Hard x-ray radiation induced dissociation of N_2 and O_2 molecules and the formation of ionic nitrogen oxide phases under pressure

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(Received 27 September 2006; revised manuscript received 24 October 2006; published 12 December 2006)

Applying hard x-ray photon radiation to a mixture of liquid N_2 and O_2 contained under pressure in a diamond-anvil cell, we break the strong covalent bonding of the molecules and form ionic compounds of complex nitrogen oxide ions at a pressure as low as 0.5 GPa previously expected for molecular phases. A new ionic $NO^+NO_3^-$ phase has been discovered at around 2 GPa. Structural characterization of the high-pressure ionic $NO^+NO_3^-$ phase with Rietveld refinement reveals an interesting layered monoclinic $P2_1/m$ structure with large elastic anisotropy, offering promises for generating materials with interesting properties and providing the basis for future theoretical studies.

DOI: 10.1103/PhysRevB.74.214107 PACS number(s): 61.50.Ks, 83.10.Tv, 68.18.Jk

Compounds formed from the second-row elements (e.g., O_2, N_2, CO, CO_2, NO_2, CH_4) exhibit extraordinary properties and intriguing behavior at high pressure. Typically existing in condensed molecular phases at low pressures with strong covalent intramolecular interaction and weak van der Waals intermolecular interaction, these compounds are expected to undergo phase transformations in which electrons within intramolecular bonds are delocalized to form extended covalent framework or polymeric solids in intermediate pressure ranges and metallic phases at high pressures.[1–6] Of the second-row compounds, nitrogen oxides have displayed more complex and poorly understood behavior. Instead of forming a framework or polymeric structure at high pressure, both N_2O and N_2O_4 were found to transform to an ionic broken-symmetry phase $NO^+NO_3^-$ at high pressures and temperatures (above 20 GPa and 1000 K).[7–10] At room temperature and low pressures, there was an apparent consensus among previous studies that nitrogen oxide existed in molecular forms. Stability studies by Song *et al.*[8,9] found $NO^+NO_3^-$ as the stable phase at high pressures, while providing evidence that suggested a molecular-phase transition at 1 GPa via an amorphous state of $NO^+NO_3^-$ between 1 and 7 GPa. An earlier study[11] did report a cubic molecular compound (α-N_2O_4) by condensing liquid N_2O_4 at 0.46 GPa; however, it was stable to at least 7.6 GPa when compressed at room temperature, although an ionic phase of $NO^+NO_3^-$ could be formed at about 3 GPa from a noncubic molecular phase (β-N_2O_4) produced by radiating α-N_2O_4 with a blue laser. On the other hand, a very recent study by Sihachakr and Loubeyre[12] has reported a crystalline $NO^+NO_3^-$ phase synthesized at 5 GPa well within the previously reported amorphous region.[8] These previous studies have provided substantial information about the behavior of nitrogen-oxide compounds, but clearly left unsettled questions regarding the stability region for the molecular phase and pointed to a potential kinetic issue associated with the transformations in nitrogen-oxide phases when pressure is the only variable. Moreover, despite the importance of the high-pressure nitrogen-oxide ionic species, no full-structure analysis has been reported previously. All the previous x-ray-diffraction studies[7,8,10,12] of $NO^+NO_3^-$ have only indexed their x-ray-diffraction patterns due to the limited data quality. While agreeing on the orthorhombic symmetry for samples synthesized in the pressure range from 5 to above 20 GPa, these studies have resulted in inconsistent unit cells and different proposed structure models.

In this study, we report: (1) the synthesis of ionic nitrogen-oxide phases at room temperature and high pressures by hard x-ray radiation-induced dissociation of nitrogen and oxygen molecules and the reaction of nitrogen and oxygen radicals; and (2) the characterization of the spectroscopy and structural properties of the ionic nitrogen-oxide phases using Raman scattering and synchrotron x-ray diffraction. Our study is carried out in a pressure region from 0.5 to 2 GPa, previously expected for a molecular phase. In the contrary, we have found the formation of ionic $NO_2^+NO_3^-$ at 0.5 GPa from a mixture of N_2 and O_2, a phase previously observed only at low temperatures and ambient pressure, and the decomposition of $NO_2^+NO_3^-$ to a new ionic $NO^+NO_3^-$ phase of monoclinic symmetry with further compression. Issues related to kinetics, ionic phase formation in nitrogen oxide, and x-ray photon radiation-induced dissociation of N_2 and O_2 are discussed.

A mixture of high-purity O_2 and N_2 (34% ± 5% N_2 in the mixture) was cryogenically loaded and sealed, inside a low-pressure container with vacuuming and gas-purging capabilities, into a sample chamber in a beryllium gasket compressed in a panoramic diamond-anvil cell. After warming up to room temperature, the sample was further compressed to 1.5 GPa based on the shift of the ruby fluorescence R_1 line with pressure, and the sample purity was confirmed by Raman spectroscopy measurements. At this pressure, both O_2 and N_2 are in liquid state; the mixture was, therefore, transparent when observed under a microscope. Samples were radiated by a 10.2 keV synchrotron x ray to induce the room-temperature reaction of O_2 and N_2 and to facilitate phase transformations with further compression. Raman spectra were recorded using the 514.5 nm excitation line of an Ar-

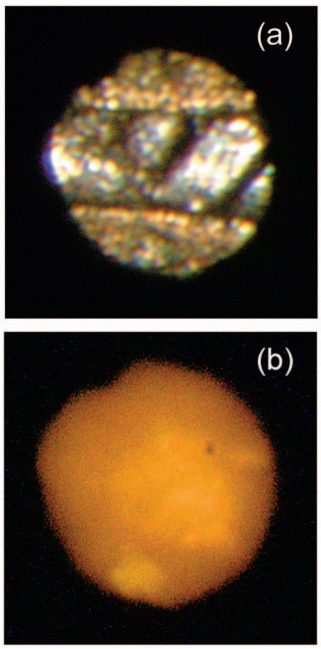

FIG. 1. (Color) Microphotographs of the high-pressure nitrogen-oxide phases. (a) The solid $NO_2^+NO_3^-$ phase formed by x-ray photon radiation of a transparent liquid mixture of N_2 and O_2. The horizontal band is the mark induced by an x-ray beam of 60 $\times 30$ μm and after a prolonged exposure time of 25 h. The sample is approximately 150 μm in diameter and 40 μm in thickness. (b) The $NO^+NO_3^-$ phase decomposed from $NO_2^+NO_3^-$ as pressure is increased. The transition was facilitated by further radiating the sample with an x-ray beam of 150×40 μm. The x-ray beam size is defined by FWHM; the base width of these beams was typically 2–3 times that of the FWHM.

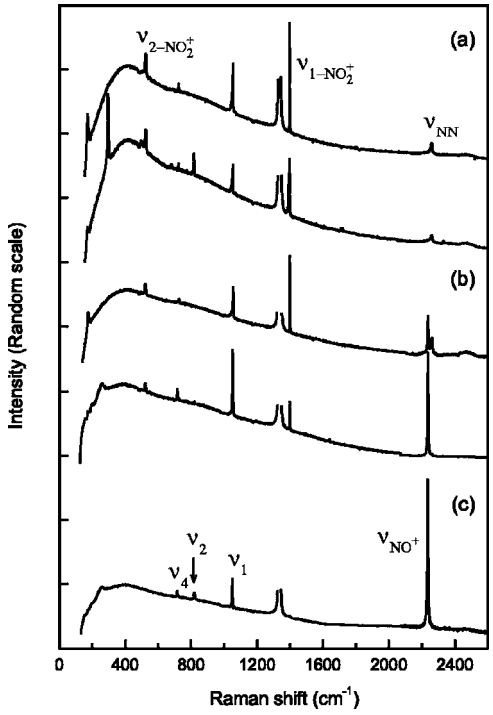

FIG. 2. Representative Raman spectra obtained during the investigation process. (a) and (b) were conducted on the sample shown in Fig. 1(a) with the top spectrum representing measurements in off-beam mark locations and the bottom spectrum within the beam-mark area; and (c) on the sample shown in Fig. 1(b). The intensity of the first-order diamond peak at 1335 cm^{-1} is partially blocked out in these spectra for clarity. (a) $NO_2^+NO_3^-$ at pressures from 0.5–1.7 GPa. The modes associated with NO_2^+ and N-N stretching are labeled as $\nu_{2\text{-}NO_2^+}$, $\nu_{1\text{-}NO_2^+}$, and ν_{NN}; vibration modes in the top spectrum without a label are attributed to NO_3^-. Additional Raman modes in the beam-mark area are due to the metastable molecular β-N_2O_4, which is an intermediate product of the reaction process. (b) $NO_2^+NO_3^-$ at 2.0 GPa showing the appearance of the NO^+ peak at 2236.5 cm^{-1} and the disappearance of the molecular β-N_2O_4 peaks. (c) $NO^+NO_3^-$ at 1.7 GPa after the sample in (b) was further radiated by a 10.2 keV x ray. The characteristic peaks of NO_3^- are labeled as ν_4, ν_2, and ν_1, and that of NO^+ as ν_{NO^+}.

ion laser. Angle-dispersive x-ray-diffraction measurements were carried out with a focused 30.162 keV monochromatic synchrotron x-ray beam (15×15 μm) and a MAR345 image plate detector to record the diffracted x rays. The diffraction patterns were processed with FIT2D,[13] Peakfit 4.0, Endeavour 1.1, and GSAS (Ref. 14) with an EXPGUI graphical interface.[15] All synchrotron experiments were conducted at the high-pressure collaborative access team (HPCAT) of the Advanced Photon Source (APS); Raman-scattering measurements were carried out at the GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS).

Due to the large covalent bond energy of the molecules, nitrogen and oxygen do not react at ambient temperature; the liquid mixture of O_2 and N_2 is transparent at 1.5 GPa (note: one of our samples was left for weeks, the sample remained as a transparent liquid mixture of the two molecules). However, after radiating the sample with a 10.2 keV synchrotron x-ray radiation for at least 6 h, we observed marked changes in the visual appearance of the sample. In contrast to the starting transparent appearance, the sample became mostly opaque and displayed grain textures as shown in Fig. 1(a). Pressure measurements indicated a significant pressure decrease in the sample from 1.5 to 0.5 GPa, consistent with a liquid-solid transformation that involves a large volume reduction. Using Raman spectroscopy and synchrotron x-ray diffraction, we identify the formation of $NO_2^+NO_3^-$, an ionic phase of N_2O_5 previously only observed at low temperatures.[16,17] In Fig. 2(a), we have shown the Raman spectra representing measurements at multiple locations in the sample. The presence of $NO_2^+NO_3^-$ is confirmed by the characteristic peaks of NO_3^- at 724.5 cm^{-1} (ν_4) and 1054.0 cm^{-1} (ν_1), and by those of NO_2^+ at 523.8 cm^{-1} (ν_2) and 1397.5 cm^{-1} (ν_1). These observations are similar to previous spectroscopic studies of the low-temperature ionic $NO_2^+NO_3^-$ phase.[16] The nitrogen vibration mode at 2259.4 cm^{-1} (ν_1) indicates an excess of nitrogen in the system after the formation of $NO_2^+NO_3^-$. X-ray-diffraction measurements at different locations within the sample show an identical pattern in Fig. 3(a) that is readily indexed as the known $P6_3/mmc$ structure with two $NO_2^+NO_3^-$ per unit cell for the low-temperature $NO_2^+NO_3^-$ phase.[17] At 1.75 GPa, the hexagonal unit cell is determined to be $a=5.3389(4)$ Å, $c=6.2964(7)$ Å, and $V=155.42(2)$ Å.[3]

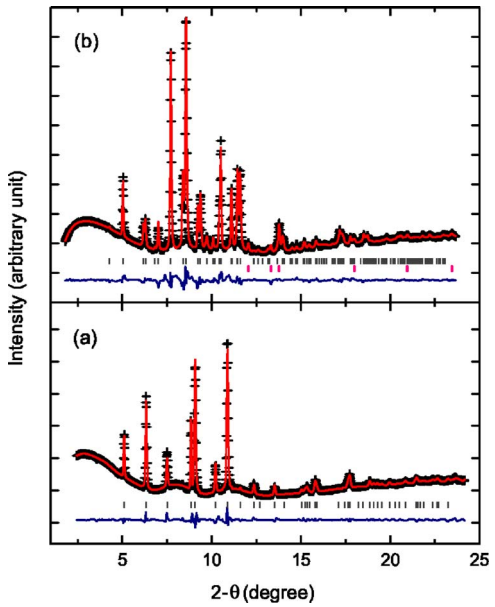

FIG. 3. (Color online) Observed (cross) and calculated (solid line) x-ray-diffraction patterns of the high-pressure hexagonal $NO_2^+NO_3^-$ phase at 1.75 GPa (a) and the new monoclinic $NO^+NO_3^-$ phase at 1.70 GPa (b). The Rietveld refinement of the monoclinic $NO^+NO_3^-$ phase was conducted based on the structure mode described by the space group $P2_1/m$ with N and O atoms at special $2e$ and general $4f$ positions (Table I). Tick marks for the $NO^+NO_3^-$ phase (upper) and Be (lower) are shown below the pattern. The difference curve is shown at the bottom. The calculated pattern for $NO_2^+NO_3^-$ in (a) is the LeBail refinement[14] using the structure of the low-temperature $NO_2^+NO_3^-$ phase at ambient pressure.[17]

The formation of $NO_2^+NO_3^-$ clearly points to a nitrogen-oxygen reaction induced by the x-ray photon radiation, which dissociates the molecules into ions or atomic forms. It is known that the triple bond of nitrogen and the double bond of oxygen can be broken by ultraviolet and x-ray photons of energy equal to or higher than 9.80 and 5.17 eV, respectively.[18] Ultraviolet and soft x-ray photon radiation-induced fragmentation of diatomic molecules including N_2 and O_2, as a means of studying the inner states of the molecules, has been reported previously.[19–22] Unlike ultraviolet photons, which break the bonding of the molecules by ionizing the valence electrons, a soft x-ray photon (up to a few keV of energy) produces an inner-shell core hole; the fragmentation of the molecules is caused by a valance (bonding) electron filling the core hole.[20,22] The mechanism for hard x-ray photon-induced dissociation of N_2 and O_2 should be the same as that by soft x-ray photons, but with a smaller absorption cross section.[23] In fact, hard x rays of 9–10.2 keV have been used to excite core-level electrons in inelastic x-ray-scattering studies.[24]

A minor molecular phase of N_2O_4 has been identified by both Raman [Fig. 2(a) (lower spectrum)] and x-ray-diffraction measurements in the sample radiated by a sharply focused x-ray beam and for a prolonged exposure time of 25 h [Fig. 1(a) (the beam mark area only)], but not in the one radiated by a wide x-ray beam and for a short exposure time of 6 h. The diffraction image of this phase from one measurement displays a few isolated weak-diffraction spots, consistent with small single crystals. When all the integrated diffraction lines from multiple measurements are considered, they are well indexed by an unstable monoclinic form of N_2O_4 (β-N_2O_4) (Refs. 25 and 26) with unit-cell parameters $a=5.851(8)$ Å, $b=4.622(7)$ Å, $c=6.298(8)$ Å, and $\beta=116.5(1)°$. The fact that this phase exists only in the x-ray-beam mark area after a long exposure time and disappears with a slight increase in pressure from 1.7 to 2.0 GPa [Fig. 2(b)] further confirms that it is a metastable form either from the intermediate reaction process or induced by the excess exposure of the sample to an intense x-ray beam.

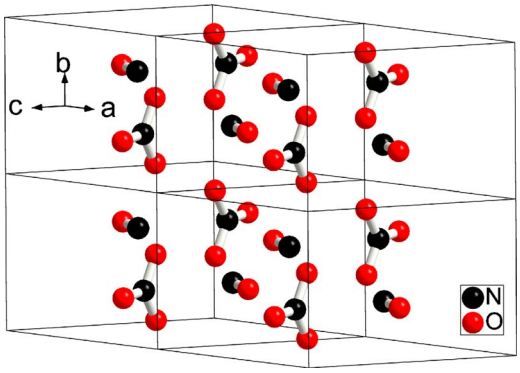

FIG. 4. (Color online) Crystal structure of $NO^+NO_3^-$ at 1.7 GPa.

The observed ionic-phase formation from atomic nitrogen and oxygen at a pressure as low as 0.5 GPa indicates that the ionic phase, instead of its parallel molecular forms, is the thermodynamically stable phase at low pressures. Comparing the densities for $NO_2^+NO_3^-$ plus $0.25N_2$ and the molecular N_2O_4 phases at the same pressure, we estimate that the $NO_2^+NO_3^-$ plus $0.25N_2$ system is about 5% and 6% denser than the corresponding α-N_2O_4 and β-N_2O_4, respectively. This implies that the formation of the ionic phase has a lower free energy. The formation of this phase only from nitrogen and oxygen radicals is indicative of a substantially high activation barrier for the transition from a molecular to an ionic phase. As a consequence, when the gas phase of N_2O_4 is cryogenically loaded into a diamond-anvil cell,[11] the molecular structure persists and the high-pressure solid phase retains the structure of a molecular compound.

A remarkable feature of nitrogen-oxide chemistry is its ability to form thermodynamically stable configurations of atoms by decomposition. For example, at above 20 GPa and 1000 K, instead of transforming to a high-pressure phase of N_2O, the thermodynamically stable configuration of atoms for a N_2O composition is $NO^+NO_3^-$ plus N_2;[7] NO was found to decompose to molecular phases of N_2O_4 and N_2O at low temperatures.[27] For the $NO_2^+NO_3^-$ phase of this study, it is certainly an interesting question whether this atom configuration is stable at elevated pressures, especially considering that both N_2O and N_2O_4 compositions adapt a $NO^+NO_3^-$ configuration at high pressures.

Increasing pressure slightly to 2.0 GPa, we found $NO_2^+NO_3^-$ becomes unstable and eventually decomposes to an ionic $NO^+NO_3^-$ phase that has not been previously de-

TABLE I. Refined atomic position and unit-cell parameters for the high-pressure monoclinic phase of $NO^+NO_3^-$ at 1.7 GPa.

	Atom	Position	x	y	z
NO^+	N1	$2e$	0.1757(10)	0.2500	0.0358(14)
	O1	$2e$	0.4450(11)	0.2500	0.1587(10)
NO_3^-	N2	$2e$	0.2690(14)	0.2500	0.5353(10)
	O2	$2e$	0.4997(10)	0.2500	0.8038(10)
	O3	$4f$	0.1750(9)	0.0370(5)	0.4058(7)

Space group: $P2_1/m$, $Z=2$
$R_{wp}=0.012$
Unit-cell parameters:
$a=5.5594(8)$ Å, $b=5.1169(7)$ Å, $c=6.8214(9)$ Å, $\beta=136.635(7)°$, and $V=133.24(2)$ Å^3

scribed in the literature. In Fig. 2(b), we show Raman spectroscopy measurements at 2.0 GPa. Although $NO_2^+NO_3^-$ is still the major phase, the spectra display a characteristic peak for NO^+ at 2236.5 cm^{-1}, indicating an instability of the $NO_2^+NO_3^-$ phase. To facilitate the transition, we further exposed the sample to a 10.2 keV x-ray radiation for 12 h. As shown in Fig. 1(b), the sample displays evident changes in color and texture, accompanied by a slight pressure drop from 2.0 to 1.7 GPa. Raman measurements conducted on the sample shown in Fig. 2(c) clearly reveal the formation of an ionic phase $NO^+NO_3^-$, with the strong NO^+ peak at 2235.4 cm^{-1} and the complete disappearance of the ν_2 and ν_1 fundamentals of NO_2^+. The NO_3^- fundamental modes at 716.5 cm^{-1} (ν_4), 820.1 cm^{-1} (ν_2), and 1050.6 cm^{-1} (ν_1), are slightly different in positions from those in $NO_2^+NO_3^-$. The formation of $NO^+NO_3^-$ is also accompanied by the disappearance of the N-N stretch mode, consistent with a reaction of the nitrogen with the oxygen from the $NO_2^+NO_3^-$ decomposition. The observed Raman lines of $NO^+NO_3^-$ are in reasonable agreement with the NO_3^- fundamental modes at 715.8 cm^{-1}, 819.9 cm^{-1}, and 1052.5 cm^{-1}, and the NO^+ peak at 2234.0 cm^{-1}, predicted for 1.7 GPa from the previous spectroscopy studies of the high-pressure $NO^+NO_3^-$ phase formed by CO_2 infrared laser heating of N_2O and N_2O_4 to 1000–2000 K under high pressures of 10–30 GPa.[7,9] However, in contrast to the previously suggested amorphous state,[8] our x-ray-diffraction study shows a well-formed crystalline phase of $NO^+NO_3^-$.

The diffraction pattern of $NO^+NO_3^-$ is markedly different from that of the hexagonal $NO_2^+NO_3^-$ (Fig. 3), and can be best indexed by a monoclinic unit cell with $a=5.5594(8)$ Å, $b=5.1169(7)$ Å, $c=6.8214(9)$ Å, $\beta=136.635(7)°$, and $V=133.24(2)$ Å^3 at 1.7 GPa. Further structural analysis yields a crystal structure described by a centrosymmetric space group $P2_1/m$ with two $NO^+NO_3^-$ per unit cell and nitrogen and oxygen atoms occupying special $2e$ and general $4f$ positions (Table I). Rietveld refinement of the structure shows good agreement between the observed and the calculated x-ray diffraction-patterns [Fig. 3(b)] with $R_{wp}=0.012$.

An interesting feature of the $NO^+NO_3^-$ structure is that the planar NO_3^- anions form layers stacking in the a-axis direction (Fig. 4) with NO^+ cations located between NO_3^- groups within the layers and the NO^+ bond at a near 60° angle from the NO_3^- plane. Such a structure usually possesses anisotropic structural and elastic properties with weak interlayer interaction, which provides the opportunity for new material formation by adding metal atoms or organic radicals between the layers.[28] Furthermore, it may be prone to framework structure formation with further compression and to phase transitions induced by rotation disorder at sufficiently high temperatures.[29] The density values of the two ionic phases $NO_2^+NO_3^-$ and $NO^+NO_3^-$ are comparable, 2.30 g/cm^3 and 2.294 g/cm^3, at the transition pressure, suggesting the decomposition transition from $NO_2^+NO_3^-$ to $NO^+NO_3^-$ is driven by the formation of stronger chemical bonding at high pressure. Being isoelectronic with N_2, NO^+ has a bond order of 3 and the shortest bond distance among the nitrogen oxide species; accordingly, it is a more stable configuration than NO_2^+. As a consequence of replacing the symmetric NO_2^+ with a nonsymmetric NO^+ unit, it is expected that the overall structure symmetry of $NO^+NO_3^-$ is lower than that for the hexagonal $NO_2^+NO_3^-$ structure.

In conclusion, the x-ray photon-induced dissociation of N_2 and O_2 molecules and the synthesis of the nitrogen-oxide phase under pressure lead to new findings. First, we demonstrate that, without or with reduced kinetic barrier, nitrogen and oxygen form ionic compounds instead of the expected molecular phases at a low-pressure region. More importantly, the high-quality x-ray-diffraction data reveals a new nitrogen-oxide phase with an interesting layered monoclinic structure of NO^+ and NO_3^- ions; the structural characterization provides the basis for future theoretical studies of nitrogen-oxide phases at high pressure. Furthermore, the x-ray photon-induced reaction of N_2 and O_2 offers a unique way to study nitrogen-oxide materials at high pressure, avoiding potential issues of ion disordering at high temperature and the data quality degradation by IR laser heating. These findings provide new insight into the nature of nitrogen-oxygen bonding under pressure and open new research areas of low-z and molecular systems at high pressure relating to kinetics, x-ray photon-radiation effects, and its application in new material synthesis.

We would like to thank HPCAT and APS for beam time, GSECARS and Vitali Prakapenka for providing the Raman spectroscopy system, Przemek Dera for useful suggestions on structure search and presentation softwares, and NASA for financial support. Use of the HPCAT facility was supported by U.S. Department of Energy (DOE)–Basic Energy Sciences, DOE-National Nuclear Security Administration, NSF, Department of Defense-Tank-Automotive and Armaments Command, and the W.M. Keck Foundation.

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[1] R. J. Hemley, Annu. Rev. Phys. Chem. **51**, 763 (2000).
[2] V. Iota, C. S. Yoo, and H. Cynn, Science **283**, 1510 (1999).
[3] C. S. Yoo, H. Cynn, G. Galli, V. Iota, M. F. Nicol, S. Carlson, D. Hausermann, and C. Maihiot, Phys. Rev. Lett. **83**, 5527 (1999).
[4] M. L. Eremets, R. J. Hemley, H. K. Mao, and E. Gregoryanz, Nature (London) **411**, 170 (2001).
[5] M. I. Eremets, A. G. Gavriliak, I. A. Trojan, D. A. Dzivenko, and R. Boehler, Nat. Mater. **3**, 558 (2004).
[6] Y. Akahama, H. Kawamura, D. Hausermann, M. Hanfland, and O. Shimomura, Phys. Rev. Lett. **74**, 4690 (1995).
[7] M. Somayazulu, A. Madduri, A. F. Goncharov, O. Tschauner, P. F. McMillian, H.-k. Mao, and R. J. Hemley, Phys. Rev. Lett. **87**, 135504 (2001).
[8] Y. Song, M. Somayazulu, H.-k. Mao, R. J. Hemley, and D. R. Herschbach, J. Chem. Phys. **118**, 8350 (2003).
[9] Y. Song, R. J. Hemley, Z. Liu, M. Somayazulu, H.-k. Mao, and D. R. Herschbach, J. Chem. Phys. **119**, 2232 (2003).
[10] C. S. Yoo, V. Iota, H. Cynn, M. F. Nicol, J. H. Park, T. Le Bihan, and M. Mezouar, J. Phys. Chem. B **107**, 5922 (2003).
[11] S. F. Agnew, B. I. Swanson, L. H. Jones, R. L. Mills, and D. Schiferl, J. Phys. Chem. **87**, 5065 (1983).
[12] D. Sihachakr and P. Loubeyre, Phys. Rev. B **74**, 064113 (2006).
[13] A. P. Hammersley, *FIT2D V10.3 Reference Manual V4.0* (European Synchrotron Radiation Facility, Grenoble, 1998).
[14] A. Larson and R. Von Dreele, General Structure Analysis System (GSAS), Los Alamos National Laboratory, Report No. LAUR 86–748, 2005.
[15] B. Toby, J. Appl. Crystallogr. **34**, 210 (2001).
[16] W. Wilson and K. O. Christe, Inorg. Chem. **26**, 1631 (1986).
[17] E. Grison, K. Eriks, and J. L. DeVries, Acta Crystallogr. **3**, 290 (1950).
[18] *CRC Handbook of Chemistry and Physics*, edited by D. R. Lide (CRC Press, Boca Raton, 1994).
[19] T. A. Carlson and M. O. Krause, J. Chem. Phys. **56**, 3206 (1972).
[20] W. Eberhardt, J. Stohr, J. Feldhaus, E. W. Plummer, and F. Sette, Phys. Rev. Lett. **51**, 2370 (1983).
[21] W. Eberhardt, E. W. Plummer, I.-W. Lyo, R. Carr, and W. K. Ford, Phys. Rev. Lett. **58**, 207 (1987).
[22] M. Kitajima, M. Ukai, S. Machida, K. Kameta, A. Ehresmann, N. Kouchi, Y. Hatano, T. Hayaishi, E. Shigemasa, and K. Ito, J. Phys. B **29**, 1711 (1996).
[23] W. H. McMaster, N. Kerr Del Grande, J. H. Mallett, and J. H. Hubbell, Lawrence Livermore National Laboratory Report, Compilation of X-ray Cross Sections, 1969.
[24] Y. Meng, H. K. Mao, P. J. Eng, T. P. Trainor, M. Newville, M. Y. Hu, C. C. Kao, J. F. Shu, D. Hausermann, and R. J. Hemley, Nat. Mater. **3**, 111 (2004).
[25] P. Groth, Acta Chem. Scand. (1947-1973) **17**, 2419 (1963).
[26] A. Obermeyer, H. Borrmann, and A. Simon, Z. Kristallogr. **196**, 129 (1991).
[27] S. F. Agnew, B. I. Swanson, L. H. Jones, and R. L. Mills, J. Phys. Chem. **89**, 1678 (1982).
[28] F. Hulliger, *Structural Chemistry of Layer-Type Phases*, (D. Reidel Publishing Company, Dordrecht-Holland/Boston-USA, 1976), Vol. 5.
[29] R. C. Evens, *An Introduction to Crystal Chemistry* (The Syndics of the Cambridge University Press, London, 1964).