

Quantum Enhancement of Charge Density Wave in NbS₂ in the Two-Dimensional Limit

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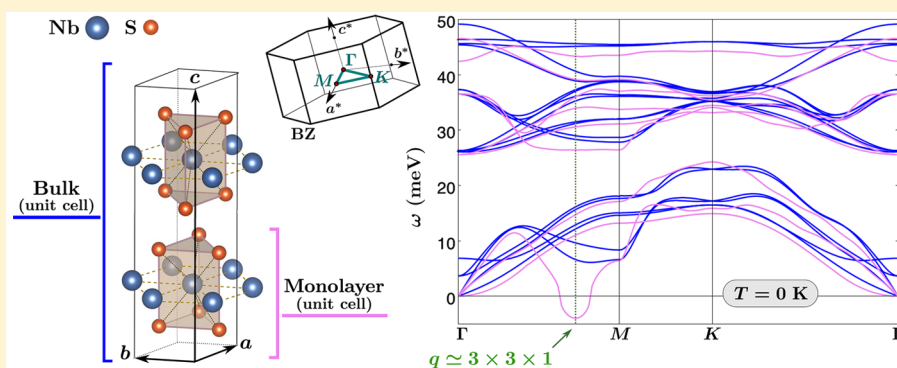
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ABSTRACT: At ambient pressure, bulk 2H-NbS₂ displays no charge density wave instability, which is at odds with the isostructural and isoelectronic compounds 2H-NbSe₂, 2H-TaS₂, and 2H-TaSe₂, and in disagreement with harmonic calculations. Contradictory experimental results have been reported in supported single layers, as 1H-NbS₂ on Au(111) does not display a charge density wave, whereas 1H-NbS₂ on 6H-SiC(0001) endures a 3 × 3 reconstruction. Here, by carrying out quantum anharmonic calculations from first-principles, we evaluate the temperature dependence of phonon spectra in NbS₂ bulk and single layer as a function of pressure/strain. For bulk 2H-NbS₂, we find excellent agreement with inelastic X-ray spectra and demonstrate the removal of charge ordering due to anharmonicity. In the two-dimensional limit, we find an enhanced tendency toward charge density wave order. Freestanding 1H-NbS₂ undergoes a 3 × 3 reconstruction, in agreement with data on 6H-SiC(0001) supported samples. Moreover, as strains smaller than 0.5% in the lattice parameter are enough to completely remove the 3 × 3 superstructure, deposition of 1H-NbS₂ on flexible substrates or a small charge transfer via field-effect could lead to devices with dynamical switching on/off of charge order.

KEYWORDS: Transition metal dichalcogenide, monolayer, charge density wave, anharmonicity, size-dependent properties, phonons

Transition metal dichalcogenides (TMDs) are layered materials with generic formula MX₂, where M is a transition metal (Nb, Ta, Ti, Mo, W, ...) and X a chalcogen (S, Se, Te). The layers, made of triangular lattices of transition metal atoms sandwiched by covalently bonded chalcogens, are held together by weak van der Waals forces, and TMDs can be readily exfoliated into thin flakes down to the single layer limit, with mechanical or chemical techniques.^{1–4} In TMDs, the interplay between strong electron–electron and electron–phonon interactions gives rise to rich phase diagrams with a

wide variety of cooperating/competing collective electronic orderings as charge-density wave (CDW), Mott insulating, and superconductive phases.^{5,6} Of the several polytypes, we focus here on the most common one for NbS₂, the H polytype,^{7,8} where the transition metal is in trigonal prismatic coordination

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with the surrounding chalcogens. In Figure 1 the 1H (monolayer) and 2H (bulk) crystal structures are shown.

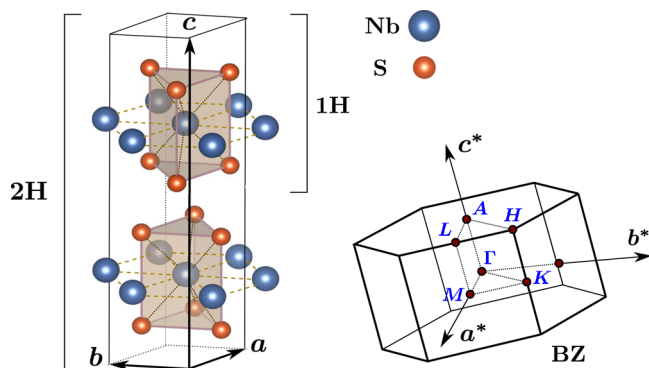


Figure 1. Left-hand side: crystal structure of trigonal NbS₂ in the 1H monolayer and in the 2H (bulk) stacking layer configuration. Right-hand side: corresponding hexagonal BZ with the high-symmetry points (in the monolayer configuration only the points Γ MK are relevant, and they are customarily indicated with a line over the letter).

Among metallic 2H bulk TMDs, NbS₂ occupies a special place as no CDW has been reported,^{9,10} contrary to its isoelectronic and isostructural 2H-TaSe₂, 2H-TaS₂, and 2H-NbSe₂. All these systems have very similar band structures and are conventional (i.e., phonon-mediated) superconductors with critical temperatures T_c that increases from a sub-Kelvin value in 2H-TaSe₂ and 2H-TaS₂ (around 0.2 and 0.5 K, respectively) up to 5.7 K in 2H-NbS₂ and 7.2 K in 2H-NbSe₂.^{11–14} They also show quite a different CDW transition strength.^{15,16} 2H-TaSe₂, 2H-TaS₂, and 2H-NbSe₂ undergo a triple incommensurate CDW transition to a superlattice with hexagonal symmetry corresponding roughly to the same wave vector $\mathbf{q}_{\text{CDW}} = \Gamma M(1 - \delta)2/3$ ($\delta \simeq 0.02$ is the incommensurate factor) of the Brillouin zone. However, the transition temperature T_{CDW} increases from 30 K for 2H-NbSe₂ to 80 K for 2H-TaS₂ and 120 K for 2H-TaSe₂ (2H-TaSe₂ actually shows a further commensurate first-order CDW transition at 92 K with δ dropping continuously to zero).¹⁷ Therefore, 2H-NbS₂ considerably stands out as it shows only an incipient instability near \mathbf{q}_{CDW} , but it remains stable even at the lowest temperatures. This circumstance is even more surprising if it is considered that 2H-NbSe₂ and 2H-NbS₂ display superconductivity at similar temperatures.

In TMDs, the behavior of the CDW ordering in the two-dimensional (2D) limit cannot be inferred from the knowledge of their bulk counterparts, because two competing mechanisms are expected to play a major role. On the one hand, reduced dimensionality strengthens Peierls instabilities (due to Fermi surface nesting) and electron–phonon interactions (due to reduced dielectric screening), thus favoring stronger CDW. On the other hand, stronger fluctuation effects from both finite temperatures and disorders should tend to destroy long-range CDW coherence in low-dimensional systems.¹⁸ In particular, the effect of dimensionality on the CDW ordering in the H polytype is a current active research area. In 1H-TaS₂, the CDW vanishes in the 2D limit,¹⁹ while in 1H-TaSe₂ it remains unchanged with respect to the bulk.²⁰ For 1H-NbSe₂ and 1H-NbS₂, the situation is more debated. In the 1H-NbSe₂ case, 3×3 CDW is observed but some controversy is still present in literature, tentatively attributed either to the sample exposure

to air or to the different substrates, concerning the thickness dependence of the T_{CDW} (lower/higher T_{CDW} of the monolayer with respect to the bulk has been reported with bilayer graphene²¹/silicon¹⁸ substrate, respectively). Supported single layers of 1H-NbS₂ have become recently available, and although no traces of CDW have been observed down to 30 K for monolayers grown on top of Au(111),²² a 3×3 CDW ordering has been observed at ultralow temperature (measurements performed below 5 K) for monolayers grown on top of graphitized 6H-SiC(0001).²³

In this Letter, we investigate from first-principles the vibrational properties of bulk 2H-NbS₂ (at zero and finite pressure) and suspended 1H-NbS₂, taking into account quantum anharmonic effects at nonperturbative level in the framework of the stochastic self-consistent harmonic approximation (SSCHA).^{24–27} For bulk 2H-NbS₂, we show that quantum anharmonic effects remove the instability found at harmonic level and give temperature-dependent phonon energies in quantitative agreement with experiment. Previous anharmonic calculations for 2H-NbS₂ anticipated the role of anharmonicity but were limited to a low-dimensional subspace of the total high-dimensional configurations space and did not account for the temperature dependence.¹⁴ We also show that quantum anharmonic effects are noticeable even at high pressure. Moreover, we demonstrate that the difference between 2H-NbS₂ and 2H-NbSe₂ is not simply ascribable to the different chalcogen mass. Finally, we analyze the 2D limit and show that freestanding single-layer 1H-NbS₂ undergoes a 3×3 CDW instability in agreement with data on 6H-SiC(0001) supported samples. However, strains smaller than 0.5% are sufficient to completely remove the instability, suggesting a strong dependence of the CDW on the environmental conditions (substrate, charge transfer, and so forth) and reconciling the apparent contradiction with supported Au(111) samples.

For bulk 2H-NbS₂, in Figure 2 we compare the computed anharmonic phonon dispersions with the results of the inelastic

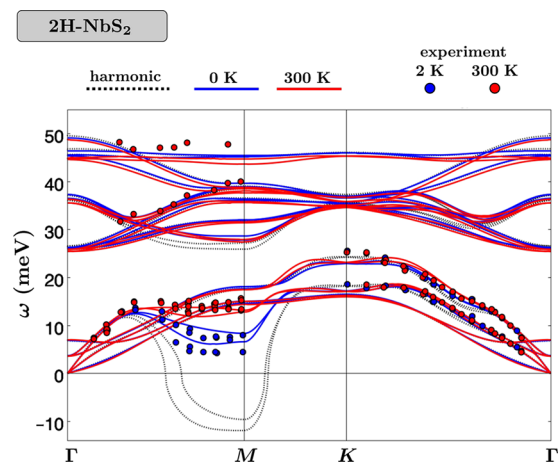


Figure 2. 2H-NbS₂ harmonic (black dashed lines) and SSCHA anharmonic phonon dispersion at 300 K (red solid lines) and 0 K (blue solid lines), calculated using the experimental lattice parameters. The results are compared with the IXS measurements of ref 7 performed at 300 K (red dots) and 2 K (blue dots). The SSCHA dispersion corrects the errors of the pure harmonic result near M: the instability of the two longitudinal acoustic and optical modes is removed and the softening on lowering temperature is well reproduced.

X-ray scattering (IXS) experiment of ref 7 at low and ambient temperature. We also show the (temperature-independent) harmonic phonon dispersion. Calculations were performed with the $a_{\text{Exp}}^{2\text{H}} = b_{\text{Exp}}^{2\text{H}} = 3.33 \text{ \AA}$ and $c_{\text{Exp}}^{2\text{H}} = 11.95 \text{ \AA}$ bulk experimental lattice parameters at zero pressure.⁷ The phonon dispersion is almost everywhere well reproduced with the harmonic calculation, except close to M , where it predicts that two longitudinal acoustic and optical modes become imaginary. Experimental phonon energies show a sensible temperature dependence in this region of the Brillouin zone (BZ) and are, obviously, always real. The SSCHA cures the pathology of the harmonic result; the anharmonic phonon dispersions do not show any instability and give a very good agreement with the experiment at both temperatures.

Because SSCHA calculations give dispersions in good agreement with experiments, we can perform a wider analysis. In the upper panel of Figure 3, we show the SSCHA phonon dispersion for different temperatures along the full high-symmetry path of the BZ. As temperature decreases, anharmonicity causes the softening of two acoustic and optical longitudinal modes close to both M and L , but there is no instability. Thus, quantum fluctuations strongly affected by the anharmonic potential stabilize 2H-NbS_2 . In the other two panels, we show the effect of hydrostatic pressure on the phonon dispersion. Because there are no available experimental lattice parameters at high pressures, we estimated them by assuming that the ratio between experimental and standard density functional theory (DFT) theoretical lattice parameters (i.e., the lattice parameters that minimize the DFT energy but do not take into account any lattice quantum dynamic effects), $a_{\text{Exp}}^{2\text{H}}(P)/a_{\text{Th-DFT}}^{2\text{H}}(P)$ and $c_{\text{Exp}}^{2\text{H}}(P)/c_{\text{Th-DFT}}^{2\text{H}}(P)$, are independent of the applied pressure P . Thus, we computed those ratios at zero pressure and for a given pressure P the calculations were performed using as lattice parameters $a = (a_{\text{Exp}}^{2\text{H}}/a_{\text{Th-DFT}}^{2\text{H}}) \times a_{\text{Th-DFT}}^{2\text{H}}(P)$ and $c = (c_{\text{Exp}}^{2\text{H}}/c_{\text{Th-DFT}}^{2\text{H}}) \times c_{\text{Th-DFT}}^{2\text{H}}(P)$. By increasing pressure the anharmonicity of the lowest energy modes around M and L decreases but remains relevant even up to 14 GPa. A similar conclusion was drawn for 2H-NbSe_2 , where large anharmonic effects and strong temperature dependence of these phonon modes were observed as high as 16 GPa, in a region of its phase diagram where no CDW transition is observed.²⁸

These results confirm the importance of quantum anharmonicity in 2H-NbS_2 to describe experimental data and the absence of a CDW instability. It is tempting at this point to use the same technique to shed light on the different CDW behavior exhibited by the very similar compound 2H-NbSe_2 . Indeed, as we showed in a previous work,²⁸ the SSCHA correctly displays the occurrence of CDW in 2H-NbSe_2 at ambient pressure. One evident difference between 2H-NbS_2 and 2H-NbSe_2 is, of course, the mass of the chalcogen atom. We then performed a SSCHA calculation at 0 K for 2H-NbS_2 with “artificial” S atoms having unaltered electronic configuration but the mass of Se. In other words, we performed a SSCHA calculation where the average displacements of the atoms from the equilibrium position is ruled by the Se mass but for each fixed position of the atoms the electronic structure is computed with the normal S atoms. The results are shown in Figure 4. Also in this case, when quantum anharmonic effects are included the system does not show any CDW instability. Thus, the different behavior of 2H-NbS_2 and 2H-NbSe_2 cannot be ascribed to a mass effect but has a more complex origin related to the different electron screening on the ions.

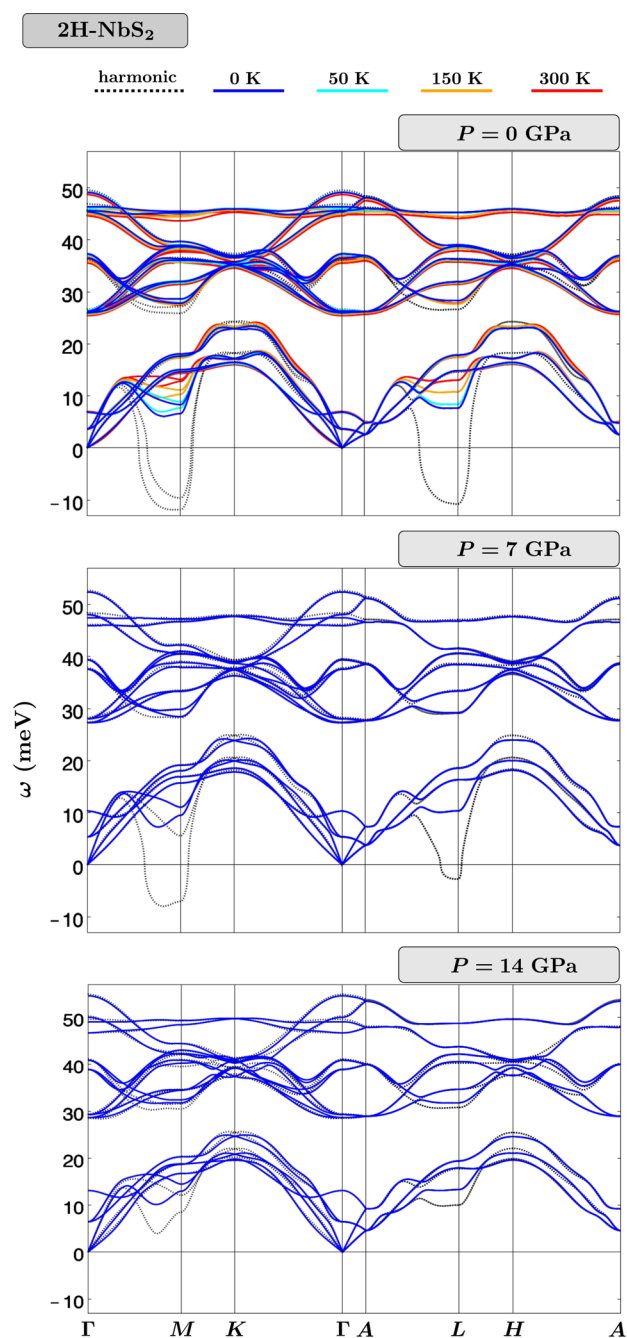


Figure 3. 2H-NbS_2 harmonic phonon dispersion (black dashed lines) and SSCHA anharmonic phonon dispersion at several temperatures (colored solid lines). Results for different pressures are shown. From the top to the bottom panel: 0, 7, and 14 GPa. The zero-pressure results are obtained using the experimental lattice parameters. The high-pressure results are obtained assuming that the ratio between experimental and DFT theoretical lattice parameters are independent of the applied pressure (more details in the main text). Anharmonicity removes the instability, obtained at harmonic level, of the longitudinal acoustic and optical modes near M and L at 0 and 7 GPa. Anharmonicity reduces as the pressure increases but it has a noticeable effect even at 14 GPa.

The validity of the results obtained with the SSCHA method on bulk 2H-NbS_2 gives us confidence that a similar calculation on the 1H-NbS_2 monolayer may shine light about the effects that dimensionality and environmental conditions (substrate, doping) can have on the CDW ordering in metallic TMDs.

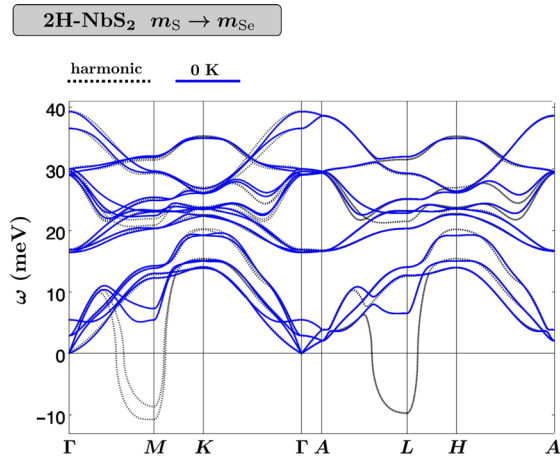


Figure 4. The 2H-NbS₂ harmonic phonon dispersion (black dashed lines) and SSCHA anharmonic phonon dispersion at 0 K (blue solid lines) at zero pressure computed replacing the mass of S with the mass of Se (more details in the main text). Anharmonicity removes the instability also in this case.

The suspended 1H-NbS₂ monolayer was simulated leaving 12.55 Å of vacuum space between a 1H layer and its periodic replica. At conventional static DFT level, we found that the theoretical zero pressure in-plane lattice parameter of the monolayer and the bulk are essentially the same, $a_{\text{Th-DFT}}^{2\text{H}} \approx a_{\text{Th-DFT}}^{1\text{H}} \approx 3.34$ Å. Therefore, for the suspended monolayer we use as in-plane lattice parameter the bulk experimental one, $a_{\text{Exp}}^{2\text{H}} = 3.33$ Å. This value is also compatible with the recent experimental measures 3.29 ± 0.03 and 3.34 Å reported for the lattice parameter of monolayer grown on substrate in ref 23 and ref 22, respectively.

In the upper panel of Figure 5, we show the harmonic and SSCHA anharmonic phonon dispersions of suspended 1H-NbS₂ at several temperatures, calculated with the lattice parameter $a_{\text{Exp}}^{2\text{H}}$. As in the bulk case, the system is unstable at harmonic level, but it is stabilized by quantum fluctuations strongly sensitive to the anharmonic potential down to 0 K. However, comparing Figures 2 and 5, we observe that even if the used in-plane lattice parameter is the same in both cases, at 0 K the softest theoretical phonon frequency is approximately 20% harder in the bulk than in the single layer case, demonstrating that there is a substantial enhancement of the tendency toward CDW in the 2D limit. In the monolayer, the theoretical phonon softening is localized in $\mathbf{q}_{\text{CDW}} = 0.72 \bar{\Gamma}\bar{M}$, which is quite close to the $\mathbf{q}_{\text{CDW}} \approx 2/3 \bar{\Gamma}\bar{M}$ of the CDW instability experimentally found in 1H-NbS₂ on 6H-SiC(0001)²³ (and in 1H-NbSe₂^{18,21}). Notice that, since the computed wave vector of the instability may be affected by the finite grids used in the calculations, we do not discard that it may be slightly shifted in the infinite grid limit.

Pressure tends normally to remove CDW ordering. Therefore, considering the proximity of the instability, it cannot be discarded that a tensile dilatation due to the substrate may induce the CDW transition observed for 1H-NbS₂ on graphitized 6H-SiC(0001). However, for the same reason we cannot exclude the more interesting prospect that the observed CDW be an intrinsic property of this system. Indeed, even small variations of the lattice parameter, compatible with the experimental uncertainty, could have a relevant impact on the results of the calculations, and a more accurate theoretical analysis of the monolayer structure is therefore necessary. As

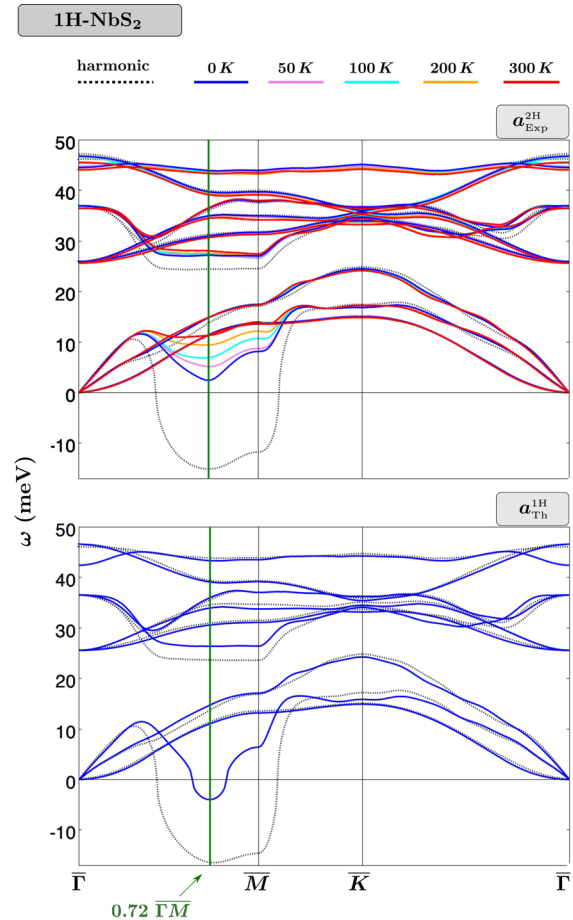


Figure 5. Suspended 1H-NbS₂ harmonic phonon dispersion (black dashed lines) and SSCHA anharmonic phonon dispersion at several temperatures (colored solid lines), at zero pressure. Top panel: results obtained with the experimental in-plane bulk lattice parameter $a_{\text{Exp}}^{2\text{H}}$. The softening of the acoustic mode, localized at $\mathbf{q}_{\text{CDW}} = 0.72 \bar{\Gamma}\bar{M}$, is more pronounced than in the 2H bulk case. However, the frequencies remain real even at 0 K. Bottom panel: results obtained with the theoretical lattice parameter $a_{\text{Th}}^{1\text{H}}$, obtained by fully relaxing the structure taking into account quantum anharmonic effects. At 0 K, the frequency at $\mathbf{q}_{\text{CDW}} = 0.72 \bar{\Gamma}\bar{M}$ becomes imaginary.

the energy of the soft-mode along $\bar{\Gamma}\bar{M}$ is of the order of ≈ 58 K, for a proper analysis of the CDW in the monolayer it is important to fully take into account quantum effects. Including quantum anharmonic contributions to strain through the technique introduced in ref 26, we find that with the used lattice parameter $a_{\text{Exp}}^{2\text{H}}$ the structure is slightly compressed with an in-plane pressure $P = 0.66$ GPa. Upon relaxation, we obtain the theoretical lattice parameter $a_{\text{Th}}^{1\text{H}} = 3.35$ Å, approximately 0.5% larger than $a_{\text{Exp}}^{2\text{H}}$.

The harmonic and quantum anharmonic phonons at 0 K calculated with the lattice parameter $a_{\text{Th}}^{1\text{H}}$ are shown in the bottom panel of Figure 5. Although at harmonic level the phonon dispersion is not substantially different from the one computed with $a_{\text{Exp}}^{2\text{H}}$, when quantum anharmonic effects are included the phonon dispersion at 0 K now shows an instability at $\mathbf{q}_{\text{CDW}} = 0.72 \bar{\Gamma}\bar{M}$ thus in agreement with the CDW observed for 1H-NbS₂ on top of 6H-SiC(0001). The obtained instability is very weak (i.e., the obtained imaginary phonon frequency is very small). Therefore, this result is also compatible with the hypothesis that charge doping from the

substrate could be at the origin of the CDW suppression for 1H-NbS₂ on top of Au(111), similarly to what it was proposed for the case of 1H-TaS₂ on top of Au(111).²⁹ Our results show that if quantum anharmonic effects are included, then even a small compression/dilatation of approximately 0.5% removes/induces the charge density wave instability on 1H-NbS₂. The extreme sensitivity of the CDW on environmental conditions therefore suggests that deposition of 1H-NbS₂ on flexible substrates^{30–32} or a small charge transfer via field effect could lead to devices with dynamical on/off switching of the 3 × 3 order.

In conclusion, we have shown that quantum anharmonicity is the key interaction for the stabilization of the crystal lattice in bulk 2H-NbS₂, as it removes the instability found at the harmonic level. The calculated temperature dependence of the phonon spectra are in excellent agreement with inelastic X-ray scattering data. Anharmonicity remains important even at large pressures. Given the good agreement between theory and experiment in bulk 2H-NbS₂, we have studied the behavior of the CDW in the 2D limit by considering single layer 1H-NbS₂. We found that suspended 1H-NbS₂ undergoes a quantum phase transition to a CDW state with approximately 3 × 3 charge ordering in the 2D limit, which is in agreement with experimental results on supported samples on 6H-SiC(0001). However, the CDW is extremely sensitive to environmental conditions, as it is very weak and compressive strains smaller than 0.5% are enough to suppress it. This explains the absence of CDW observed in 1H-NbS₂ on top of Au(111). This also suggest that devices with dynamical on/off switching of the 3 × 3 charge order can be obtained with deposition of 1H-NbS₂ on flexible substrates or through a small charge transfer via field effect.

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Notes

The authors declare no competing financial interest.

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(27) All the calculations were performed from first-principles with the QUANTUM ESPRESSO package³³ by computing the energy/forces of the configurations used by the SSCHA within density-functional theory and the harmonic dynamical matrices within density-functional perturbation theory. We used the generalized gradient approximation for the exchange-correlation functional, under the Perdew–Burke–Ernzerhof parametrization.³⁴ For the unit-cell calculation in the bulk and in the monolayer, the integration in reciprocal space was performed on a $24 \times 24 \times 8$ and a $40 \times 40 \times 1$ Monkhorst–Pack grid³⁵ of the Brillouin zone, respectively. These meshes were adjusted accordingly in the supercell calculations. We used ultrasoft pseudopotentials,³⁶ a plane-wave cutoff energy of 35 Ry for the kinetic energy and 400 Ry for the charge density, and a Methfessel–Paxton smearing of 0.005 Ry.³⁷ The SSCHA calculations were performed on a $4 \times 4 \times 1$ supercell for the bulk and on a $6 \times 6 \times 1$ supercell for the monolayer. The short-range part of the anharmonic dynamical matrices were computed with SSCHA in the static approximation for the phonon self-energy, retaining only the so-called “bubble term”.^{25,38} The long-range part of the anharmonic dynamical matrices were obtained first by Fourier interpolating the difference between the SSCHA and the harmonic dynamical matrices to finer grid and then adding the harmonic contribution calculated on this grid (for $6 \times 6 \times 4$ the bulk and for $16 \times 16 \times 1$ the monolayer). The phonon dispersion along high-symmetry paths were subsequently obtained by Fourier interpolation.

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