	AgF_2	single c.	81	19
	AgFBF_4	powder	76	24
	AgFBF_4	single c.	78	22
	La_2CuO_4	single c.	74	26
K	AgF_2	powder	9	91
	La_2CuO_4	single c.	3	97

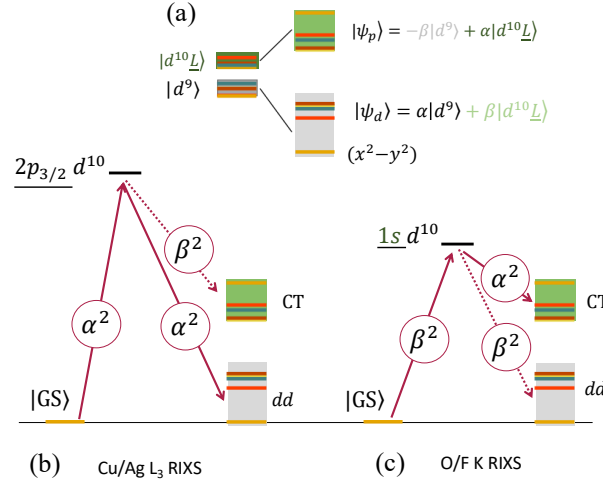


Figure 6.19: (a) Ionic levels (left) and hybridized levels (right) according to Eq. 6.4. The parameters to obtain these levels are the same as Ref. [46]. The hybridized levels are the same as shown in Fig. 6.15. (b) Processes involved for the transition metal L_3 -edge RIXS. Circles indicate the probabilities of the transitions due to projection onto the ionic configurations. (c) Same for ligand K -edge RIXS. An underline in labels indicates a hole.

The integral is over the orientation of the polarization vector of outgoing photons, since they are not discriminated in the experiment.

The operators in Eq. 6.7 act only on the d^9 component of the wave functions Eq. 6.4. Therefore, the expression can be put as,

$$I(dd) = \sum_{\nu} W_{\nu} \alpha_{\nu}^2 \quad (6.8)$$

with the weights,

$$W_{\nu} = \langle n_d \rangle \int d\Omega' |\langle d^9, x^2 - y^2 \downarrow | (\hat{\epsilon}' \cdot \hat{r}) P_{3/2}(\hat{\epsilon}' \cdot \hat{r}) | d^9, \nu \sigma \rangle|^2 \quad (6.9)$$

and with $\langle n_d \rangle \equiv \alpha_{x^2-y^2}^2$ the ground state d -occupancy. Similarly, for the CT intensity, substituting $d \rightarrow p$ in Eq. (6.7) we obtain,

$$I(CT) = \sum_{\nu} W_{\nu} \beta_{\nu}^2 \quad (6.10)$$

Figure 6.19 (a) shows the electronic levels in a cluster computation. Panel (b) shows the relevant transitions for a transition metal L_3 RIXS process. For the core electron to be excited, it should find a hole in the d shell (probability $\alpha_{x^2-y^2}^2$). Then the excited state can decay again on a d state (probability α_{ν}^2) or in a CT excitation (probability β_{ν}^2).

Defining

$$\begin{aligned} \overline{\alpha^2} &= \frac{\sum_{\nu} W_{\nu} \alpha_{\nu}^2}{\sum_{\nu} W_{\nu}} \\ \overline{\beta^2} &= \frac{\sum_{\nu} W_{\nu} \beta_{\nu}^2}{\sum_{\nu} W_{\nu}} \end{aligned} \quad (6.11)$$

we find $I(dd)/I(CT) = \overline{\alpha^2}/\overline{\beta^2}$. Since $\overline{\alpha^2} + \overline{\beta^2} = 1$, we can estimate $\overline{\alpha^2}$, $\overline{\beta^2}$. Because of technical reasons, $I(dd)'$ was determined, excluding the quasielastic part. We can crudely take into account

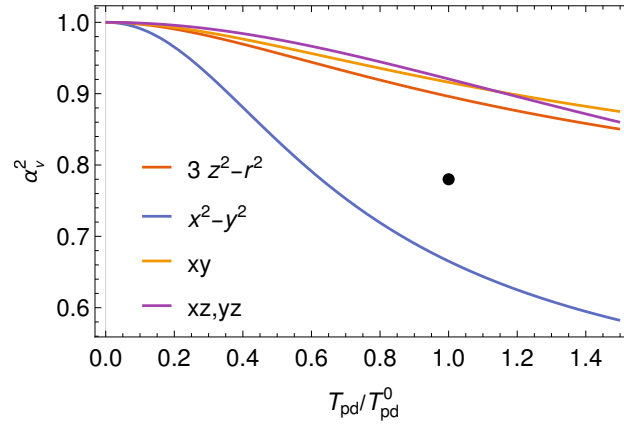


Figure 6.20: α_v^2 from cluster computations compared with the value of $\overline{\alpha^2}$ for LCO obtained integrating the spectral weight on the Cu L_3 edge (black dots). For the cluster computations, we used the charge transfer energy $\Delta_{pd} = 2.75$ eV. The hybridizations were rescaled by the factor T_{pd}/T_{pd}^0 with $T_{pd}^0 = 2.5$ eV corresponding to the parameter used in Ref. [50]. T_{pd} is equal to twice the hopping integral between a copper d and a oxygen p orbital. The factor of 2 is related to the symmetrized combinations of orbitals used in cluster computations.

this by reducing the intensity by a $(4/5)$ factor. Therefore, $I'(dd)/I(CT) \approx (4/5)\overline{\alpha^2}/\overline{\beta^2}$. As an example, Fig. 6.20 shows the α_v^2 for LCO obtained with the parameters of Ref. [50] and the hybridizations rescaled to modify the degree of covalency. The dot is the value of $\overline{\alpha^2}$ deduced from the spectral weight analysis. Clearly, it is not very far from the average of the previous values. The similarity of the intensity ratio in La_2CuO_4 and AgF_2 indicates a very similar degree of covalency, with La_2CuO_4 somewhat more covalent than AgF_2 .

A precise determination will require a more accurate determination of the cross sections as the ultra-short life time approximation may break down, especially in the case of LCO, which has a narrower L_3 core hole lineshape than AgF_2 . Another difficulty is that the resonance profile of the dd and CT transitions may be different. In particular, a different width or several resonances may distort the relative weights. Misalignment from the resonance maximum may lead to small distortion of the weights.

A similar analysis can be done at the K edge of the ligand, Figure 6.19 (c). In this case, the role of α and β are interchanged, so the larger relative weight of the dd transitions in the K edge of AgF_2 respect to LCO (Table 6.1 suggest that AgF_2 is the more covalent material). However, as discussed in Ref. [46], in this case, also Coulomb intersite matrix elements can influence the intensity, so this apparently contradictory result may reflect stronger intersite Coulomb matrix elements.

6.5 Conclusions

We have presented XAS and RIXS measurements on the Ag L_3 edge of two silver fluoride crystals and Ag_2O as a reference. The XAS results were compared with DFT computations, which allowed us to identify the origin of the main features in the spectra. The approximation used with a localized frozen core hole worked relatively well.

The AgF_2 Ag L_3 RIXS results complement previous K edge RIXS measurements. In addition, we present the RIXS spectra of AgFBF_4 , which is believed to host a spin-liquid ground state.

The Ag L_3 edge belongs to the tender X-ray range (3.35 keV), making it a challenging experi-

ment in commonly available facilities. In addition, the strong reactivity of silver fluorides and the sensitivity to radiation damage further complicate the measurements. Despite these difficulties, very informative RIXS spectra were obtained.

The K -edge measurements of Ref. [46] already demonstrated a striking similarity between the cuprate and the fluoride electronic structure. The present measurements independently confirm this trend.

Notwithstanding the low resolution available in the present L_3 measurements, the silver fluorides show clear dd and CT features very similar to the ones in cuprates. The positions of peaks coincided very well with the results of previous cluster computation and the measurements at the K -edge.[46]

The results were extended to the very interesting one-dimensional quantum antiferromagnet, AgFBF_4 . The position of the dd and CT peaks was located at very similar positions as for AgF_2 , suggesting that the local electronic structure is determined mainly by the octahedral-like structure and depends weakly on the global structural details.

We argue that the spectral weight ratio between the CT and dd features is a measure of the covalency of the materials. Making very rough estimates, the degree of covalency of cuprates and fluorides appears very similar in the present experiment. They suggest a slightly stronger covalency in the cuprates, while the K -edge experiment suggests stronger covalency in the fluoride. We argue, however, that this last result may be influenced by intersite matrix elements as already proposed in Ref. [46], which may enhance the spectral weight of dd excitations in the K -edge.

It is interesting that for a negative charge transfer material, the ratio of intensities inverts[182], confirming this ratio as a tool to evaluate covalency.

The finding that RIXS experiments are feasible at the Ag L_3 edge of silver fluorides calls for high-resolution spectra that allow investigating low-energy excitations as magnons, phonons, and plasmons. Recently available single crystals[158] may allow the characterization of the full momentum dependence of the excitations.

Overall, the strong similarity of the spectra in the two edges strongly supports the idea that, from the electronic structure point of view AgF_2 is an excellent clone of cuprates. This provides a strong motivation to pursue the synthesis of doped compounds in the search for new avenues for high- T_c superconductivity and quantum magnetism.

Chapter 7

Conclusions

This thesis presented a comprehensive experimental investigation of silver fluoride compounds, with a particular focus on AgF_2 , in the broader context of high-temperature superconductivity and its analogies with cuprate materials. Motivated by the structural and electronic similarities between AgF_2 and the prototypical cuprate La_2CuO_4 , the research aimed to explore the synthesis, surface reactivity, and spectroscopic properties of silver fluorides using a combination of advanced experimental techniques.

The first part of the work was dedicated to the design and construction of custom UHV systems tailored for fluoride synthesis. This included the realization of an innovative fluorination setup capable of generating in situ monatomic fluorine and a novel PLD chamber. These systems provided the necessary environment for growing and modifying silver-based compounds under clean and well-controlled conditions.

The direct fluorination of crystalline silver was studied using scanning tunneling microscopy, which enabled visualization of individual fluorine adatoms. The experiments confirmed that fluorine can be deposited on silver surfaces in a controlled manner and that various adsorption configurations can be stabilized. Complementary DFT simulations were used to interpret the STM results and to identify the nature of the observed adsorption sites. Thermodynamic modeling further indicated that fluorination remains favorable well beyond the dilute limit, suggesting the feasibility of forming more extended fluorinated layers.

At intermediate surface coverages, fluorine adatoms exhibited evidence of phase separation. This phenomenon was modeled using a simplified 2D Van der Waals gas framework, which reproduced key features observed experimentally, such as the emergence of disordered and amorphous overlayer phases. The agreement between model predictions and experimental data provided strong support for the underlying physical interpretation.

To probe the bulk electronic properties of silver fluorides, resonant inelastic X-ray scattering and X-ray absorption spectroscopy were performed on pellet samples of AgF_2 . These measurements were compared with reference data from La_2CuO_4 . The results revealed a remarkable similarity between the two materials in terms of their dd and charge-transfer excitations, in measurements conducted at the Ag L_3 absorption edge.

Among the most significant outcomes of this thesis are the successful design and implementation of specialized UHV apparatus for fluoride synthesis; the first STM-based characterization of fluorine adatoms on Ag(100) and Ag(110) surfaces; the experimental observation and theoretical modeling

of phase transitions in two-dimensional fluorine adlayers and the acquisition of RIXS data from AgF_2 , providing a direct comparison with cuprate electronic structures.

These findings highlight the potential of silver fluorides as a novel platform for investigating the physics of strongly correlated materials and unconventional superconductivity. The close electronic and magnetic parallels between AgF_2 and parent cuprates suggest that silver fluorides—especially in the form of flat or strained layers—could serve as fertile ground for the emergence of high-temperature superconductivity. Future research efforts may focus on the growth of high-quality AgF_2 thin films via epitaxial methods, in situ measurements of magnetic excitations using RIXS, and experimental investigation of electronic properties of overlayer F-structures on Ag-surfaces by means of X-ray Photoemission Spectroscopy.

In summary, this thesis opens several promising directions for the continued exploration of silver-based quantum materials and establishes a robust experimental foundation for future investigations into the rich physics of fluorinated transition metal compounds.

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Appendix A

Transient motion of "hot" adatoms

Dissociative adsorption of molecular gases on metallic surfaces is of particular interest due to the high reactivity of "hot" adatoms emerging after cleavage of the molecular bond. They may travel for long distances (up to several lattice constants) with high initial speed dissipating energy produced by chemisorption. In [183] it was studied dissociative adsorption of Oxygen on Al(111) and the migration of "hot" oxygen adatoms for distances up to 80Å. After reaching equilibrium, oxygen adatoms stay immobile at 300K, which was proved by periodic STM measurements. Very low coverage was demonstrated ($\theta \approx 10^{-3}ML$), so only a few adatoms were found on terraces, and coverage was computed just by counting them over the unit of area. There was no correlation found between final positions of adatoms, however, in a set of articles [86, 134] devoted to studying the transient motion of "hot" Oxygen adatoms on Ag(001) pairing effect was found. Oxygen adatoms formed pairs with typical interparticle distances of 4nm and 2nm, which matched with 2 possible dissociation processes happening. In the first case Oxygen molecule dissociated directly after being chemisorption, which corresponds to a longer interparticle separation (4nm). In the second case molecule was adsorbed from the precursor state, travelling over the surface before chemisorption, which leads to dissipation of energy and smaller interparticle distances (2nm). In [184] adsorption of Oxygen on Pt(111) surface was studied. The mechanism of molecule dissociation producing pairs of oxygen "hot" adatoms was confirmed, though interparticle distances within one pair were found to be much shorter. Indeed, reasonable computation, presented in the article, revealed impossible for "hot" adatom to travel such long distances as in [183]. The explanation of this phenomenon was found in [185], where it was proposed the ballistic movement of adatoms after dissociation. It was proved that this way interpair distances can reach large values. Moreover, it was considered a type of dissociative adsorption called abstraction, first observed for F_2 on Si surface in [106]. During this process, molecular fluorine dissociates during adsorption, but only one adatom chemisorbs to the surface, while the second is scattered in the vacuum. In this case, the release of energy during the chemisorption of one fluorine adatom prevails over the bond energy of the incident molecule. Additionally, this mechanism redistributes the energy produced by chemisorption between two adatoms unequally, so in the case of large chemisorption energy, an excess of it can be transformed into the kinetic energy of the scattered Fluorine atom.

Appendix B

Van der Waals equation solved numerically

Table B.1: Phase coexistence points in the p - V - T phase space of the van der Waals fluid. The data columns versus temperature are labeled by the pressure and volume notations in Fig. 5.3 panel (b). Table is taken from [122]

T/T_c	p_X/p_c	V_G/V_c	V_F/V_c	V_D/V_c	V_C/V_c	T/T_c	p_X/p_c	V_G/V_c	V_F/V_c	V_D/V_c	V_C/V_c
1.00	1.000	1.000	1.000	1.000	1.000	0.57	6.419e-02	0.4241	0.5246	3.158	2.191e+01
0.99	9.605e-01	0.8309	0.8946	1.128	1.243e+00	0.56	5.764e-02	0.4214	0.5209	3.232	2.411e+01
0.98	9.219e-01	0.7755	0.8561	1.189	1.376e+00	0.55	5.158e-02	0.4188	0.5173	3.308	2.661e+01
0.97	8.843e-01	0.7376	0.8283	1.240	1.496e+00	0.54	4.598e-02	0.4163	0.5137	3.387	2.947e+01
0.96	8.476e-01	0.7082	0.8059	1.287	1.612e+00	0.53	4.081e-02	0.4138	0.5102	3.469	3.274e+01
0.95	8.119e-01	0.6841	0.7870	1.330	1.727e+00	0.52	3.607e-02	0.4114	0.5068	3.553	3.652e+01
0.94	7.771e-01	0.6637	0.7704	1.372	1.844e+00	0.51	3.174e-02	0.4091	0.5034	3.641	4.089e+01
0.93	7.432e-01	0.6459	0.7556	1.412	1.963e+00	0.50	2.779e-02	0.4068	0.5000	3.732	4.598e+01
0.92	7.102e-01	0.6302	0.7422	1.451	2.087e+00	0.49	2.420e-02	0.4045	0.4967	3.827	5.195e+01
0.91	6.782e-01	0.6161	0.7299	1.490	2.215e+00	0.48	2.097e-02	0.4023	0.4934	3.925	5.897e+01
0.90	6.470e-01	0.6034	0.7186	1.529	2.349e+00	0.47	1.806e-02	0.4002	0.4902	4.028	6.729e+01
0.89	6.167e-01	0.5918	0.7080	1.567	2.489e+00	0.46	1.545e-02	0.3981	0.4870	4.134	7.722e+01
0.88	5.874e-01	0.5811	0.6981	1.605	2.636e+00	0.45	1.313e-02	0.3960	0.4838	4.246	8.915e+01
0.87	5.589e-01	0.5712	0.6888	1.644	2.791e+00	0.44	1.108e-02	0.3940	0.4807	4.362	1.036e+02
0.86	5.312e-01	0.5620	0.6800	1.682	2.955e+00	0.43	9.283e-03	0.3921	0.4776	4.483	1.212e+02
0.85	5.045e-01	0.5534	0.6717	1.721	3.128e+00	0.42	7.710e-03	0.3901	0.4746	4.611	1.429e+02
0.84	4.786e-01	0.5453	0.6637	1.760	3.311e+00	0.41	6.347e-03	0.3883	0.4716	4.744	1.698e+02
0.83	4.535e-01	0.5377	0.6561	1.800	3.506e+00	0.40	5.175e-03	0.3864	0.4686	4.883	2.036e+02
0.82	4.293e-01	0.5306	0.6489	1.840	3.714e+00	0.39	4.175e-03	0.3846	0.4656	5.030	2.465e+02
0.81	4.059e-01	0.5238	0.6419	1.880	3.936e+00	0.38	3.332e-03	0.3828	0.4627	5.184	3.015e+02
0.80	3.834e-01	0.5174	0.6352	1.921	4.172e+00	0.37	2.627e-03	0.3811	0.4597	5.346	3.729e+02
0.79	3.616e-01	0.5113	0.6288	1.963	4.426e+00	0.36	2.044e-03	0.3794	0.4568	5.518	4.670e+02
0.78	3.406e-01	0.5055	0.6225	2.005	4.698e+00	0.35	1.567e-03	0.3777	0.4540	5.699	5.926e+02
0.77	3.205e-01	0.5000	0.6165	2.049	4.990e+00	0.34	1.183e-03	0.3761	0.4511	5.890	7.631e+02
0.76	3.011e-01	0.4947	0.6107	2.092	5.304e+00	0.33	8.785e-04	0.3745	0.4483	6.093	9.986e+02
0.75	2.825e-01	0.4896	0.6051	2.137	5.643e+00	0.32	6.401e-04	0.3729	0.4455	6.308	1.330e+03
0.74	2.646e-01	0.4848	0.5996	2.183	6.009e+00	0.31	4.569e-04	0.3713	0.4426	6.537	1.806e+03
0.73	2.475e-01	0.4801	0.5943	2.229	6.406e+00	0.30	3.188e-04	0.3698	0.4399	6.781	2.506e+03
0.72	2.311e-01	0.4756	0.5891	2.277	6.835e+00	0.29	2.170e-04	0.3683	0.4371	7.041	3.560e+03
0.71	2.154e-01	0.4713	0.5841	2.326	7.302e+00	0.28	1.437e-04	0.3668	0.4343	7.321	5.193e+03
0.70	2.005e-01	0.4672	0.5792	2.376	7.811e+00	0.27	9.225e-05	0.3654	0.4315	7.620	7.801e+03
0.69	1.862e-01	0.4632	0.5744	2.427	8.366e+00	0.26	5.723e-05	0.3639	0.4288	7.943	1.211e+04
0.68	1.726e-01	0.4593	0.5698	2.479	8.973e+00	0.25	3.417e-05	0.3625	0.4260	8.291	1.951e+04
0.67	1.597e-01	0.4556	0.5652	2.532	9.639e+00	0.24	1.953e-05	0.3612	0.4233	8.668	3.276e+04
0.66	1.475e-01	0.4520	0.5608	2.587	1.037e+01	0.23	1.063e-05	0.3598	0.4205	9.077	5.767e+04
0.65	1.358e-01	0.4485	0.5564	2.644	1.118e+01	0.22	5.477e-06	0.3585	0.4178	9.524	1.071e+05
0.64	1.249e-01	0.4451	0.5522	2.702	1.207e+01	0.21	2.647e-06	0.3571	0.4150	10.01	2.116e+05
0.63	1.145e-01	0.4419	0.5480	2.761	1.305e+01	0.20	1.189e-06	0.3558	0.4122	10.55	4.485e+05
0.62	1.047e-01	0.4387	0.5439	2.823	1.415e+01	0.19	4.909e-07	0.3546	0.4095	11.14	1.032e+06
0.61	9.550e-02	0.4356	0.5399	2.886	1.537e+01	0.18	1.836e-07	0.3533	0.4067	11.80	2.615e+06
0.60	8.687e-02	0.4326	0.5359	2.951	1.673e+01	0.17	6.113e-08	0.3521	0.4039	12.54	7.416e+06
0.59	7.878e-02	0.4297	0.5321	3.018	1.826e+01	0.16	1.773e-08	0.3508	0.4011	13.37	2.406e+07
0.58	7.123e-02	0.4269	0.5283	3.087	1.997e+01	0.15	4.360e-09	0.3496	0.3982	14.31	9.174e+07

