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The effect of high pressure on the lattice structure and dynamics of phenacenes

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Abstract. We studied the effect of high pressure on three phenacenes, aromatic molecules with a zig-zag configuration of the benzene rings. The lattice structure and vibrational dynamics of crystalline phenanthrene ($C_{14}H_{10}$, three benzene rings), chrysene ($C_{18}H_{12}$, four), and picene ($C_{22}H_{14}$, five) were investigated by means of X-ray diffraction and Raman measurements. Raman spectra were compared with theoretical ones obtained from *ab-initio* Density Functional Theory calculations. Experimental and theoretical results allowed to identify the onset of a structural transition in phenanthrene at 7.8 GPa under hydrostatic conditions and at 5.7 GPa under non-hydrostatic conditions. We found that this transition is related to a reorientation of the molecules in the *ab* plane. On the contrary, chrysene and picene do not undergo any phase transition in the investigated pressure range, thus suggesting that molecular size plays an important role in the occurrence of pressure induced structural modifications in aromatic compounds.

1. Introduction

Phenacenes are a class of polycyclic aromatic hydrocarbons (PAHs) characterized by a zig-zag configuration of the aromatic rings in the molecular structure. Like other PAHs, they are prototypical organic systems where molecules are held together in the crystalline state by weak intermolecular interactions. Intermolecular distances can thus be conveniently reduced by the application of an external pressure, which finely tunes structural [1–3], electronic [4, 5] and vibrational properties [3, 6] of the system. When the pressure exceeds a critical threshold, usually a few tens of GPa, it also induces irreversible reactions leading to new and peculiar structural phases [7–9]. Moreover, experimental investigations of aromatic hydrocarbons provide new useful benchmarks for theoretical calculations [10, 11].

In this respect, experimental studies on phenacenes under pressure are still low in number and not systematic. The first three members of phenacene are phenanthrene $C_{14}H_{10}$ which is



made of three fused benzene rings, chrysene $C_{18}H_{12}$ (four rings) and picene $C_{22}H_{14}$ (five rings). Phenanthrene has been recently investigated under pressure by means of X-ray diffraction (XRD) and Raman spectroscopy [3]. In this work, two structural phase transitions at 2.3 and 5.6 GPa were claimed. Concerning chrysene, preliminary spectroscopic works have been performed in the past at very low pressure [12, 13], whereas high pressure structural studies have never been performed. Picene has been studied only by means of optical measurements [5, 6, 14] showing the absence of any structural phase transition up to 23 GPa, where an irreversible transformation to hydrogenated amorphous carbon occurs [5].

Here, we report a first step towards a systematic investigation of the effect of high pressure (HP) on phenacenes by studying the structural and vibrational properties of phenanthrene, chrysene and picene up to 20 GPa. Our results show that only phenanthrene undergoes a phase transition whereas chrysene and picene keep their original structure up to the maximum pressure. The comparison among the three compounds points out the key role of the molecular size in determining the occurrence of a structural transition.

2. Methods

2.1. Experimental

Phenanthrene and chrysene powder samples were purchased from Sigma Aldrich. Picene powder was obtained through a newly developed synthesis procedure [15].

High pressure XRD measurements were performed at ID-09 beamline of the ESRF synchrotron (Grenoble, France) with a fixed wavelength of 0.4127 Å. The sample-to-detector distance and the image plate orientation angles were calibrated using CeO_2 standard. The two-dimensional diffraction images, acquired from a MAR555 detector, were converted to one dimensional 2θ diffraction patterns using the FIT2D software [16]. Pressure on the sample was generated by a membrane diamond anvil cell (DAC) equipped with IA diamonds (culet size 400 μm) and a stainless steel gasket. A $\sim 50\mu m$ sample was loaded, together with Helium as hydrostatic medium, inside a 150 μm hole which was previously drilled in the gasket.

High pressure Raman measurements on phenanthrene and chrysene were carried out with a LabRam Infinity and a LabRam HR Evo micro-spectrometers, respectively. Both instruments are by Horiba Jobyn-Yvon and are installed at the Department of Physics of the Sapienza University of Rome. Samples were excited by a He-Ne laser through a 50x long working distance objective which also collected the scattered radiation from the samples (backscattering geometry). Both the spectrometers allowed a spectral resolution better than 3 cm^{-1} . A screw driven DAC equipped with 700 μm culet IIA diamonds was used to pressurize the sample. A 250 μm hole was drilled in gasket and filled with sample without any pressure transmitting medium. A ruby sphere was added near to the culet center (no farther than 50 μm) for measuring the pressure *in situ* by the ruby fluorescence technique [17]. At each pressure step, Raman spectra were collected from three different points almost equidistant from the ruby and separated by $\sim 50\mu m$ one from the other. This allowed to check the homogeneity of the pressure response over the sample [18]. The comparison among these spectra showed that peak frequencies never exceeded a 2 cm^{-1} difference among the three acquisition points, thus witnessing the absence of strong pressure gradients.

2.2. Theoretical

Raman and IR cross sections of crystalline phenanthrene were calculated at selected pressures using Density Functional Perturbation Theory (DFPT) [19, 20], as implemented in the *quantum-espresso* package [21]. We used norm-conserving pseudopotentials [22] together with the local density approximation. The plane-wave (charge density) cutoff energy was set to 100 Ry (400 Ry) for all calculations. We used a uniform $3 \times 4 \times 3$ grid for \mathbf{k} -space integration. We checked

the choice of the plain wave cutoff by performing calculations under pressure keeping constant the number of plane waves by increasing/decreasing the cutoff according to $E_{\text{cutoff}} \propto V^{-\frac{2}{3}}$.

3. Results and Discussion

At ambient conditions, phenanthrene [23], chrysene [24] and picene [25] crystallize in a monoclinic unit cell where molecules are arranged in a herringbone configuration in the ab plane and are stacked along the c axis. In particular, phenanthrene and picene have the same space group $P2_1$ and two molecules per unit cell ($Z = 2$), whereas the space group of chrysene is $I2/c$ with $Z = 4$.

The XRD patterns of the three compounds have been collected in the 0-20 GPa pressure range. Data at selected pressures are shown in figure 1. At ambient conditions, a Le Bail fit of the diffraction patterns provides the following lattice parameters: $a = 8.458(2)$ Å, $b = 6.164(2)$ Å, $c = 9.482(5)$ Å, $\beta = 98.11(2)^\circ$ for phenanthrene; $a = 8.352(3)$ Å, $b = 6.205(2)$ Å, $c = 25.16(2)$ Å, $\beta = 115.84(4)^\circ$ for chrysene; $a = 8.196(3)$ Å, $b = 6.324(2)$ Å, $c = 13.82(5)$ Å, $\beta = 93.75(6)^\circ$ for picene. All these parameters are in agreement with the literature [23–25]. On increasing pressure, Bragg peaks shift towards higher angular values (lower interplanar distances) as a consequence of the volume reduction. This shift is continuous for chrysene, figure 1(b), and picene, figure 1(c), where also the overall shape of the diffraction patterns keeps constant over the whole pressure range. This indicates that the ambient pressure crystalline lattice of chrysene and picene is maintained, although compressed, up to 20 GPa. In other words, chrysene and picene do not undergo any structural transition in the investigated pressure range.

On the contrary, phenanthrene undergoes a phase transition at about 7.8 GPa. As a matter of fact, around this pressure value, the intensity of the lowest angle Bragg peak decreases and a new peak appears around $2\theta \sim 2.8^\circ$ (look at the 8.7 GPa pattern in figure 1). Other subtle changes are observed for the reflections around $2\theta \sim 8^\circ$. It is worth noting that our data does not show any other phase transition, at variance with the results reported by Huang *et al.* in Ref.[3], where a transition at 2.3 GPa and another one at 5.6 GPa were claimed. The comparison between our XRD patterns, figure 1(a), and those from Ref.[3] shows that the transition found by Huang *et al.* at 5.6 GPa is the same we found at 7.8 GPa. The two different values of the transition pressure are likely due to different hydrostatic conditions since here we employed helium as hydrostatic medium, whereas no medium was used by Huang and coworkers [3]. As to the phase transition found at 2.3 GPa by Huang *et al.*, our diffraction patterns do not show any anomaly around this pressure value. The absence of the phase transition at 2.3 GPa and the lowering of the pressure value under non-hydrostatic conditions for the other transition are further confirmed by our Raman measurements, which will be discussed in the following.

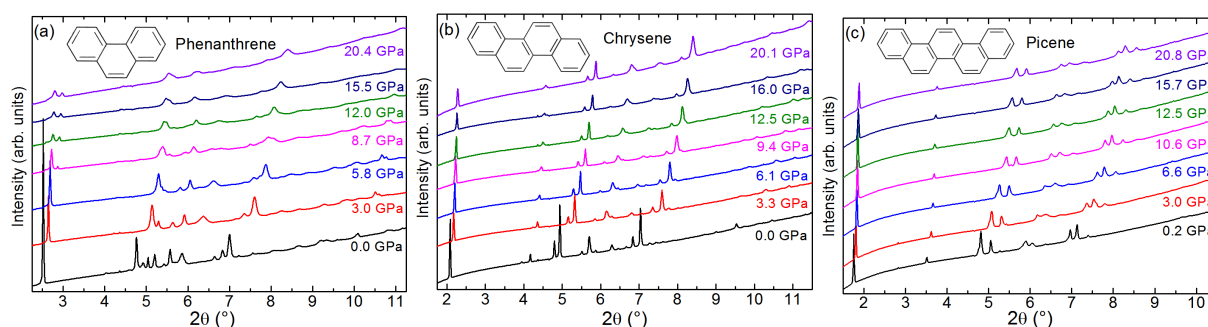


Figure 1. X-ray diffraction patterns of phenanthrene (a), chrysene (b) and picene (c) at selected pressures. Sketches of the molecular structures are also shown.

In Ref.[26], we analysed the diffraction patterns of phenanthrene using a structural model generated from an algorithm for crystal structure prediction and we identified a triclinic $P1$ unit cell with $Z=3$ formula units as the best structural candidate for the HP phenanthrene phase [26]. The lattice parameters of this phase obtained from a Le Bail fit of experimental data at 7.8 GPa are $a = 6.951(10)$ Å, $b = 8.967(10)$ Å, $c = 9.522(5)$ Å, $\alpha = 100.42(11)^\circ$, $\beta = 106.86(9)^\circ$, $\gamma = 106.03(9)^\circ$. In the HP phase, phenanthrene molecules are arranged in a parallel fashion within the ab plane, thus pointing out that the herringbone arrangement typical of phenacenes is no longer energetically convenient at HP (see Ref.[26]). This *motif* transition in the ab plane implies a rotation of the molecular units under pressure. This reorientation is easier when the steric hindrance of the molecules is smaller, especially when the available volume is reduced by pressure. This considerations strongly suggest a prominent role of the small molecular size of phenanthrene (three benzene rings) for the occurrence of the HP structural transition. Therefore, the bigger steric hindrance of chrysene (four benzene rings) and picene (five benzene rings) is likely responsible for the structural stability of these systems at least up to 20 GPa.

The occurrence of a phase transition can be also revealed by a vibrational spectroscopy. In fact, when the symmetry of the system changes across a phase transition, as in the case of phenanthrene (from $P2_1$ to $P1$), the vibrational selection rules change and a more or less pronounced variation can be observed in the vibrational spectrum of the system.

We thus performed Raman measurements on the three phenacenes as a function of pressure in the 0-8 GPa range. The pressure dependence of the Raman spectra of phenanthrene and chrysene are shown in figure 2. The spectra of picene are instead reported in Ref.[6] and do not show any indication of a phase transition, in agreement with the XRD data shown in figure 1 and with the infrared measurements under pressure reported in Ref.[5].

In any case, the investigated pressure range is limited by the appearance of a strong pressure induced luminescence background which prevents to collect Raman data above 8.5 GPa for phenanthrene, 7.7 GPa for chrysene and 6 GPa for picene [6]. This phenomenon has been observed in several aromatic hydrocarbons under pressure and it is generated by crystalline defects which increase under pressure [4].

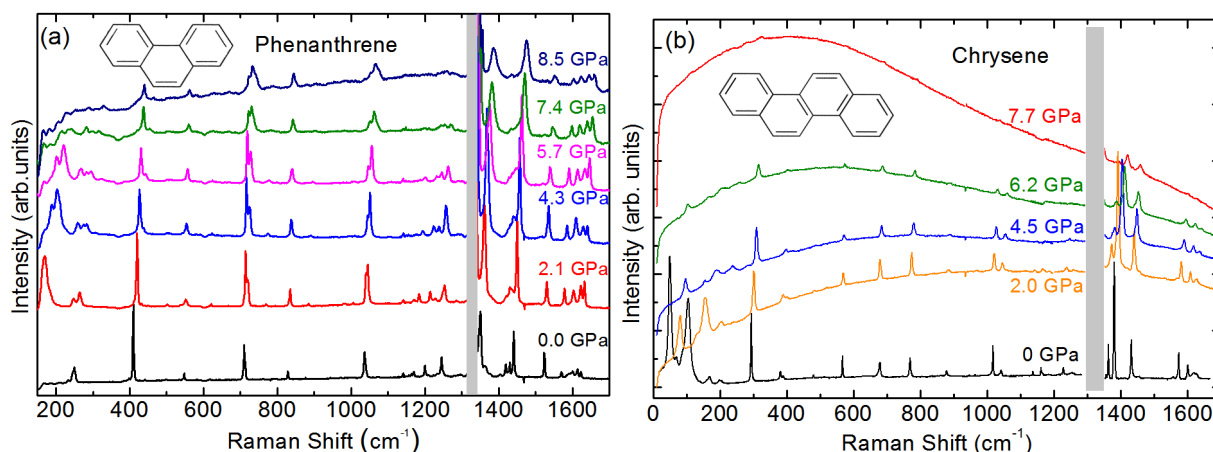


Figure 2. Raman spectra of phenanthrene (a) and chrysene (b) at selected pressures. The grey area around 1330 cm^{-1} masks the Raman peak of the diamond.

As to figure 2, a hardening of the vibrational frequencies and a broadening of the peaks is observed on increasing pressure. In particular, the Raman peaks below 200 cm^{-1} , ascribed to intermolecular vibrations [27, 28], show the strongest hardening. Indeed, pressure can easily

modify the intermolecular distances owing to the weakness of the intermolecular interactions.

The shift of the Raman peaks of chrysene under pressure is continuous (see figure 2(b)), without signs of any phase transition in agreement with XRD data.

On the other hand, some pressure induced spectral changes (such as peaks splitting, intensity enhancement/reduction, appearance of new peaks) can be observed in the Raman spectra of phenanthrene (see figure 2(a)). In the 0-6 GPa pressure range, these spectral changes can be nicely reproduced by DFT calculations based on the low pressure $P2_1$ phase of phenanthrene. Above 6 GPa, measured spectra are no longer well reproduced by calculations, especially some new peaks appearing in the experimental data, thus suggesting the occurrence of a phase transition in agreement with XRD data.

We report in figure 3 the comparison of the measured and calculated Raman spectra for two frequency regions: around 730 cm^{-1} , panels (a)-(c), and 1050 cm^{-1} , (d)-(f). The lineshape analysis of the experimental spectra is based on a standard least-square fitting procedure with Lorentzian or Gaussian functions. The theoretical spectra shown in panels (c) and (f) are calculated using the monoclinic $P2_1$ structure of phenanthrene at 0, 4, 8 GPa with relaxed internal positions. At 0 GPa, the experimental spectra can be fitted with a two component

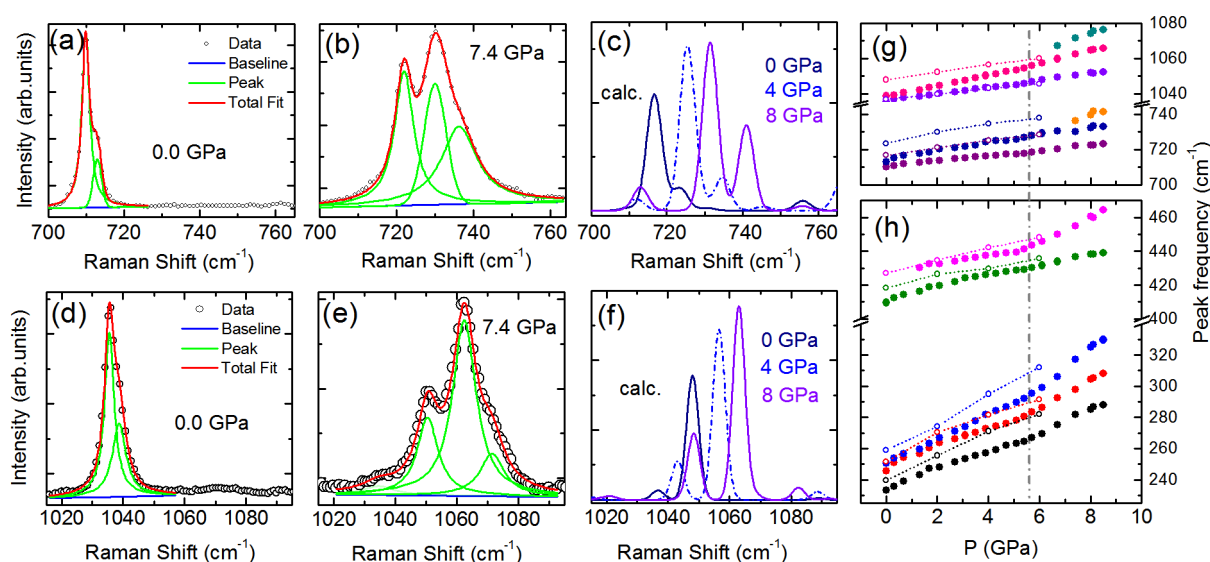


Figure 3. Lineshape analysis of the Raman spectra of phenanthrene within the $700\text{--}760\text{ cm}^{-1}$ and $1000\text{--}1080\text{ cm}^{-1}$ ranges at 0 GPa, panels (a)-(d), and 7.4 GPa, (b)-(e). Panels (c)-(f): DFT calculated spectra at 0, 4, 8 GPa for the $P2_1$ phase of phenanthrene. Panels (g)-(h): Measured (full points) and calculated (empty points) vibrational frequencies of some selected modes as a function of pressure (g)-(h). The vertical grey dotted line marks the pressure value where a slope change is observed.

model in both spectral regions (see panels (a),(d)), in agreement with the calculated spectra (see panels (c),(f)). Above 5.7 GPa, a considerable broadening is observed in both regions. Moreover, there is an inversion of the intensity of the two components of the spectral feature around 710 cm^{-1} (compare panels (a) and (b)). The spectral analysis at 7.4 GPa, panels (b) and (e), reveals a change in the relative Raman cross section of the two components and the appearance of a shoulder on the high frequency side in both the spectral regions. In contrast, the Raman spectra calculated in the $P2_1$ structure are characterized by only two components at all pressures and do not show the appearance of any new peak (see panels (c),(f)). Therefore, the appearance of the high frequency shoulders in the experimental spectra indicates a structural

change from the $P2_1$ structure to a high pressure phase of phenanthrene with reduced symmetry. This agrees with the results of our XRD analysis under hydrostatic compression which shows a transition to a structure with $P1$ symmetry and $Z=3$ molecules in the unit cell.

The analysis of experimental spectra also provided the vibrational frequencies of the observed peaks. The pressure dependence of some of these frequencies is shown in figure 3(g)-(h), where the calculated values of the corresponding vibrational modes of the $P2_1$ phase is also shown for comparison. Both calculated and measured frequencies increase as a function of pressure, with similar slopes. The theoretical values are systematically $\sim 10 \text{ cm}^{-1}$ higher than the experimental ones. This amounts to 1 % relative error, which is within the typical accuracy of LDA-DFPT calculations for phonon frequencies [6, 29].

More interestingly, above 5.7 GPa, a slope change of the experimental frequencies occurs, *i.e.* they increase more rapidly under pressure. Such a slope change demonstrates that pressure has a different and stronger effect on the vibrational frequencies above 5.7 GPa. This behavior is often observed when the system enters a new phase [30]. On further increasing pressure, two new peaks, already shown in panels (b) and (e), appear around 740 and 1070 cm^{-1} and persist up to the maximum pressure investigated (orange and dark cyan points). Therefore, both the slope change and the appearance of new peaks indicates the occurrence of a phase transition in phenanthrene at high pressure.

Yet, the phase transition in the XRD data is at 7.8 GPa whereas the phase transition deduced from the Raman spectra occurs at 5.7 GPa. This disagreement can be ascribed to the different experimental conditions. In fact, the XRD data were collected with helium as a pressure transmitting medium (hydrostatic conditions), whereas the Raman spectra were collected without a medium. The non-hydrostaticity thus explains the lower transition pressure of about 5.7 GPa, which is indeed in agreement with the value obtained from the non-hydrostatic XRD measurements reported in Ref.[3].

4. Conclusions

In this paper, we studied the effect of high pressure on the lattice structure and vibrational spectra of crystalline phenanthrene, chrysene and picene, by means of X-ray diffraction, Raman spectroscopic measurements and DFT calculations. We showed that the onset of a structural transition occurs in phenanthrene at 7.8 GPa under hydrostatic conditions, whereas chrysene and picene keep the same structure up to the maximum pressure here investigated of about 20 GPa. Bearing in mind the shorter length of phenanthrene (three aromatic rings) molecules compared to chrysene (four) and picene (five), we conclude that the molecular size strongly affects the pressure induced modifications of the structure of phenacenes.

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References

- [1] Oehzelt M, Aichholzer A, Resel R, Heimel G, Venuti E and Della Valle R G 2006 *Phys. Rev. B* **74** 104103
- [2] Fabbiani F P A, Allan D R, Parsons S and Pulham C R 2006 *Acta Crystallogr. B* **62** 826–42
- [3] Huang Q W *et al.* 2013 *J. Chem. Phys.* **139** 104302
- [4] Dreger Z A, Lucas H and Gupta Y M 2003 *J. Phys. Chem. B* **107** 9268–74
- [5] Fanetti S, Citroni M, Malavasi L, Artioli G A, Postorino P and Bini R 2013 *J. Phys. Chem. C* **117** 5343–51
- [6] Capitani F *et al.* 2013 *Phys. Rev. B* **88** 144303
- [7] Ciabini L, Santoro M, Gorelli F A, Bini R, Schettino V and Raugai S 2007 *Nat. Mater.* **6** 39–43
- [8] Wen X D, Hoffmann R and Ashcroft N W 2011 *J. Am. Chem. Soc.* **133** 9023–35
- [9] Fitzgibbons T C, Guthrie M, Xu E s, Crespi V H, Davidowski S K, Cody G D, Alem N and Badding J V 2015 *Nat. Mater.* **14** 43–47

- [10] Schatschneider B, Monaco S, Liang J J and Tkatchenko A 2014 *J. Phys. Chem. C* **118** 19964–74
- [11] Schatschneider B, Monaco S, Tkatchenko A and Liang J J 2013 *J. Phys. Chem. A* **117** 8323–31
- [12] Offen H W 1966 *J. Chem. Phys.* **44** 699–703
- [13] Baldwin B A and Offen H W 1967 *J. Chem. Phys.* **46** 4509–14
- [14] Joseph B *et al.* 2012 *J. Phys. Condens. Matter* **24** 252203
- [15] Protti S, Artioli G A, Capitani F, Marini C, Dore P, Postorino P, Malavasi L and Fagnoni M 2015 *RSC Adv.* **5** 27470–5
- [16] Hammersley A P, Svensson S O, Hanfland M, Fitch A N and Hausermann D 1996 *High Pressure Res.* **14** 235–48
- [17] Mao H K, Bell P, Shaner J W and Steinberg D J 1978 *J. Appl. Phys.* **49** 3276
- [18] Capitani F, Fasolato C, Mangialardo S, Signorelli S, Gontrani L and Postorino P 2015 *J. Phys. Chem. Solids* **84** 13–6
- [19] Baroni S, de Gironcoli S, Dal Corso A and Giannozzi P 2001 *Rev. Mod. Phys.* **73** 515–62
- [20] Lazzeri M and Mauri F 2003 *Phys. Rev. Lett.* **90** 036401
- [21] Giannozzi P *et al.* 2009 *J. Phys. Condens. Matter* **21** 395502
- [22] We used the pseudopotentials C.pz-vbc.UPF and H.pz-vbc.UPF from <http://www.quantum-espresso.org>
- [23] Trotter J 1963 *Acta Crystallogr.* **16** 605–8
- [24] Burns D M and Iball J 1960 *Proc. R. Soc. London A* **257** 491–514
- [25] De A, Ghosh R, Roychowdhury S and Roychowdhury P 1985 *Acta Crystallogr. C* **41** 907–9
- [26] Capitani F, Höppner M, Malavasi L, Marini C, Artioli G A, Hanfland M, Dore P, Boeri L and Postorino P 2016 *J. Phys. Chem. C* **120** 14310–6
- [27] Godec J and Colombo L 1976 *J. Chem. Phys.* **65** 4693–700
- [28] Colangeli L, Mennella V, Baratta G A, Bussoletti E and Strazzulla G 1992 *Astrophys. J.* **396** 369–77
- [29] Brown-Altwater F, Rangel T and Neaton J B 2016 *Phys. Rev. B* **93**(19) 195206
- [30] Capitani F, Trequattrini F, Palumbo O, Paolone A and Postorino P 2016 *J. Phys. Chem. B* **120** 2921–28