PHYSICAL REVIEW B **73**, 174111 (2006)

Solid ammonia at high pressure: A single-crystal x-ray diffraction study to 123 GPa

F. Datchi,* S. Ninet, M. Gauthier, A. M. Saitta, B. Canny, and F. Decremps
IMPMC, Physique des Milieux Denses, CNRS UMR 7590, Université Pierre et Marie Curie, 140 rue Lourmel, 75015 Paris, France

(Received 21 March 2006; published 11 May 2006)

The high-pressure phases of solid ammonia have been investigated by x-ray diffraction in a diamond anvil cell at room temperature. Despite the first-order solid phase transition at 4 GPa, quasi-single crystals of NH_3 and ND_3 could be obtained and compressed to 123 and 62 GPa, respectively. The observed reflections above 4 GPa are compatible with the structure determined by neutron diffraction on ND_3. We found strong evidence for an isosymmetric transition at 12 GPa in NH_3 and 18 GPa in ND_3. This transition is more likely due to rearrangements of the hydrogen atoms, whereas the N atoms remain on their quasi-hcp sites. The experimental equation of state (EOS) is compared to the one derived from first-principles calculations. A stiffening of the EOS above 55 GPa could indicate the onset of a quantum-disordered regime for some of the H bonds.

DOI: 10.1103/PhysRevB.73.174111 PACS number(s): 62.50.+p, 61.10.Nz, 61.50.Ks, 64.70.Kb

I. INTRODUCTION

Ammonia belongs to the important group of simple molecular ices with a large abundance in the solar system. Because they are major constituents of Jovian planets, knowledge of the high-pressure properties of these compounds and their mixtures is needed for modeling the interior of these planets. There is also a fundamental interest in ammonia as an archetype of hydrogen-bonded solids. Compared to H_2O, the hydrogen bonds are weaker in the low-pressure solid since the single electronic lone pair of the nitrogen atom bonds to three H atoms of neighboring molecules. A long-standing issue concerns the occurrence in dense ammonia of a symmetric phase with centered hydrogen bonds. As a general rule, symmetric hydrogen bonds are found for low values of the donor-acceptor distance. Nonsymmetric phases at ambient pressure may thus become symmetric under load, as is the case, e.g., in HCl,[1] HBr,[2] and H_2O.[3] Whether such a scenario holds in ammonia remains thus far an unsettled issue.

At room temperature, ammonia crystallizes at 1 GPa in a rotationally disordered, face-centered-cubic phase (phase III, space group $Fm\bar{3}m$).[4] A first-order transition occurs at 4 GPa to solid IV. It was initially described as hexagonal close-packed (hcp) by x-ray diffraction experiments,[5,6] but neutron diffraction on ND_3 revealed an orthorhombic structure (space group $P2_12_12_1$) with rotationally ordered molecules.[7,8] Phase IV was found stable in the neutron diffraction experiments up to 9 GPa. At higher pressure, the experimental findings are quite confusing: a phase transition was detected at about 14 GPa in Raman[9] and Brillouin[10] studies of NH_3, but no change was seen in the Raman spectra of ND_3 up to 40 GPa (Ref. 11) nor in the x-ray powder pattern of NH_3 to 56 GPa.[6] Gauthier *et al.*[9] also reported a phase transition at 60 GPa that was interpreted as the signature of H-bond symmetrization. More recently, two phase changes at 40 and 70 GPa were inferred from a IR absorption study,[12] but no evidence of symmetrization could be seen up to 120 GPa. Finally, the most recent powder x-ray experiment up to 40 GPa suggested a monoclinic structure for phase IV and a transition to an undetermined phase at 12 GPa.[13] Clearly, more structural data are needed to clarify this situation. Because the path to symmetrization of the H-bonds in ammonia is directly correlated to the solid structure, determining the latter is one of the most important issue. As a matter of fact, recent theoretical studies[14,15] found that if the orthorhombic structure determined by Loveday *et al.*[8] remains stable, symmetrization should not occur before a pressure of the order of 1–2 TPa at 0 K, i.e, out of present experimental reach. It is the aim of this work to probe the structure of solid ammonia by x-ray diffraction to very high pressures. We overcame many problems encountered in previous powder experiments by using single-crystal techniques. This allowed us to determine the equation of state of NH_3 and ND_3 and obtain structural parameters up to 123 GPa.

II. EXPERIMENTAL DETAILS

Previous powder XRD studies on NH_3 at high pressures were all limited by very poor statistics due to low-quality samples. Starting from the liquid, it is indeed extremely difficult to obtain a large enough number of randomly oriented crystallites inside the sample volume of a diamond anvil cell. On the other hand, the single-crystal technique has been successfully used in the recent past on light compounds such as H_2O.[16] Performing single-crystal x-ray diffraction on ammonia seemed, therefore, the way to proceed. In this case, however, the presence of the III-IV first-order transition at 4 GPa—and because phase IV is not accessible from the liquid—appeared, until now, as a strong obstacle to the single-crystal technique above the transition pressure.

The experimental volume of membrane diamond anvil cells (DAC) were filled with liquid NH_3 or ND_3 (isotopic purity ≥99.66%) at 5 bar and 278 K. Rhenium gaskets were used but as in Ref. 16, we embedded the samples in a gold ring to reduce the fragmentation of the crystal due to nonhydrostatic compression. Pressure was measured with the luminescence from a ruby ball or $SrB_4O_7:Sm^{2+}$ powder, using the recently revised ruby scale,[17] and from the equation of state (EOS) of gold.[18]

Single crystals of NH_3 or ND_3 were grown by slowly compressing the liquid phase up to the room temperature melting pressure. This generally produced a few crystallites that eventually coalesced to form a single germ in equilib-

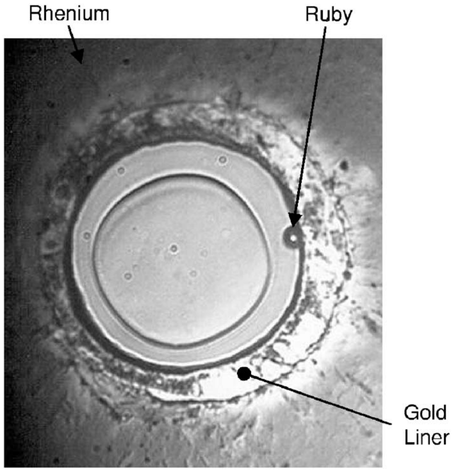

FIG. 1. Photograph of the NH_3 sample at 1 GPa, 300 K, as viewed through the diamond anvil. A single crystal of phase III is in equilibrium with its melt. The hole size is 70 μm, and the gold liner separating the sample from the rhenium gasket is ~10 μm thick.

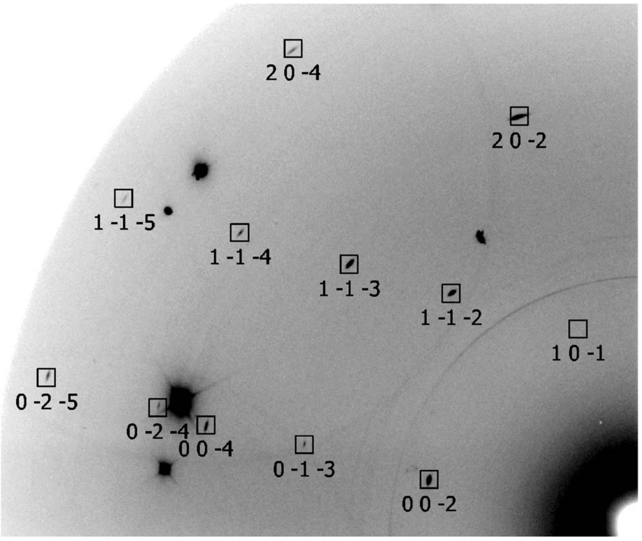

FIG. 2. Detail of the diffraction pattern of NH_3 phase IV at 4.5 GPa, overlaid with the indexing of reflections from the NH_3 crystal. The nonindexed spots are from the diamond anvils.

rium with the melt (Fig. 1). With further load, the single crystal occupied the whole sample space. Pressure was increased very slowly at each step in order to prevent crystal fragmentation as best as possible.

The x-ray diffraction (XRD) experiments were performed at beamlines ID30 and ID09A of the European Synchrotron Radiation Facility (Grenoble, France). We used an angular-dispersive setup with a monochromatic beam ($\lambda \simeq 0.4$ Å) focused down to below 20 μm and either a MAR345 image plate or a Bruker Smart 6500 CCD detector. The DAC could be rotated around the vertical axis, perpendicularly to the x-ray beam (ω rotation). The cell presents a large x-ray aperture ($2\theta_{\text{max}}=37°$) thanks to the use of quasi x-ray transparent diamond seats built out of c-BN or B_4C.

III. RESULTS

Three different samples of NH_3 were compressed up to 31.5, 99, and 123.8 GPa, respectively, and one sample of ND_3 to 62 GPa. The observed reflections below 4 GPa agree with the $Fm\bar{3}m$ space group of phase III.[4] The transition to phase IV is detected by a rapid pressure drop of a few tenths of gigapascal—due to a volume jump of 1.5%—and a noticeable change of diffraction pattern. As shown in Fig. 2, the latter is characteristic of a single-crystal pattern, although the mosaicity is relatively large (a few degrees), indicating a fragmentation of the initially very high-quality crystal. We note, however, that this fragmentation appears to be rather due to nonhydrostatic compression than to the transition, for the mosaicities just before and after the transition are similar. Using a rotation method, the orientation matrix of the crystal was determined which could account for all the observed spots.

Up to 47 reflections were observed down to a resolution of 0.9 Å. They were all very well indexed by an orthorhombic unit cell with $a=3.2671(3)$ Å, $b=5.6819(19)$ Å, and $c=5.3692(4)$ Å at 4.3 GPa, very close to the one found in Ref. 8 for ND_3. As described in this paper, the nitrogen atoms in phase IV are only slightly displaced (within 0.11 Å) with respect to the relative position of the hcp structure. Thanks to the high resolution of our experiments and the use of single-crystal techniques, we were able to resolve the 0.005 Å difference in the d spacings of peaks that correspond to equivalent reflections in the hcp structure. Further, very weak non-hcp peaks are nonambiguously seen on XRD patterns [for example, the $(0\bar{1}\bar{3})$ reflection in Fig. 2]. The observed extinctions points to $P2_12_12_1$ space group as the most probable one, in agreement with the refinement of the neutron data.[8] Unfortunately, we were unable to extract reliable intensities from our diffraction images, which precluded a refinement of the structure. This is a combinated effect of the relatively poor crystal quality and of the extinction of the primary beam by the intense Bragg peaks from the front diamond anvil: most reflections are affected by this extinction in a manner that is difficult to correct.

By increasing pressure above 12 GPa for NH_3 and 18 GPa in ND_3, a different diffraction pattern was systematically obtained. More specifically, the pattern was composed of the Bragg peaks previously observed in the patterns of solid IV and additional spots. The latter reflections do not belong to the initial crystal and cannot be indexed using a supercell. Actually, they correspond to d spacings that are compatible with the unit cell parameters of phase IV at this pressure. As shown in Fig. 3, the diffraction pattern at 13 GPa can be interpreted as originating from two different crystals, sharing the same orthorhombic unit cell, but differently oriented. No systematics was found in the relative orientation of these two crystals. We stress that this phenomenom was observed at the same pressure with all samples, independent of their size and initial orientations, and that no more additional peaks appeared with further increase in pressure (below and above 12 GPa, only angular broadening of the reflections is observed as a consequence of nonhydrostatic compression). This strongly suggests that a phase transition occurs at this pressure, causing a splitting of the crystal

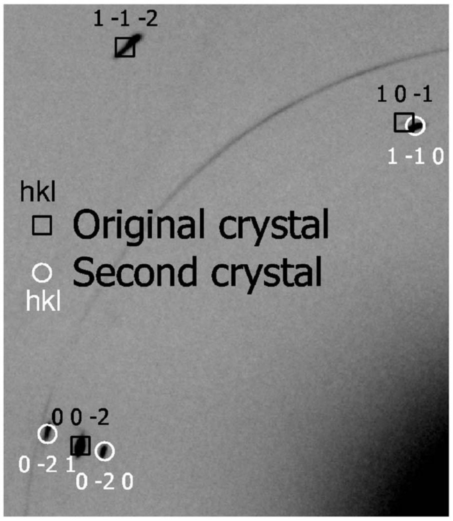

FIG. 3. Detail of the diffraction image of the NH_3 sample at 13 GPa, overlaid with the indexing of reflections from the original (squares) and second (circles) crystals.

in two components. The high-pressure phase, however, presents the same orthorhombic symmetry and, most likely, the same space group as phase IV (all peaks above 12 GPa follow the extinction rules characteristic of $P2_12_12_1$). This transition is further supported by the occurrence, at the same pressure, of a kink in the c/a-axis ratio (Fig. 4): initially slowly increasing up to 12 GPa (respectively, 18 GPa) in NH_3 (respectively, ND_3), it then starts to decrease at a higher rate. A similar evolution is observed for c/b, whereas the b/a ratio shows a rather continuous, slow decrease up to 123 GPa. The solid above 12 GPa thus presents a larger compressibility in the c-axis direction. We may then understand the observed splitting of the crystal as the consequence of a sudden change in the strain state of the sample.

Within the precision of our measurements (~ 0.1 Å$)^3$, no volume jump is detected across the transition, but the kink in the c/a ratio, added to the observed crystal splitting, suggests a first-order transition. As a matter of fact, Landau's theory of phase transition tells us that a transition between isosymmetric phases must be discontinuous.[19,20] Other examples of isostructural transitions where no volume discontinuity was detected can be found in the literature, such as, for instance, in ice VIII,[21,22] CsI,[23,24] and NH_4PF_6.[25] In the first two cases, the transition involved a discontinuous change in the symmetry-unconstrained fractional coordinate, while in the latter, a radical change in the orientation of the spontaneous strain components was found although the transition appeared continuous by XRD or NMR. In phase IV, all atoms are on general positions, and the transition may thus result from the movements of any of them; however, considering the large difference in the transition pressure between the two isotopes and the similarity between the XRD patterns, it is more likely that movements of the hydrogen or deuterium atoms are involved.

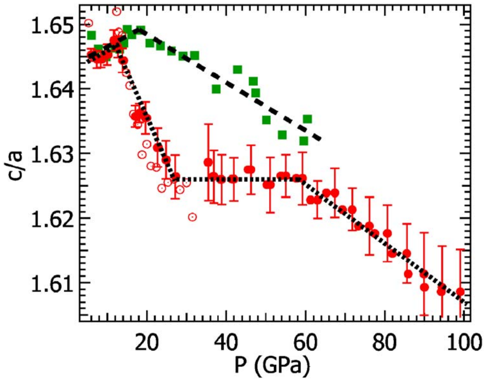

FIG. 4. (Color online) c/a-axis ratio. Solid and dotted circles are experimental data for NH_3 and solid squares for ND_3. The dotted and dashed lines are guides to the eye.

TABLE I. Parameters of the Vinet equation of state[27] fitted to the present experimental data for NH_3 and ND_3, and to the *ab initio* calculations for NH_3.

Fit range	NH_3		ND_3	Calc. (NH_3)
(GPa)	4–55	4–123	4–62	2–100
V_0 (Å^3/mol)	33.0(8)	39.7(23)	31.9(4)	33.0(2)
B_0 (GPa)	7.1(11)	2.0(7)	8.1(6)	6.1(2)
B_0'	5.97(20)	7.5(3)	6.09(9)	6.36(4)
χ^2	3.98	26.35	0.55	0.08

As recalled above, the occurrence of a phase transition from solid IV to V was already inferred at ca. 14 GPa by Brillouin[10] and Raman[9] studies. In the former, the frequency shift of the Brillouin peak presented a small discontinuity, supporting a first-order transition. In the Raman experiment, the transition was associated with a change of slope in the $\nu(P)$ of the lattice modes and the growth of an additional mode in the $\nu_1-\nu_3$ band. From group theory, we expect 12 $(4\nu_1+8\nu_3)$ Raman-active modes for this band in the orthorhombic unit cell and only a total of three and four modes were, respectively, observed below and above the transition. There is thus no contradiction with a transition between isosymmetric phases. It is also interesting to note that in the Raman experiments, the shape of the vibron band evolved continuously up to 30 GPa. Here, the c/a ratio decreases linearly from 12 to 30 GPa, pressure beyond which it becomes stable again.

The equation of state (EOS) of NH_3 is represented in Fig. 3. The volume was calculated using all observed reflections (22 of them from 8 different classes were still visible at 100 GPa). There is no sign of large deviatoric stress developing in ammonia up to the megabar range: the d spacings of equivalent reflections remain within experimental uncertainty and the R band of ruby is still resolved at 100 GPa. The agreement between measurements on different samples is also excellent, within experimental accuracy on pressure and volume. The large number of measured points constrain very well the equation of state up to a compression factor V/V_0 of 0.36.

We tested various forms proposed in the literature[26–28] to fit the experimental EOS. The results for the Vinet form, which produced the best fits, are given in Table I. Although we could obtain excellent fits for NH_3 up to 55 GPa and ND_3

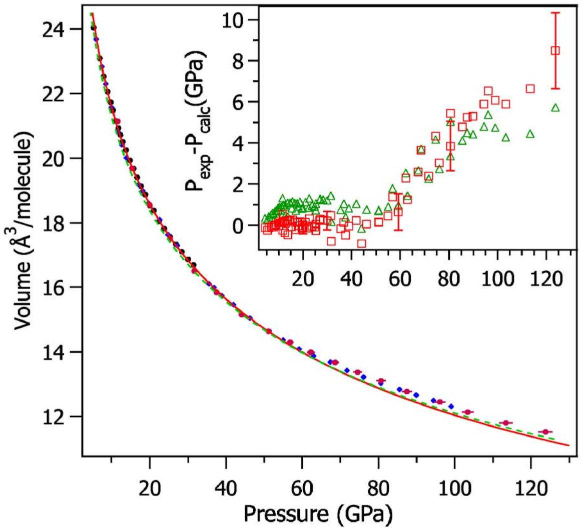

FIG. 5. (Color online) Equation of state of solid ammonia (NH_3). Different symbols represent experimental data from different runs. The solid line is the Vinet fit to the NH_3 data up to 55 GPa, and the dashed line is the EOS given by present *ab initio* calculations. The inset shows the difference between experimental pressure and the one predicted either by the Vinet model fitted to 55 GPa (squares) or by the *ab initio* calculations (triangles).

up to 62 GPa, all these models failed to represent the NH_3 data at higher pressures. An increasing difference between experimental and model-predicted pressure can be observed in the inset of Fig. 5.[29] Actually, the parameters obtained by fitting the whole pressure range substantially differ from those obtained by restraining the fit to the data below 55 GPa, and the χ^2 values are much larger (see Table I). To explain this, we may either suppose that the tested EOS models are inadequate in this large compression range or that there is an intrinsic change in the compressibility behavior of NH_3 at $P > 55$ GPa. In order to test the former hypothesis, we performed first-principles calculations of the volume of solid NH_3 at 18 pressures between 2 and 100 GPa.[30] We started from the experimental unit cell of phase IV and optimized the cell axis and atomic positions at each pressure. The results are in very good agreement with those of Refs. 14 and 15. The calculated EOS is very well fitted by a Vinet form (Table I). For $P < 55$ GPa, it closely follows the experimental EOS, whereas at $P > 55$ GPa, we basically find the same deviation as with the Vinet model (inset of Fig. 3). This deviation appears, therefore, to be an intrinsic effect and might be the signature of a phase transition. As a matter of fact, we also observe another decreasing regime in the c/a ratio beyond 55 GPa. We note, however, that there is no obvious change in the diffraction pattern and no volume discontinuity can be measured. We did not observe such an effect in ND_3 either; however, considering the 50% isotopic shift in the IV-V transition pressure, we might expect it at a higher pressure than achieved here.

In their Raman study, Gauthier *et al.*[9] observed a small jump (~ 5 cm^{-1}) at 60 GPa in the frequency of the vibron mode, which appeared at 14 GPa, whereas the other vibrons, and in particular, the symmetric stretching ν_1 mode, were no longer visible. They interpreted this as a transition to another phase, solid VI. This pressure is close to the one where we detect the anomaly of the EOS. Gauthier *et al.*[9] proposed cubic structures for solid VI that could accommodate symmetric H bonds, but these can be ruled out by the present work. This confirms the theoretical study of Cavazzoni[14] who found the cubic structures unstable in his simulations. Our experiments show that solid ammonia retains the orthorhombic symmetry of solid IV up to 123 GPa. Phase V, and possibly phase VI, should therefore mainly differ from phase IV in the arrangements of the hydrogen atoms while the nitrogen atoms keep their quasi-hcp positions. It is thus likely that the deformation of the ammonia molecule already initiated in phase IV (Ref. 8) becomes larger and larger with increasing pressure. As a matter of fact, with increasing strength of hydrogen bonds under pressure, the large difference in bond lengths and angles found for phase IV should induce a larger delocalization of the H atoms involved in the stronger bonds. This could even mean that H-bond symmetrization in ammonia could be achieved for some bonds and not the others, or for all bonds but at different pressures.

The present experiments do not allow us to state whether symmetrization occurs in the probed pressure range. On the one hand, the observed stiffening of the EOS is reminiscent of the one observed in ice VII (Ref. 3) at the onset of the so-called quantum disordered regime,[31] and concurs with the disappearance of the Raman-active symmetric stretching ν_1 mode reported by Gauthier *et al.*[9] On the other hand, Sakashita *et al.*[12] were able to follow the IR-active ν_1 mode up to 120 GPa, which is not in favor of symmetrization (we note that the IR-active ν_1 mode is not Raman active, such that both observations are compatible). Furthermore, as mentioned in the Introduction, first-principles simulations of Refs. 14 and 15 put the transition to the symmetric state at much higher pressures than discussed here; however, it was pointed out that it may be achieved at much lower pressure via a first-order process to a different structure and that inclusion of quantum effects in the simulations would also act to bring the symmetrization transition to a lower pressure. The importance of quantum effects in dense ammonia is indirectly supported by the fact that these calculations and ours, which treat H atoms as classical particles, do not exhibit the experimentally observed changes at 12 and 55 GPa.

Finally, we found no evidence for phase transitions at 40 and 70 GPa as reported by Sakashita *et al.*[12] These transitions were mainly supported by the splitting of ν_4 modes in the infrared (IR) spectra. However, there are six IR-active ν_4 modes in the orthorhombic structure, and only two, three, and four are successively observed. It could well be then that the additional modes are ones that were not resolved at lower pressures.

In conclusion, we have shown that single crystals of hydrogenous and deuterated ammonia phase IV can be obtained despite the III-IV first-order transition and have studied them by x-ray diffraction up to 123 and 62 GPa, respectively. The orthorhombic structure of phase IV was confirmed for both isotopes. A subtle phase transition has been detected at 12(18) GPa for NH_3 (ND_3) to another structure, which appears isosymmetric to phase IV. We have measured the room-temperature equation of state with high accuracy, which allowed us to detect a change of compressibility in

NH_3 above 55 GPa. This indicates a modification of the intermolecular interactions and could be associated to the onset of a quantum disordered regime for some of the H bonds. Further work is needed, including full quantum mechanical simulations, in order to determine the exact nature of the observed changes.

ACKNOWLEDGMENTS

We thank A. C. Dhaussy, M. Mezouar, and M. Hanfland at ESRF for their help with the experiments, and Ph. Pruzan for fruitful discussions.

---

*Electronic address: datchi@impmc.jussieu.fr

[1] K. Aoki, E. Katoh, H. Yamawaki, M. Sakashita, and H. Fujihisa, Physica B **265**, 83 (1999).

[2] E. Katoh, H. Yamawaki, H. Fujihisa, M. Sakashita, and K. Aoki, Phys. Rev. B **59**, 11244 (1999).

[3] P. Pruzan, J. C. Chervin, E. Wolanin, B. Canny, M. Gauthier, and M. Hanfland, J. Raman Spectrosc. **34**, 591 (2003), and references therein.

[4] R. B. V. Dreele and R. C. Hanson, Acta Crystallogr., Sect. C: Cryst. Struct. Commun. **C40**, 1635 (1984).

[5] R. L. Mills and B. Olinger (unpublished).

[6] J. W. Otto, R. F. Porter, and A. L. Ruoff, J. Phys. Chem. Solids **50**, 171 (1989).

[7] S. Klotz, M. Gauthier, J. M. Besson, G. Hamel, J. S. Loveday, R. J. Nelmes, R. M. Wilson, and W. G. Marshall, Appl. Phys. Lett. **67**, 1188 (1995).

[8] J. S. Loveday, R. J. Nelmes, W. G. Marshall, J. M. Besson, S. Klotz, and G. Hamel, Phys. Rev. Lett. **76**, 74 (1996).

[9] M. Gauthier, P. Pruzan, J. C. Chervin, and J. M. Besson, Phys. Rev. B **37**, 2102 (1988).

[10] M. Gauthier, P. Pruzan, J. C. Chervin, and A. Polian, Solid State Commun. **68**, 149 (1988).

[11] P. Pruzan, M. Gauthier, and J. Chervin, Int. J. Thermophys. **11**, 259 (1990).

[12] M. Sakashita, H. Yamawaki, H. Fujihisa, and K. Aoki, Rev. High Pressure Sci. Technol. **7**, 796 (1998).

[13] M. Gauthier, J. P. Iti, A. Polian, D. Hasermann, and M. Hanfland, in *High Pressure Science and Technology*, edited by W. A. Trzeciakowski (World Scientific, Singapore, 1996), pp. 372–374.

[14] C. Cavazzoni, Ph.D. thesis, SISSA (1998).

[15] A. D. Fortes, J. P. Brodholt, I. G. Wood, and L. Vočadlo, J. Chem. Phys. **118**, 5987 (2003).

[16] P. Loubeyre, R. LeToullec, E. Wolanin, D. Hausermann, and M. Hanfland, Nature (London) **397**, 503 (1999).

[17] W. Holzapfel, J. Appl. Phys. **93**, 1813 (2003).

[18] A. Dewaele, P. Loubeyre, and M. Mezouar, Phys. Rev. B **70**, 094112 (2004).

[19] J.-C. Toldano and P. Toldano, *The Landau Theory of Phase Transitions* (World Scientific, Singapore, 1987).

[20] A. G. Christy, Acta Crystallogr., Sect. B: Struct. Sci. **51**, 753 (1995).

[21] J. M. Besson, S. Klotz, G. Hamel, W. G. Marshall, R. J. Nelmes, and J. S. Loveday, Phys. Rev. Lett. **78**, 3141 (1997).

[22] D. D. Klug, J. S. Tse, Z. Liu, X. Gonze, and R. J. Hemley, Phys. Rev. B **70**, 144113 (2004).

[23] H. Mao, Y. Wu, R. Hemley, L. Chen, J. Shu, L. Finger, and D. Cox, Phys. Rev. Lett. **64**, 1749 (1990).

[24] B. Winkler and V. Milman, J. Phys. C **9**, 9811 (1987).

[25] I. Swainson, R. Hammond, J. Cockcroft, and R. Weir, Phys. Rev. B **66**, 174109 (2002).

[26] F. Birch, J. Geophys. Res. **83**, 1257 (1978).

[27] P. Vinet, J. Ferrante, J. Smith, and J. Rose, J. Phys. C **19**, L467 (1986).

[28] W. Holzapfel, Europhys. Lett. **16**, 67 (1991).

[29] This deviation is observed in the same manner when plotting the linearized form of the Vinet EOS (not shown) (Ref. 3).

[30] These calculations, based on density functional theory, used the PWSCF code (www.pwscf.org), which implements a pseudopotential/plane wave scheme, with a cutoff of 70 Ry and a $4\times4\times4$ *k*-points grid.

[31] The quantum disordered regime is characterized by a translational disorder along the bond due to a low potential barrier and strong tunneling and is an intermediate state between the molecular and symmetric phases.