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Raman spectroscopy of $B_{12}As_2$ and $B_{12}P_2$ up to 120 GPa: Evidence for structural distortion

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We report results of Raman spectroscopy studies on single crystals of $B_{12}P_2$ and $B_{12}As_2$ under pressure to 120 GPa at 300 K. In the 75–85 GPa range in both compounds several additional modes appear while several other split. These results evidence a transition to a distorted structure with a strong deformation of the icosahedra. The Raman spectra measured at ambient down from 120 GPa show that this transformation is reversible.

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I. INTRODUCTION

Boron and boron-rich solids are materials with unusual structures. B_{12} distorted icosahedra are the primary building blocks of pure boron and many boron-rich solids. B atoms within icosahedra participate in strong covalent bonds with neighboring atoms in adjacent icosahedra and other structural elements. As a consequence of this bonding, these compounds are very stable, with a melting temperature up to 2700 K. The bonding within icosahedra is metallike: internal bonding electrons are delocalized over the surface of each icosahedron with densities that peak at the centers of the triangular faces formed by three neighboring boron atoms. Such distinctive bonding has some extremely interesting consequences, such as self-healing resistance to radiation damage.[1] Hence, the stability range of icosahedrally builded compounds presents interest both from fundamental and application points of view.

In the structures of the simplest boron-rich solids, B_{12} icosahedra are centered at the vertices of a rhombohedral unit cell. The simplest elemental boron crystal, α boron, takes this simple structure as illustrated in Fig. 1(a). Other polymorphs of elemental boron have more complex structures.[2] For example, β boron has 105 atoms in its rhombohedral unit cell. Despite its relative complexity, the structure of β boron is also based on icosahedral B_{12} units, together with B_{20} units that can be viewed as the fusion of three icosahedra. The icosahedral boron pnictides $B_{12}As_2$ and $B_{12}P_2$ have related structures. Here [Fig. 1(b)], B_{12} icosahedra remain at the vertices of the rhombohedral unit cell. Two-atom As-As or P-P dumbbells lie along the long body diagonal of the unit cell. Details of the intericosahedral bonding are provided in the caption of Fig. 1.

The relatively open crystal structures of icosahedral boron-rich solids have prompted long-standing interest in their stability under high pressures. Many recent studies have focused on the stability and transformations of complex forms of elemental boron at high pressure.[3–20] Although interesting phenomena such as superconductivity,[21,22] semiconductor-to-metal transitions,[3,7,9] and pressure-induced amorphization[8] have been reported at high pressures in these complex forms of boron, we find no reports of pressure-induced phase transitions in icosahedral borides.

α boron has been studied under pressure up to the 100 GPa range mostly by x-ray diffraction,[17] Raman scattering,[6,17,20] and resistance measurement.[16] One very interesting result of these studies is, beside the very broad stability range of this compound, the peculiar pressure dependence of the icosahedron librational mode, 524 cm^{-1} at ambient. Indeed, its frequency increases very slowly with pressure up to 20 GPa and decreases at higher pressure. The only study of the pressure dependence of the boron pnictides is a Raman study performed on $B_{12}As_2$ up to 15 GPa.[23]

In this Rapid Communication, we present Raman spectra obtained on single crystals of $B_{12}As_2$ and $B_{12}P_2$ at pressures up to 120 GPa. In the pressure range 75–85 GPa in both compounds we observe the appearance of several new Raman modes, and splittings among several of the modes present at ambient pressure. The appearance of low-frequency modes that are rapidly hardened with further pres-

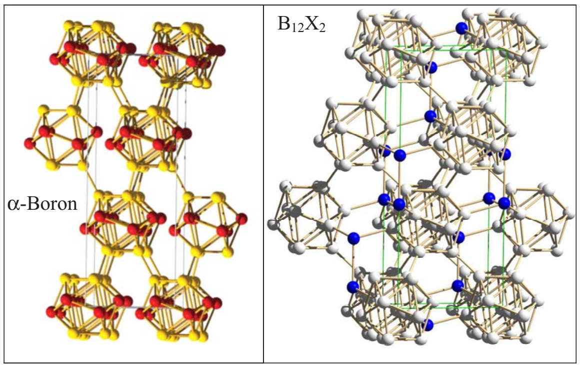

FIG. 1. (Color online) Structure of α-B_{12} and $B_{12}X_2$. In α-B_{12}, the atoms at polar positions [light (yellow) spheres] form covalent bonds to atoms at polar positions of adjacent icosahedra. Atoms at equatorial positions [dark (red) spheres] participate in three centers bonds with equatorial atoms in each of two adjacent icosahedra. In $B_{12}X_2$, these three-center bonds are replaced by covalent bonds to pnictide atoms, which form a two-atom chain along the body diagonal of the rhombohedral unit cell. Pnictide atoms, As or P, are shown as blue spheres.

surization evidences a transition to a distorted structure. The Raman spectra measured on the samples recovered at ambient from high pressure show that this transformation is reversible.

II. TECHNIQUE

The experiments were carried out in a membrane diamond-anvil cell[24] equipped with beveled diamonds of culet 100/300 μm. A rhenium gasket preindented down to 20 μm and drilled with a 50 μm hole and neon pressure-transmitting medium were used.[25] The Raman spectra were excited with the 514.5 nm line of an Ar laser at a power of 300 mW and were recorded using a T64000 Jobin-Yvon triple grating monochromator. Pressure in the diamond-anvil cell was determined from the shift of the ruby luminescence line. Above 96 GPa the signal from the ruby became undetectable and pressures to 120 GPa were deduced from an extrapolation of the pressure shift of the diamond Raman line from the anvils.[26] The samples were small single-crystalline unoriented pieces broken from larger crystals. At each measurement point the pressure difference across the samples was measured and it was found to be lower than 0.5–1 GPa.

The transparent single crystals of $B_{12}As_2$ and $B_{12}P_2$ were grown and characterized following a method described elsewhere.[27] The nonpolarized Raman spectra were measured in the backscattering geometry on flakelike samples of $\sim$1–2 μm in thickness and $\sim$5–10 μm in diameter. Two sets of experiments were performed, the first one to 96 GPa, and the second one to 120 GPa, each time with $B_{12}P_2$ and $B_{12}As_2$ together in the cell. At each pressure each sample was probed by Raman in several points. The spectra were investigated in a range from $\sim$20 to 3000 cm^{-1}. The first-order Raman mode of the diamond anvils cut the spectra above 1340 cm^{-1} and to $\sim$1600 cm^{-1} (to 120 GPa). Above 1600 cm^{-1} no peak could be detected.

III. RESULTS AND DISCUSSION

$B_{12}P_2$ and $B_{12}As_2$ belong to the same space group as α boron, i.e., $R\bar{3}m$. There are 14 atoms in the unit cell (one B_{12} icosahedron and two pnictogen atoms), and therefore 42 vibrational modes, whose irreducible representations at the Γ point are: $5A_{1g}$, $2A_{2g}$, $7E_g$, $2A_{1u}$, $5A_{2u}$, and $7E_u$. The Raman active modes are $5A_{1g}$ and $7E_g$, i.e., 12 different frequencies corresponding to 19 degrees of freedom. At ambient conditions, 11 modes have been observed,[24,27] like in the related compound B_6O.[27–29] The pressure dependence of these 11 vibrational modes was only established in $B_{12}As_2$ and up to 15 GPa.[23]

Typical Raman spectra and their pressure dependence up to 120 GPa are shown in Figs. 2–4. There is a good agreement with the published results,[23,27–30] although no mode is observed below 200 cm^{-1} in the present study (see Ref. 31). These plots show more than the 12 expected first-order modes (17 for $B_{12}As_2$ and 16 for $B_{12}P_2$). With prior authors, we speculate that this might be due to multiphonon processes.

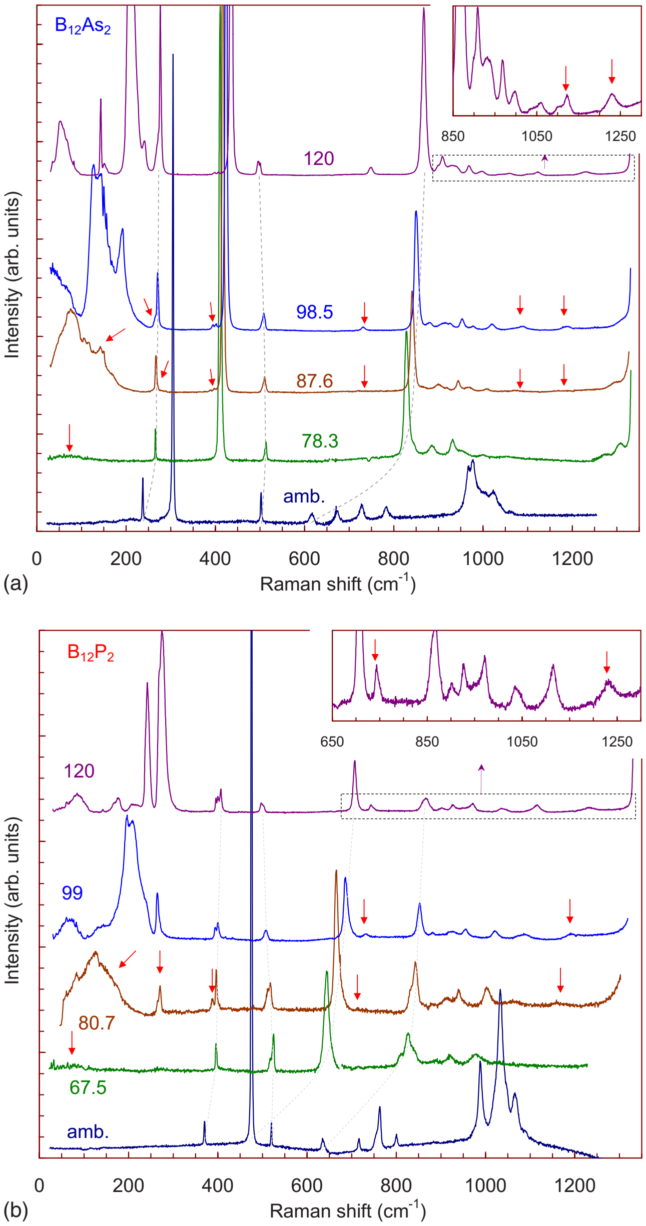

FIG. 2. (Color online) Raman spectra of (a) $B_{12}As_2$ and (b) $B_{12}P_2$ at selected pressures. The numbers above the curves are the pressures in gigapascal; arrows point out some of new peaks.

The two low-frequency modes, namely, 240 and 310 cm^{-1} for $B_{12}As_2$ and 371 and 478 cm^{-1} for $B_{12}P_2$ do not exist in pure α-B_{12}, and hence should be related to vibrations of the X-X and X-B bonds. The ratios of the frequencies ($371/240=1.546\approx 478/310=1.542$) are simply explained by the difference between As and P atomic masses $(M_{As}/M_P)^{1/2}=1.555$. This simple relation proves that the restoring forces involved in the atomic displacement pattern of these modes are equivalent in both crystals.

Up to 50–60 GPa both compounds exhibit a conventional behavior with a hardening of almost all the Raman modes owing to shrinking of the chemical bonds (Fig. 3). Only the equivalent of the librational mode of α boron, 507 cm^{-1} in $B_{12}As_2$ and 521 cm^{-1} in $B_{12}P_2$, presents a small pressure coefficient, reaches a maximum and then decreases(Fig. 4).

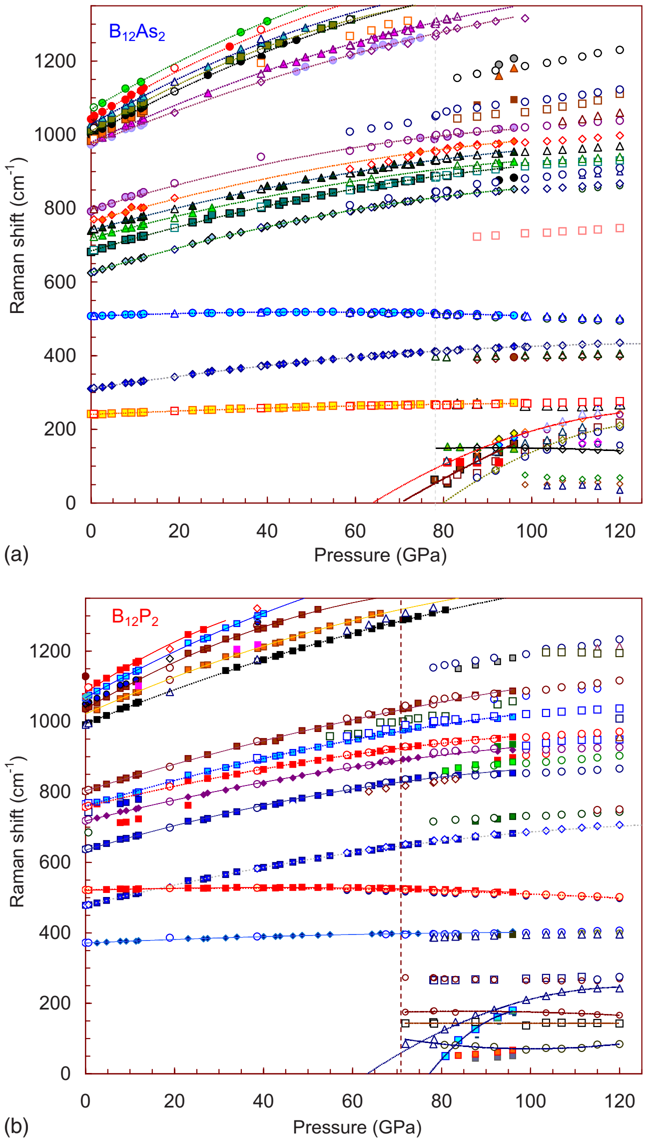

FIG. 3. (Color online) Pressure dependence of the wave numbers of (a) $B_{12}As_2$ and (b) $B_{12}P_2$ at ambient temperature. The vertical dashed lines indicate the appearance of new peaks.

At higher pressure, noticeable modifications occur in the Raman spectra. First, (i) the decrease in the librational modes frequency and (ii) the appearance of weak modes below 200 cm^{-1}. Then above 70–75 GPa in $B_{12}P_2$ and 80–85 GPa in $B_{12}As_2$ (iii) multiple splitting of the high-frequency modes, and (iv) the appearance of new peaks in the high-frequency region (Figs. 2–4). The Raman spectra of both compounds following their return to ambient pressure are almost identical to those obtained before pressurization, showing that all the transitions are reversible.

Our experimental results provide evidence for pressure-induced structural distortions in icosahedral borides based on the α-boron structure. We have no structural data to describe these distortions. However, the association of the various Raman bands with vibrations of different structural elements allows for the following discussion.

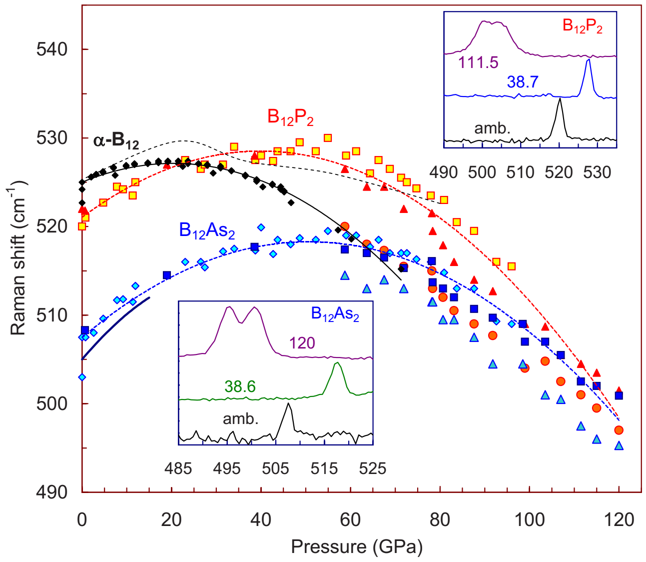

FIG. 4. (Color online) Pressure dependence of the low-frequency librational mode in α-B_{12} single crystal (black diamonds) (Ref. 17) and powder (dashed line) (Ref. 16), and in $B_{12}As_2$ and $B_{12}P_2$ [points fitted by dashed lines—present work; thick solid line—data for $B_{12}As_2$ to 15 GPa (Ref. 21)].

The main transformations of the Raman spectra are: (i) strong pressure-induced modification of the low-frequency spectra (below 200 cm^{-1}); (ii) rapid hardening of the new features (Fig. 2); (iii) persistence of all the basic modes of the ambient crystal structure, some of them splitted. All these characteristics suggest a transition to a distorted structure of lower symmetry. In the present case, the decrease in the librational modes frequency, which might be associated with a structural predestabilization, is seen already near 50 GPa for $B_{12}P_2$ and ~60 GPa for $B_{12}As_2$ (Fig. 4). The existence of low-frequency modes is distinctly detected at somewhat higher pressures. The appearance of low-frequency modes in the 200 cm^{-1} range under pressure as broad bands (Fig. 2) apparently evidences a structural instability, possibly with a doubling of the unit cell, and hence a folding of the Brillouin zone (Fig. 1). To 120 GPa, the highest pressure achieved in the present experiment, the shape of these broad bands gradually transform to those that are typical for ordered solids (Fig. 2), and the strong pressure dependencies of their wave numbers are tending to a saturation to ~250 cm^{-1} (Fig. 3). Therefore, this sluggish transition to a distorted structure is almost completed to 120 GPa. The new modes found above 70–75 GPa in $B_{12}P_2$ and 80–85 GPa in $B_{12}As_2$ in the high-frequency range (Figs. 2 and 3) evidence the beginning of a distortion of the crystal structure.

It should be emphasized, that the appearance of the broad low-frequency structures (Fig. 2) are not related to gradual amorphization of the materials, contrary to the case of β-B_{105} near 100 GPa.[8] Furthermore, no sign of metallization in the samples were noticed (color change, decrease in peaks' intensities, appearance of electron scattering background, etc.).

From the drastic changes in a part of the intraicosahedral modes one can surmise that the shape of the icosahedron in a distorted structure is essentially different than the conventional one. Furthermore, the librational mode, 507 cm^{-1} in $B_{12}As_2$ and 521 cm^{-1} in $B_{12}P_2$ that are believed to be related to icosahedra, splits in a doublet in the distorted phase (Fig.

4). This fact is also consistent with a doubling of the unit cell (folding of the Brillouin zone). The hypothesis of the survival of the icosahedra in the high-pressure phase with a distorted shape is reinforced by the reversibility of the transition: if they would have been destroyed, a large amount of energy would be necessary to rebuild them. The very high-frequency modes disappear in the very strong diamond Raman mode above 1340 cm^{-1}

The small changes in the phonons associated with vibrations of the X-B and X-X bonds could match with a minor modification of the associated bonds. The bends in the pressure dependencies of the wave numbers (Fig. 3) propose higher bulk modulus in the distorted phase.

In summary, pressure-induced changes in our Raman spectra of icosahedral boron pnictides provide evidence of pressure-induced distortions of the crystal structures, and of the icosahedra. We know of no evidence of similar phase transitions in other similar icosahedral borides. One should recall that no apparent phase transformation was found in α boron at room temperature up to 100 (Ref. 17) and even 200 GPa.[32] Very recent theoretical calculations[33] find that above 20 GPa another form of boron, namely, γ-B_{28} is energetically more favorable, but very strong kinetic barriers prevent a transition at ambient temperature. It might explain why no transformation in the crystal structure of α-B_{12} was found so far.[16,17,32] Alternatively, the transformation we observe might be a peculiarity of only α-B_{12} compounds ($B_{12}X_2$ and $B_{12}C_3$) in which extra atoms in the intericosahedral space favor the distortion of the icosahedra above some critical pressure.

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