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Phase transitions of cesium azide at pressures up to 30 GPa studied using *in situ* Raman spectroscopy

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Cesium azide has been studied by Raman spectroscopy at pressures up to ≈30 GPa at room temperature. The sequence of phase transitions to Phase III (at 0.5 GPa), Phase IV (at 4.3 GPa), and Phase V (at ≈19 GPa) has been observed in agreement with recent X-ray diffraction studies. Phase III has been found to adopt a monoclinic $C2/m$ structure with two azide anions in nonequivalent positions, where one set of azide anions appears to be orientationally disordered according to the observed Raman spectra. The transition to Phase IV has been associated with orientational ordering of azide anions, while the transition to Phase V has been shown to proceed with a lowering of crystal symmetry. Moreover, spectroscopic features indicate a possible change of bonding in CsN_3 toward formation of covalent bonds at high pressures. © *2015 AIP Publishing LLC*.
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I. INTRODUCTION

The set of physical and chemical properties of inorganic azides[1] determined their applications as industrial chemicals, particularly as a source of chemically pure nitrogen, as initial explosives, and even as photographic materials at low temperature. This practical aspect causes considerable interest in the electronic structure and optical properties of metal azides in order to understand the decomposition mechanism.[2–9] Furthermore, metallic azides are of interest as model systems for studying the main regularities of fast chemical reactions in solids with complex chemical bonding.[1]

Alkali azides possessing a linear molecular anion, N_3^-, provide a new challenge for calculations of crystal structure, lattice dynamics, and electronic structure, representing the next-level model of ionic compounds beyond the extensively studied (as model systems) alkali halides. Inorganic azides exhibit a variety of crystal structures with nevertheless simple structural principles: the arrangement of the cations and anions is the same as that of the alkali halides (distorted because of the nonspherical shape of the anion), including the dimorphism of NaCl- and CsC1-type packing. It would be worthwhile to compare the structural behavior of metal azides with other systems with symmetric, quadrupolar anions (HF_2^-), as well as with systems with asymmetric, dipolar anions (KSCN family). Furthermore, metal azides could also serve well as precursor model systems for still more complex ionic solids with molecular anions and cations (NH_4^+, thallium thiocyanates).[10]

Metal azides exhibit a broad range of crystal stabilities with respect to explosive decomposition. It is believed that subtle differences in the chemical bonding of the azides are at the origin of their different stability and decomposition behaviors. Thus, an investigation of the crystal structure and lattice dynamics of azide crystals at high pressure is considered to provide valuable data for testing these ideas because application of pressure affects the interaction and therefore the bonding properties in a substance.

There are significant difficulties in carrying out experimental studies of heavy-metal azides because of their explosive nature. Fortunately, alkali metal azides are much more benign in behavior, and therefore crystal structures and lattice dynamics of alkali azides have been well studied at ambient pressure. However, until recently, high-pressure phase diagrams of azides were studied only in a narrow pressure range below 4 GPa.[11–17] Discovery of the polymerization of nitrogen at a pressure near 120 GPa (Ref. 18) renewed interest in inorganic azides as a precursor for the synthesis of extended nitrogen allotropic structures at lower pressures, and their pressure-induced phase transitions have been intensively studied over a wide range of pressures, both theoretically and experimentally.[19–41]

Cesium azide (CsN_3) has been studied using *in situ* X-ray diffraction up to pressures above 55 GPa.[23] In addition to the known low-pressure phase transition from Phase II to Phase III at 0.4 GPa,[11,14] there are two further phase transitions to Phase IV at 4.4 GPa and to Phase V at 15.4 GPa. However, X-ray illumination can cause radiation damage in inorganic azides, affecting the results of X-ray diffraction studies.[12,25] Therefore, it is of interest to investigate the

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sequence of phase transitions[23] using an optical spectroscopic technique. Here, we present the results of experimental studies of CsN_3 using *in situ* Raman spectroscopy under high pressures up to above 30 GPa at room temperature.

II. EXPERIMENTAL METHODS

The finely powdered samples of CsN_3 were loaded into a diamond anvil cell (DAC) with a stainless steel gasket. The diamond anvils had flat culets of diameter 500 μm. To avoid sample contamination, loading of the sample was performed in a glove box in an atmosphere of pure argon, containing <0.1 ppm of oxygen and water. Silicone oil was used as a pressure transmitting medium or pressure was applied without any medium to avoid possible contamination of the sample, with identical results in both sets of experiments. The sample in the DAC was structurally characterized in Phase II at 0.1 GPa and in Phase III at 1 GPa using angle-dispersive X-ray diffraction at beamline ID-09, ESRF (wavelength $\lambda = 0.4149$ Å).

A Melles Griot 25-LHP-928-230 HeNe laser with a nominal power of 35 mW (accounting for losses on the optical elements, the laser power at the sample position can be estimated as ≈26 mW) was used as the exciting source of the Raman spectra. Raman spectra were recorded in backscattering geometry using a custom Raman optical microscope system for diamond anvil cells (similar to that described in Ref. 42) with a single-imaging spectrograph, Princeton Instruments Acton SP 2500 (focal length 500 mm), equipped with a 1200 grooves mm^{-1} diffraction grating and a liquid nitrogen cooled charge-coupled device detector. The spectral resolution in the studied spectral range was $\approx 1\,cm^{-1}$. The Raman spectrometer was calibrated using Ne spectral lines with an uncertainty of $\pm 1\,cm^{-1}$.

The pressure was determined using the fluorescence lines of a ruby chip, which was loaded in contact with the sample.

III. RESULTS AND DISCUSSION

The diffraction patterns of CsN_3 collected at a pressure of 0.1 GPa (Fig. 1) can be unambiguously indexed to the tetragonal *I*4/*mcm* structure with lattice parameters $a = 6.544 \pm 0.001$ Å and $c = 8.105 \pm 0.003$ Å, in good agreement with the literature data.[23,43] The lattice consists of layers of Cs^+ and N_3^- ions and can be considered as a distorted CsCl-type structure because of the rod shape of the anion.

Our Raman spectra at low pressures (Figs. 2(a) and 2(b)) are also in agreement with the published data.[14,44,45] According to group theory for the tetragonal lattice of CsN_3,[46] there are three Raman active lattice modes: two librational E_g and B_{1g} modes because of hindered rotational motion of the azide anion and a translational E_g mode corresponding to cationic translations parallel to the (001) plane. The Raman active internal vibrations spectrum contains a correlation field split pair of A_{1g} and B_{2g} modes involving the symmetric stretching mode (ν_1) of the azide anion. Both librational modes E_g and B_{1g} are observed in our spectra at frequencies of $\approx 120\,cm^{-1}$ and $\approx 151\,cm^{-1}$ (at a pressure of 0.1 GPa) in good agreement with the literature data,[14] while for CsN_3 the translation E_g mode (located at $42\,cm^{-1}$)[14] lies beyond the cut-off edge used in our experiment's razor filter; therefore, its pressure dependence could not be studied. The correlation field splitting of the internal ν_1 stretching is very small, and so the A_{1g} and B_{2g} components are unresolved in the spectra of internal vibrations and only one peak is observed at $\approx 1329\,cm^{-1}$ at 0.1 GPa, again in agreement with

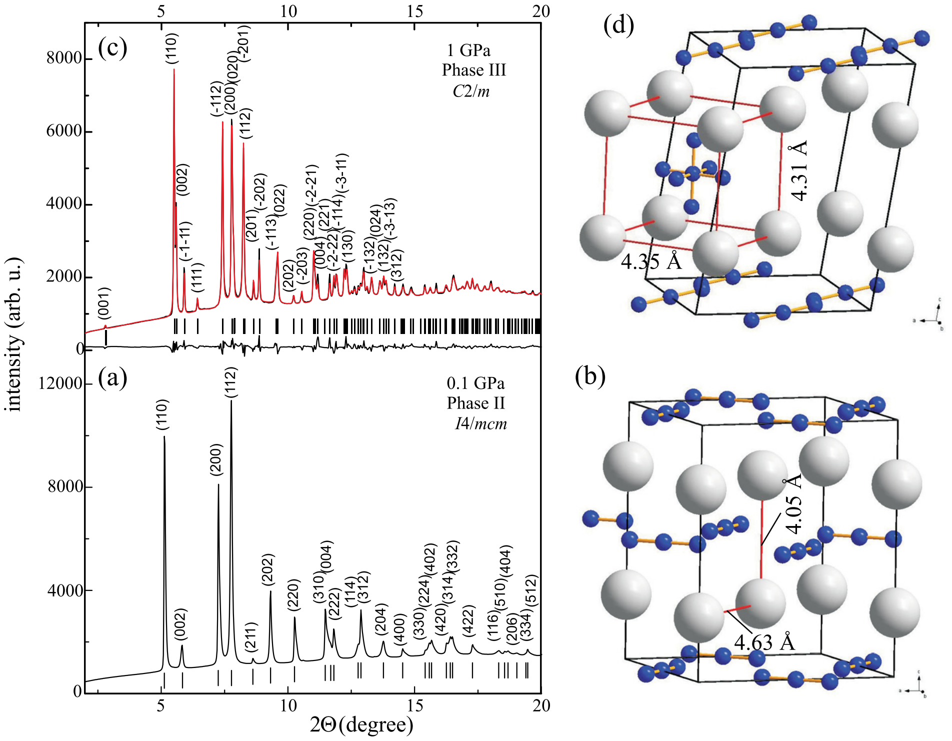

FIG. 1. X-ray diffraction patterns of CsN_3 in Phase II at a pressure of 0.1 GPa (a) and in Phase III at 1 GPa (c). The tick marks below the patterns show the calculated reflection positions of tetragonal *I*4/*mcm* structure (b) of Phase II and monoclinic *C*2/*m* structure of Phase III (d). The Cs ions in the *C*2/*m* structure of Phase III form nearly cubic cages in which azide anions are randomly oriented parallel to the edges of the cube (three possible orientations of the anion are shown in the highlighted cage of Cs cations), similar to the orientationally disordered high-temperature cubic phase *I*.[46] The red solid line in the upper panel is the calculated profile obtained by the Rietveld refinement of the *C*2/*m* structure, whereas the black solid line below the pattern represents the difference between observed and calculated intensities.

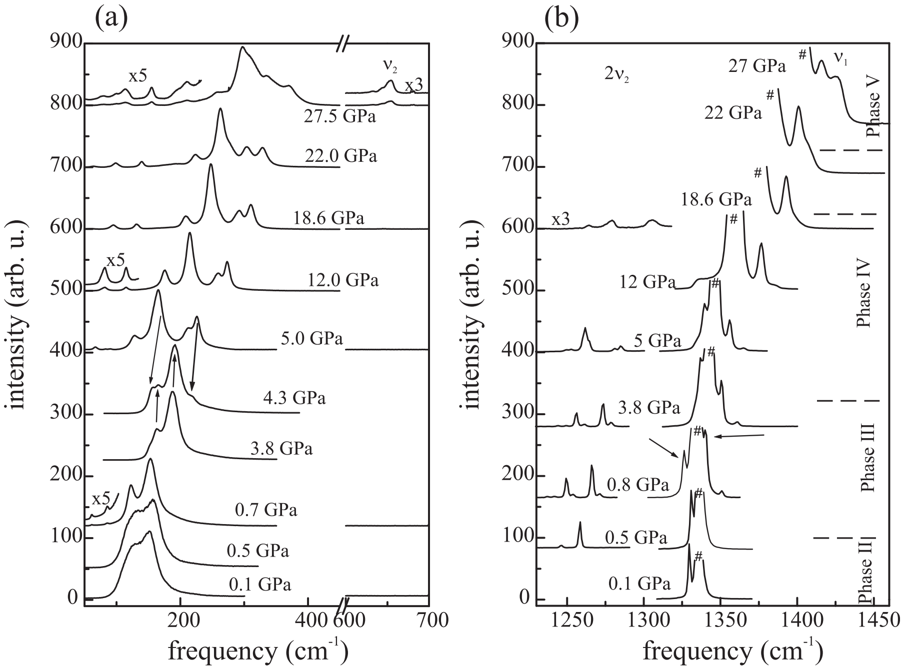

FIG. 2. Representative Raman spectra of CsN_3 external lattice modes and internal fundamental ν_2 bending mode (a), internal $2\nu_2$ bending overtone, and ν_1 symmetric stretching modes (b) collected at different pressures. Weak lattice excitations, fundamental ν_2, and overtone $2\nu_2$ bending mode peaks are magnified for clarity. The spectrum at 4.3 GPa in panel (a) demonstrates coexistence of Phase III and Phase IV, as indicated by arrows showing corresponding lines of low- and high-pressure phases. The strong Raman band of stressed diamond anvils is denoted with # in panel (b). Arrows in panel (b) indicate splitting of the ν_1 symmetric stretching mode at the Phase II to Phase III transition. The low frequency internal ν_1 mode is screened by a strong diamond Raman band at pressures above 7 GPa.

the published data.[14,45] In addition to the abovementioned fundamental vibrational modes, Raman spectra at 0.1 GPa contain some relatively weak peaks at $\approx 1248\,\mathrm{cm}^{-1}$ and $\approx 1256\,\mathrm{cm}^{-1}$, corresponding to the first overtone of the N_3^- bending (ν_2) mode. Detailed assignment of the observed band at ambient pressure of the $2\nu_2$ species in CsN_3 is given in Ref. 45. The importance of these spectral features comes from the insight that they give on the Fermi resonance between the ν_1 and $2\nu_2$ levels of the azide ions. Therefore, the pressure dependence studies of these features could provide valuable data for investigating the Fermi resonance, which is, however, beyond the scope of this work.

In the pressure range of 0–0.5 GPa, frequencies of all observed modes monotonically increase. In agreement with recent high-pressure X-ray diffraction studies,[23] the phase transition to Phase III at pressures of ≈0.5–0.6 GPa is observed as indicated by a sizable decrease in the bandwidth of the librational lines, splitting of internal vibration modes, and the appearance of two weak low-frequency peaks at $65\,\mathrm{cm}^{-1}$ and $90\,\mathrm{cm}^{-1}$ (Figs. 2(a) and 2(b)). The observed spectroscopic changes at the Phase II to Phase III transition are in full agreement with previous high-pressure Raman studies.[14]

X-ray diffraction patterns of CsN_3 also indicate a phase transition (Fig. 1) to Phase III. The diffraction pattern collected at 1 GPa can be unambiguously indexed with a monoclinic structure with refined lattice parameters $a = 6.19 \pm 0.02$ Å, $b = 6.10 \pm 0.02$ Å, $c = 8.62 \pm 0.03$ Å, $\beta = 98.56 \pm 0.03°$, and the extinction rules are compatible with the space group $C2/m$ in agreement with recent X-ray diffraction studies.[23] The cell volume of Phase III is $V = 321.9$ Å^3, implying four formula units per unit cell.

Comparing the lattice parameters of Phase III with those of Phase II, we can assume that Phase III also possesses a layered structure with Cs^+ ions and the centers of the azide anions arranged within layers, similar to that in the ambient pressure phase. Thus, the transition to Phase III represents a shift of layers of Cs^+ and N_3^- ions parallel to the (001) plane.

The layered arrangement of ions in the monoclinic $C2/m$ structure of Phase III, similar to that in the low-pressure phase, is achieved by placing the Cs^+ cations in the $4i(x, 0, z)$ sites (with x and z close to the values 0 and 1/4, respectively), whereas the centers of the azide anions are at two nonequivalent sites, $2b(0.5, 0, 0)$ and $2d(0, 0.5, 0.5)$.[23] The Rietveld refinement of the diffraction pattern at 1 GPa (Fig. 1) with this structural model provides the fractional coordinates of Cs cations $4i(-0.051, 0, 0.247)$.

The large splitting of ν_1 internal stretching modes in Phase III, $\approx 13\,\mathrm{cm}^{-1}$, (Fig. 3) is consistent with the suggestion that Phase III contains two sets of crystallographically nonequivalent azide-anion sites. At the same time, each of the two nonequivalent azide anions should generate an A_g and B_g pair of librational modes in the Raman spectrum because of rotational motions around the *a*- and *b*-axes, whereas only two librational peaks are observed in the spectra of Phase III.

It is important to note that the (001)-plane distance sizably increases at the transition to Phase III. The shortest Cs–Cs distance in the ambient pressure $I4/mcm$ structure (4.05 Å at ambient pressure, Fig. 1(b)) is along the *c*-direction, and it is significantly shorter than the Cs–Cs distance within the (*ab*)-plane (4.63 Å), while at the transition to Phase III ($C2/m$ structure, Fig. 1(d)) the Cs–Cs distance along the *c*-direction increases (4.31 Å at 1 GPa) and it is very close to the nearest Cs–Cs distance within the (*ab*)-plane (4.35 Å). Therefore, Cs^+ ions in Phase III form nearly cubic cages confining in their centers azide anions located in $2d(0, 0.5, 0.5)$ sites. This arrangement resembles the arrangement of the ions in the high-temperature cubic $Pm3m$ Phase I, which is stable at ambient pressure at temperatures above 414 K with cubic unit cell dimension ≈4.5 Å at ambient pressure.[11,47] This phase is orientationally disordered with azide

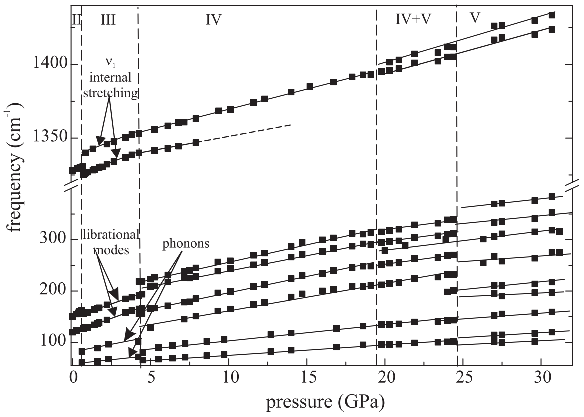

FIG. 3. External and internal ν_1 mode frequencies as a function of pressure. Solid lines drawn through the data points are eye guides only. Dashed vertical lines represent phase boundaries, and phases are assigned with Roman numbers, as in Ref. 23.

ions statically randomly oriented parallel to the edges of the unit cell. Thus, by analogy, we can suppose that in the high-pressure Phase III the azide anions with centers located in 2*d*(0, 0.5, 0.5) sites are confined in the nearly cubic cages of the Cs^+ ions and are statically disordered, whereas other azide anions occupying 2*b*(0.5, 0, 0) sites are orientationally ordered (Fig. 1(d)). The structure with partial orientational disordering of azide anions in Phase III would explain the number of observed Raman-active modes. Furthermore, the structural model with partial orientational disordering of the azide anions accounts for the discrepancy between the pressures of the phase transitions in CsN_3 observed experimentally[23] and theoretically calculated[38] because *ab initio* calculations[38] are limited to ordered structures.

According to the Raman spectroscopy data (Figs. 2 and 3) the $C2/m$ Phase III remains stable up to a pressure near 4 GPa, above which changes in the spectra indicate the onset of the next phase transition (Figs. 2 and 3), in agreement with the X-ray diffraction studies.[23] In lattice excitation spectra, doubling of the librational lines is observed at the phase transition to Phase IV (Figs. 2(a) and 3). At the same time, in the internal excitations spectra, only two ν_1 modes are still observed. It cannot be completely ruled out that the number of ν_1 internal modes also increases in Phase IV, and that the additional ν_1 species are screened by the diamond Raman band. However, the number of $2\nu_2$ components remains unchanged at the phase transition (Fig. 2(b)). Thus, it can be assumed that the number of ν_1 modes also remains unchanged in Phase IV, and therefore, the primitive unit cell of the Phase IV structure contains two nonequivalent formula units, similar to that of Phase III. No appreciable change in the frequencies of the ν_1 modes was observed in the course of the Phase III to Phase IV transition, while the slope of their pressure dependences decreased slightly, indicating that no large volume decrease occurs at the phase transition. Thus, the assignment of Phase IV to primitive $P2_1/m$ or $P2_1$ unit cells with eight formula units and with significantly reduced volume[23] compared with the Phase III unit cell seems to be inappropriate because of the poor quality of the diffraction patterns. The spectroscopic changes observed at the Phase III to Phase IV transition indicate that this is an apparently isostructural phase transition associated with orientational ordering of the disordered azide anions in Phase III. The structure of Phase IV might be related to the $C2/m$ structure found to be stable at pressures above 6 GPa in the recent *ab initio* calculations.[38]

Very recently, rubidium azide (RbN_3), which is closely related to CsN_3, was studied at high pressures at room temperature by means of *in situ* X-ray diffraction.[39] It was found that the first pressure-induced phase transition in RbN_3 occurs at a pressure of 6.5 GPa (significantly higher than the Phase II to Phase III but close to the Phase III to Phase IV transitions in CsN_3) in the high-pressure γ-phase assigned to the $C2/m$ space group. In this context, a high-pressure Raman spectroscopy study of RbN_3 would be of interest to gain more insight on structure and lattice dynamics of the structurally related heavy alkali azides.

No fundamental azide anion bending ν_2 modes have been observed in the Raman spectra of Phase IV. Therefore, the azide anions in this phase most probably remain linear and symmetric.

Phase IV appears to be stable up to a pressure of $\approx$18.5 GPa (Figs. 2 and 3) above which the onset of the next phase transition to Phase V is indicated by the observed changes in the Raman spectra. This phase transition is rather sluggish, with a large range of coexistence of Phases IV and V from $\approx$19 to 24.7 GPa, in agreement with X-ray diffraction studies.[23] The Raman spectra of Phase V are characterized by multiple splittings of all of the observed spectral peaks, indicating lowering of the symmetry at the phase transition. All of the observed peaks are apparently broadened because of the large volume decrease at the phase transition. The line broadening and screening of the spectral range of internal vibrations by the Raman band of the stressed diamond preclude any conclusive suggestion about the possible symmetry of Phase V. Again, it would be of interest to compare the Raman spectra of CsN_3 Phase V observed here with those of δ-RbN_3 found in X-ray studies[39] to be stable above 16 GPa and assigned to the orthorhombic structure.

An intriguing property of the CsN_3 Phase V is the appearance of a weak band in the region of the fundamental azide anion bending ν_2 (Fig. 2(a), spectrum at 27.5 GPa). The fundamental ν_2 bending vibrations are Raman inactive in the linear symmetric azide anion, but they become active in Raman scattering in covalent azides (e.g., HN_3), where the azido group appears to be slightly distorted. The appearance of this mode in the Raman spectra of Phase V might be an indication of the azide anion linear symmetry breaking because of changes of the chemical bonding in CsN_3 toward formation of covalent bonds at high pressures. This bonding change might be a reason for the relatively low pressure of nitrogen polymerization in CsN_3 predicted theoretically.[38]

IV. CONCLUSION

High-pressure Raman spectroscopy studies revealed three structural phase transitions at pressures of $\approx$0.5, 4.3, and $\approx$19 GPa to Phases III, IV, and V, respectively, in agreement with recent X-ray diffraction studies. Phase III is confirmed to adopt monoclinic $C2/m$ symmetry with two nonequivalent azide anions. The observed Raman spectra of Phase III can be explained by partial orientational disordering of azide anions in the $C2/m$ structure. The changes in the Raman spectra at the Phase III to Phase IV transition indicate that this is most probably an isostructural phase transition associated with the orientational ordering of the azide anions. The subsequent Phase V, which is stable above 19 GPa, has a lower symmetry. The appearance of the fundamental ν_2 bending vibrations in the spectra of this phase indicates a change of the chemical bonding in CsN_3 toward formation of covalent bonds at high pressures.

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