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Novel high-pressure nitrogen phase formed by compression at low temperature

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Raman spectroscopy and powder x-ray diffraction methods have been used to characterize a novel phase of nitrogen which forms on compression from ambient pressure at low temperatures. The new, λ, phase exhibits an exceptionally wide range of pressure stability from below 1 to 140 GPa, overlapping nine other known phases. On heating, its transformations are different to those observed in other phases, implying that the phase nitrogen adopts depends not only on P-T path, but also on the initial structural configuration, which greatly complicates its phase diagram.

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The phase diagram of nitrogen has been studied both experimentally and theoretically in a wide pressure and temperature range. The plethora of structural configurations include 11 solid molecular phases [1–6], an amorphous state [2], and two nonmolecular phases [7,8]. All these phases can be accessed when nitrogen is kept above 90 K during compression, as is the usual case where the sample is clamped in the gas state at 300 K or where the sample is warmed after cryoloading at low pressure [1]. At 300 K, nitrogen freezes at 3 GPa to β-N_2, and further compression results in the δ, δ_{loc}, ϵ, ζ, and κ phases at 5, 11, 16, 60, and 115 GPa, respectively [4,9–12]. These phases show decreasing symmetry of the lattice with pressure. Finally, at around 150 GPa, the amorphous η state is reached in a transition which exhibits substantial pressure hysteresis [2,13]. The phase diagram also shows significant metastability, particularly with the phases recovered from high temperature synthesis [3,14]. Heating ζ-N_2 at 65 GPa first yields ϵ-N_2, then transforms to ι-N_2 at 750 K, which can be quenched to room temperature and is stable on decompression to 23 GPa. Heating at 95 GPa yields θ-N_2 at 600 K, which can also be quenched to room temperature and is stable down to 30 GPa [3]. The ι and θ phases appear to differ substantially from the family of phases which makes the transition chain from δ to κ-N_2 [3].

There are considerable disagreements between the theoretical understanding of nitrogen under high pressure and experimental observations. Theory predicts the formation of atomic solid nitrogen at around 50 GPa [15–17], however, experimentally this was not observed until 110 GPa, where the cubic gauche structure is recovered after heating above 2000 K [7]. Theoretical calculations also predict a variety of unobserved low enthalpy molecular phases [17,18] at a range of pressures above 40 GPa. The difficulty in connecting theory with experiment may be linked to the high energy barrier of transitions which results in the metastability of phases, particularly at lower temperature [6,14,16]. Various experimentally observed phases, which can be quenched to 300 K, are only seen to form at high temperatures, where such energy barriers may be overcome. It is therefore unclear whether these predicted low temperature phases have not been observed because they are thermodynamically unfavorable or if experiments have failed to produce them. At 40 GPa, where several phases are predicted, many phases of nitrogen can exist at room temperature, and depending on the P-T path taken, any of ϵ, θ, and ι may be observed after synthesis.

Here, we present a new phase of nitrogen, referred to as λ-N_2, which is formed by compression at low temperature (77 K) up to >32 GPa. The observation of a new phase obtained via this route highlights the dependence of the nitrogen phase obtained on its history in P-T space.

λ-N_2 was synthesized by the compression of high purity liquid nitrogen at 77 K from ambient pressure. To obtain λ-N_2 at room temperature, the pressure must exceed 32 GPa and can be as high as 100 GPa. Warming at lower pressure always results in the formation of ϵ-N_2 as formed by the standard route at 300 K. Once synthesized, λ-N_2 is stable over an exceptionally wide range of pressures at room temperature, as shown in the phase diagram in Fig. 1. Under what conditions λ-N_2 is the equilibrium phase, as opposed to being metastable with respect to other phases, is difficult to determine experimentally, however, at room temperature it exhibits no phase transformations from 32 to 140 GPa. Above 140 GPa, Raman activity is lost, though the sample remains transparent; this is attributed to λ-N_2 entering the amorphous η state, similarly to ζ-N_2 at 150 GPa [2]. When cooled to 10 K, λ-N_2 can be decompressed to 0.3 GPa and, as such, it can exist over a region of P-T space in which the ϵ, ζ, κ, ι, θ, η, γ, cubic gauche, and layered polymeric phases of nitrogen are all observable [4,7–12].

Raman spectra were taken using the 514 nm line of an Ar^+ ion laser with a custom built confocal Raman system with pressure measured by the ruby fluorescence method. The Raman spectrum of λ-N_2 (see Fig. 2) is very distinct, consisting of four well-defined low frequency modes (282, 352, 417, and 465 cm^{-1} at 40 GPa). The low frequency modes shift at approximately 2 cm^{-1}/GPa, remaining intense over the full range of pressures studied. λ-N_2 has three vibrons, ν_1, ν_2, ν_3, at frequencies of 2357, 2385, and 2396 cm^{-1}, respectively, at 40 GPa. The central vibron ν_2 is five times more intense than ν_3 at higher frequency, with the lower frequency vibron

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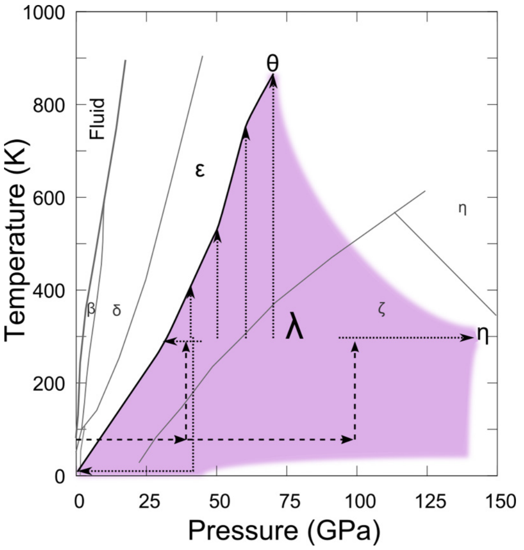

FIG. 1. Transformation and phase diagram of nitrogen. The colored section and black line show the observed transitions from λ-N_2. The black dashed lines show some of the P-T paths which will produce λ-N_2 at low temperature and the dotted lines show some of the key P-T paths used to investigate its phase transitions and the phase obtained. The gray lines show the phase diagram of nitrogen previously observed under compression at 300 K [1,3,14].

ν_1 being very weak below 60 GPa and undetectable above 100 GPa, where it overlaps ν_2. Interestingly, all low frequency modes are much better defined, while the frequencies of the vibrons in λ-N_2 (as well as θ-N_2) are lower than those of the other phases found at the same P-T conditions on standard compression (see Fig. 2).

Diffraction data were collected at beamline 16-ID-B (HPCAT) at the Advanced Photon Source using focused, monochromatic beam of 0.42418 Å. The data were collected at room temperature from 32 to 90 GPa. Due to the small sample size, weak scattering from nitrogen atoms, and graininess of the sample, full Reitveld refinement was not possible. However, recent density functional theory (DFT) calculations [17] predict four low enthalpy phases at 40 GPa and low temperatures with space groups $P2_1/c$, $Pbcn$, $P4_12_12$, and $C2/c$ that have been previously unobserved experimentally. A LeBail fit of data taken at 34 GPa gives a good fit to a monoclinic structure with lattice parameters $a = 3.051(7)$, $b = 3.066(5)$, $c = 5.705(13)$ Å with $\beta = 131.65(5)^\circ$, which is in excellent agreement in terms of both lattice parameters and allowed symmetry with the predicted $P2_1/c$ structure. Figure 3 shows the integrated patterns and fit together with the unintegrated pattern (inset). By inserting the fractional atomic coordinates given by theory, the layered structure shown in Fig. 4 could be obtained.

To investigate the high temperature transitions of λ-N_2, we have performed several heating cycles using resistively heated diamond anvil cells equipped with secondary resistive elements around the diamonds. Isobaricity was ensured using the high frequency edge of the first order diamond Raman mode [19] while temperature was measured using a thermocouple in contact with the diamond. At pressures between 32 and 65 GPa, λ-N_2 transforms into ϵ-N_2 at high temperature. At 32 GPa the transition temperature is 300 K, after which the transition temperature rapidly increases with pressure up to 750 K at 60 GPa. An example of the change in the Raman spectrum over the transition is shown in Fig. 5. At 70 GPa, where ϵ-N_2 is known to transform into ι-N_2 at 750 K [3], λ-N_2 slowly transforms to θ-N_2 at higher temperatures above 800 K,

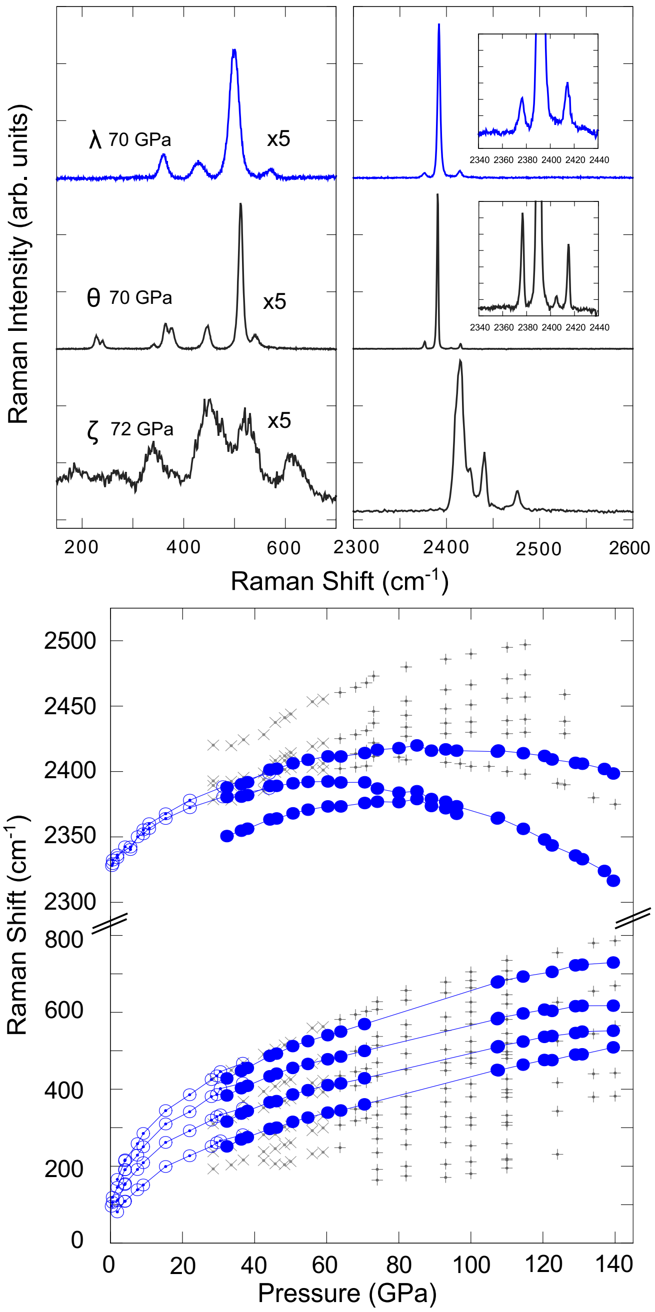

FIG. 2. Raman spectra of selected nitrogen phases. Top: Raman spectra of ζ, θ, and λ phases around 70 GPa showing the lower frequency vibrons of λ and θ and the low frequency (presumably) lattice modes. The weaker vibrons are shown in the inset. The λ and θ spectra are from the same sample before and after heating. Bottom: Positions of Raman peaks vs pressure. Circles show λ-N_2 with lines as a guide for the eye, solid circles are room temperature measurements, and open circles are those from low temperatures. Gray points show ϵ (diagonal crosses) and ζ (vertical crosses) phases obtained via compression at 300 K.

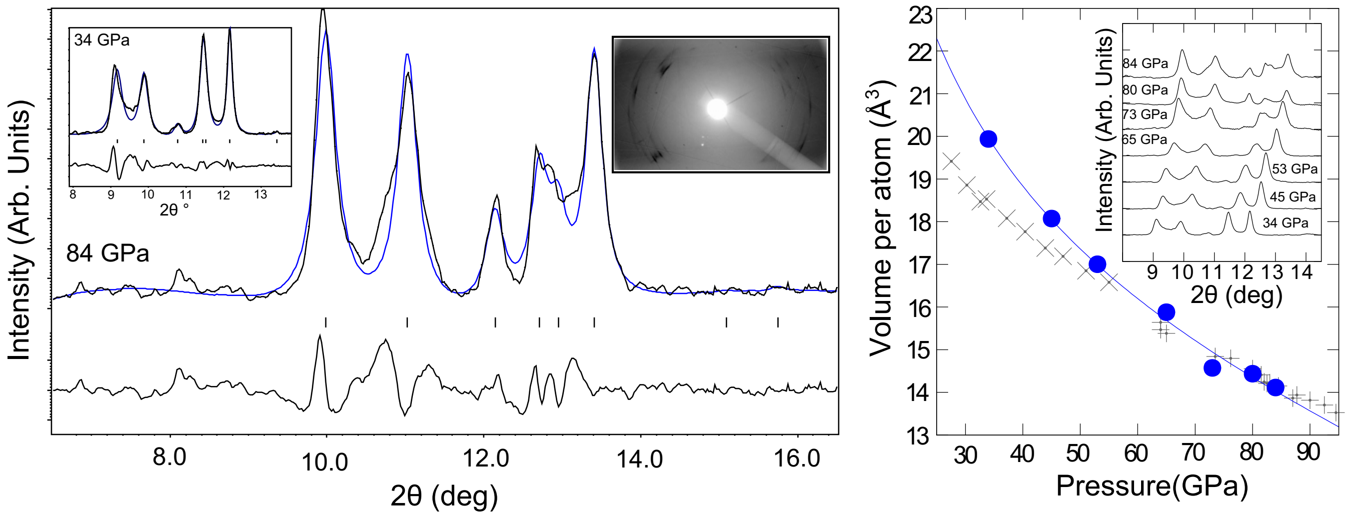

FIG. 3. X-ray powder diffraction of λ-N_2 using 0.424 18 Å radiation. Left: The integrated powder diffraction pattern (black) and LeBail fit (blue) with residuals taken at 84 GPa. Inset left: The same at 34 GPa. Inset right: The unintegrated pattern at 84 GPa. Right: Volume per nitrogen atom vs pressure. Blue circles are λ-N_2, and uncertainties are significantly smaller than the plotting points (about 0.5%). The fitted Vinet equation of state is shown by the blue line. Diagonal crosses show data for ϵ-N_2 and vertical crosses show data for ζ-N_2. Inset: The integrated powder diffraction data at various pressures.

as shown in Fig. 6. The Raman spectra of a sample before and after heating at 70 GPa are shown in Fig. 2 and show the similarities between the Raman spectra of λ and θ-N_2. While θ-N_2 appears to have a more complex structure, as shown by its extra vibron and eight lattice modes compared to the four of λ-N_2, they both exhibit well-defined lattice modes and vibrons of lower frequency than are seen in other phases at the same P-T conditions. This suggests that they are related phases and could explain the different phases obtained when heating λ and ϵ-N_2 at 70 GPa. Since the high temperature transitions are different between the initially low temperature compressed λ-N_2 and the standard compression phases, the phase diagram is far more complex, as shown in Fig. 1. Ascertaining the relative roles of kinetics and thermodynamics in these transitions poses a challenge to theory.

The wide region of P-T space in which λ-N_2 may be observed is remarkable when considering the large degree of metastability which exists in the nitrogen phase diagram. In addition to the ϵ-N_2/ζ-N_2 phases observed under gradual compression, both ι-N_2 and θ-N_2 are also observed to be stable in this pressure range after synthesis at high temperature [3] or on quenching from the melt [14]. Recent DFT calculations [17] have found that the $P2_1/c$ (λ-N_2) structure is more stable than ϵ-N_2 by 24 meV per atom at 40 GPa and low

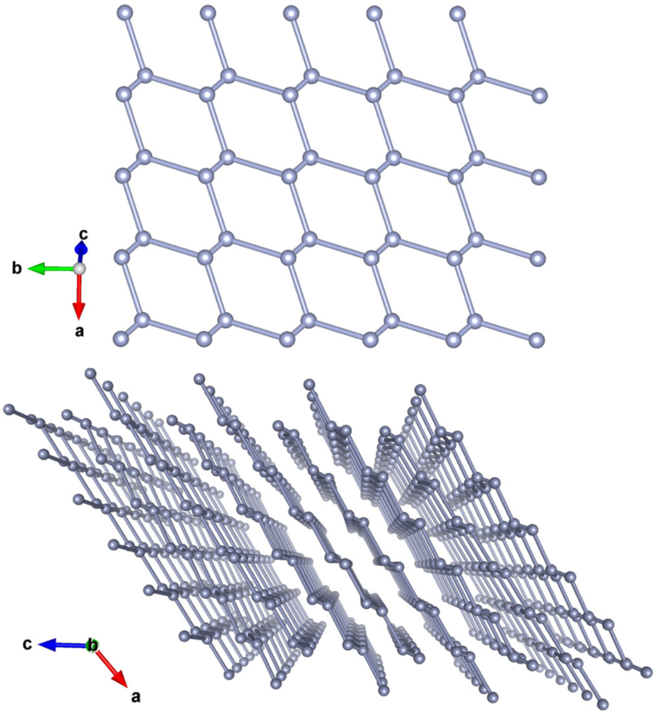

FIG. 4. The structure of λ-N_2 using the atomic positions from theory [17]. Bonds are shown between nearest and next nearest neighbors to illustrate the layered structure. Top: A single layer of λ-N_2 showing the symmetric intermolecular bonds. Bottom: Viewed down the b axis parallel to the sheets.

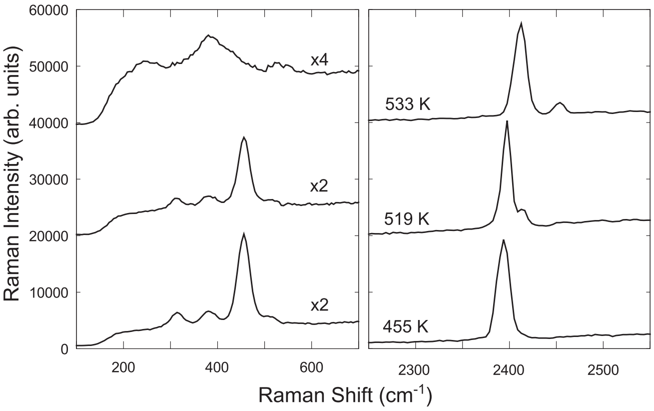

FIG. 5. Raman spectra of λ-N_2 being heated at 50 GPa showing the dramatic changes on conversion to the ϵ-N_2 phase starting at 519 K and completed by 533 K.

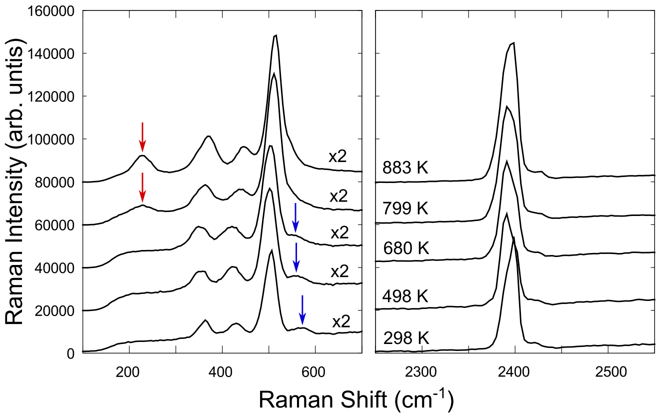

FIG. 6. Raman spectra of λ-N_2 being heated at 70 GPa. The transition to θ-N_2 is characterized by the emergence of the low frequency mode (marked with red arrows) at 229 cm^{-1} starting just below 800 K and becoming more intense as the transition goes to completion. The highest frequency lattice mode (marked with blue arrows) is also lost into the strongest one in this transition.

temperature, with increasing pressure further enhancing its stability, making λ-N_2 the most thermodynamically stable of the observed nitrogen phases in at least this region. The higher pressure stability of λ-N_2 is also implied by the rapid increase of the decomposition temperature of λ-N_2 with pressure.

After the transition to ϵ-N_2 at high temperature, the transition does not reverse on cooling and λ-N_2 is not obtained. However, this does not necessitate that it is less thermodynamically stable—λ-N_2 is a low temperature phase and its formation from ϵ-N_2 might be kinetically hindered rather than thermodynamically unfavorable. A similar argument can explain why ζ-N_2 forms from ϵ-N_2 at low temperature with an increase in pressure [1]. ϵ and ζ-N_2 are related phases and would be expected to have a lower energy barrier to the transition between them than that to λ-N_2, so, regardless of which is thermodynamically most stable, the transition to λ-N_2 cannot occur for kinetic reasons. The many competing phases suggest that the potential energy landscape of nitrogen must be quite flat in this region, and there is the possibility that there are many other competing phases not yet observed due to the barriers which prevent transitions to the thermodynamically stable phase. The observation of the ζ′ phase [2,14] supports this idea as some slight modification to the ζ phase with a sufficient barrier to transformation to differentiate them.

The similarities in the Raman spectra of λ-N_2 and θ-N_2 are striking. It is interesting to note that λ-N_2 forms at low temperature and modest pressure (<90 K, <32 GPa) while θ-N_2 is observed to form at high pressure and high temperature (70 GPa, over 850 K from λ-N_2 or 95 GPa, over 600 K from ϵ-N_2). Both phases are observed over a wide range of P-T space as θ-N_2 can be recovered to 30 GPa on room temperature decompression [3], a similar pressure to λ-N_2. It is possible then that the high-pressure and temperature conditions under which θ-N_2 forms are needed to overcome the energy barrier to formation and should not be interpreted as it being a high P-T phase.

The transition from λ to ϵ-N_2 on heating is isobaric and therefore entropy driven, which further suggests a highly ordered structure for λ-N_2, as indicated by the well-defined lattice modes. Using the atomic positions predicted by theory for the $P2_1/c$ structure [17] gives a structure which consists of sheets of nitrogen molecules, as shown in Fig. 4. The distances between the nonbonded atoms within the sheets are shorter in comparison to the distance between the sheets, coupled with the low frequency of the vibron, suggesting that intermolecular interactions in the sheet play a significant role in the properties of λ-N_2. The intermolecular interactions and weakened molecular bond, as evidenced by the soft vibron, make λ-N_2 an appealing starting material in the search for new routes to atomic phases of nitrogen as there would be less kinetic hinderance to breaking the molecular triple bond.

Kinetics plays a large role in the phase diagram of nitrogen. This opens the possibility of more unknown transitions and phases and may explain the many disagreements between theory and experiment. The dependence of the phase transitions on the starting material, as seen on comparing the behaviors of λ-N_2 and ϵ/ζ-N_2 when heated, may also open the possibility to find other phases via a correct selection of the starting phase. By minimizing the energetic barriers to transformation, most likely by selecting a structurally similar precursor, it may be possible to tailor transitions to novel atomic forms at lower pressure and temperature, as predicted to exist by theory. When the potential role of compression temperature is also considered, the options become multitudinous.

In conclusion, a novel phase of nitrogen, λ-N_2, has been synthesized through low temperature compression and is observed to have a remarkably wide stability range. Comparisons between the distinct features in the Raman spectra, powder x-ray diffraction data, and previous theoretical studies strongly suggest that λ-N_2 adopts a $P2_1/c$ structure. Although the discovery of this new phase by performing compression at low temperature reconciles differences in experiment and theory, the P-T conditions under which λ-N_2 is the thermodynamic equilibrium are unknown and pose an interesting challenge for future theoretical studies. The degree of metastability exhibited by the new λ phase is unexpected, as is the extent of the dependence of the phase adopted by dense nitrogen on both the P-T path and the initial configuration, making the search for further phases far wider.

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[1] R. Bini, L. Ulivi, J. Kreutz, and H. J. Jodl, J. Chem. Phys. **112**, 8522 (2000).

[2] E. Gregoryanz, A. F. Goncharov, R. J. Hemley, and H.-k. Mao, Phys. Rev. B **64**, 052103 (2001).

[3] E. Gregoryanz, A. F. Goncharov, R. J. Hemley, H.-k. Mao, M. Somayazulu, and G. Shen, Phys. Rev. B **66**, 224108 (2002).

[4] E. Gregoryanz, A. F. Goncharov, C. Sanloup, M. Somayazulu, H.-k. Mao, and R. J. Hemley, J. Chem. Phys. **126**, 184505 (2007).

[5] M. J. Lipp, J. P. Klepeis, B. J. Baer, H. Cynn, W. J. Evans, V. Iota, and C.-S. Yoo, Phys. Rev. B **76**, 014113 (2007).

[6] M. I. Eremets, R. J. Hemley, H.-k. Mao, and E. Gregoryanz, Nature (London) **411**, 170 (2001).

[7] M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, and R. Boehler, Nat. Mater. **3**, 558 (2004).

[8] D. Tomasino, M. Kim, J. Smith, and C.-S. Yoo, Phys. Rev. Lett. **113**, 205502 (2014).

[9] W. E. Streib, T. H. Jordan, and W. N. Lipscomb, J. Chem. Phys. **37**, 2962 (1962).

[10] M. Hanfland, M. Lorenzen, C. Wassilew-Reul, and F. Zontone, Rev. High Press. Sci. Technol. **7**, 787 (1998).

[11] M. I. Eremets, A. G. Gavriliuk, N. R. Serebryanaya, I. A. Trojan, D. A. Dzivenko, R. Boehler, H. K. Mao, and R. J. Hemley, J. Chem. Phys. **121**, 11296 (2004).

[12] E. Gregoryanz, C. Sanloup, R. Bini, J. Kreutz, H. J. Jodl, M. Somayazulu, H.-k. Mao, and R. J. Hemleya, J. Chem. Phys. **124**, 116102 (2006).

[13] A. F. Goncharov, E. Gregoryanz, H.-k. Mao, Z. Liu, and R. J. Hemley, Phys. Rev. Lett. **85**, 1262 (2000).

[14] A. F. Goncharov, J. C. Crowhurst, V. V. Struzhkin, and R. J. Hemley, Phys. Rev. Lett. **101**, 095502 (2008).

[15] A. K. McMahan and R. LeSar, Phys. Rev. Lett. **54**, 1929 (1985).

[16] C. Mailhiot, L. H. Yang, and A. K. McMahan, Phys. Rev. B **46**, 14419 (1992).

[17] C. J. Pickard and R. J. Needs, Phys. Rev. Lett. **102**, 125702 (2009).

[18] Y. Ma, A. R. Oganov, Z. Li, Y. Xie, and J. Kotakoski, Phys. Rev. Lett. **102**, 065501 (2009).

[19] Y. Akahama and H. Kawamura, J. Appl. Phys. **96**, 3748 (2004).