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# Pressure-induced isostructural phase transformation in $\gamma$ -B<sub>28</sub>

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Isostructural phase transformations (ISPhTs) so far were reported only for heavy elements and their compounds with complex electronic and/or magnetic structures. Studies of one of the lightest elemental material, high-pressure boron  $\gamma$ -B<sub>28</sub>, by means of *in situ* single-crystal x-ray diffraction and Raman spectroscopy reveal abrupt changes in the compressional behavior and Raman spectra at 40 GPa. Combined experimental and *ab initio* theoretical analysis of the structural and vibrational properties of  $\gamma$ -B<sub>28</sub> suggests that the ISPhT under compression is due to the changes in the polarity of the covalent bonds between the boron atoms in the complex quasimolecular structure of  $\gamma$ -B<sub>28</sub>.

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## I. INTRODUCTION

Isostructural phase transformations are particular cases of isosymmetric transformations and include discontinuous isostructural transitions and crossovers. They are rare, intriguing phenomena in solids often associated with a significant volume collapse, giant magnetoelastic coupling, or negative thermal expansion.<sup>1–5</sup> Elemental boron and boron-rich compounds have been given a particular scientific and technological attention because of their specific physical properties: high melting temperatures, a wide energy band gap, high hardness, strong absorbance of neutrons, etc. The structures of these materials are based on icosahedral units as a common feature. Even high pressure does not destroy the rigid units so that the very recently described high-pressure boron phase<sup>6–8</sup>  $\gamma$ -B<sub>28</sub> consists of B<sub>12</sub> icosahedra typical for rhombohedral  $\alpha$ - and  $\beta$ -boron. Consisting of only B<sub>12</sub> units,  $\alpha$ -boron does not show any phase transitions on compression to at least 80 GPa at ambient temperature. The arrangement of B<sub>12</sub> icosahedra in  $\beta$ -boron is complex and its structure contains partially occupied sites.<sup>9,10</sup> The  $\beta$ -boron is more compressible (the bulk modulus  $K_{300}$ =185–210 GPa) in comparison with  $\alpha$ -boron ( $K_{300}$ =213–224 GPa).<sup>11,12</sup> The resistivity measurements<sup>13</sup> indicate a transformation from  $\beta$ -boron into yet unknown superconducting phase at about 160 GPa. At pressures above 8.5 GPa and temperatures higher than 1500 °C pure boron crystallizes as a  $\gamma$ -B<sub>28</sub> phase with a *Pnnm* space group.<sup>6–8</sup> It contains 28 atoms in the unit cell. The structure consists of B<sub>12</sub> icosahedra and B<sub>2</sub> dumbbells linked covalently<sup>6,7</sup> (Fig. 1). The  $\gamma$ -B<sub>28</sub> phase was demonstrated<sup>7</sup> to be stable at least to 30 GPa and 2000 K. However, experimental information about the high-pressure behavior of the  $\gamma$ -B<sub>28</sub> phase is so far limited. Here we present the results of the high-pressure Raman spectroscopy study of  $\gamma$ -B<sub>28</sub> up to 105 GPa and its single-crystal x-ray diffraction over 65 GPa.

## II. METHODS

Single crystals and polycrystalline aggregates of  $\gamma$ -B<sub>28</sub> were grown as described in our previous publications (see Refs. 6 and 7).

### A. Diamond-anvil cell experiments

In different runs the sample was clamped between diamond anvils with culets of 300, 250, or 120  $\mu$ m in diameter. Rhenium (in the Raman spectroscopy experiments) or steel (in single-crystal x-ray diffraction experiments) gaskets were indented to the thickness of about 50  $\mu$ m and holes with a diameter of 100 or 80  $\mu$ m were drilled in the center. Small isometric pieces of the high-pressure boron phase synthesized in a multianvil apparatus were loaded into the holes along with ruby balls served as pressure markers. As a pressure transmitting medium Ne or He were loaded at 1.4 kbar

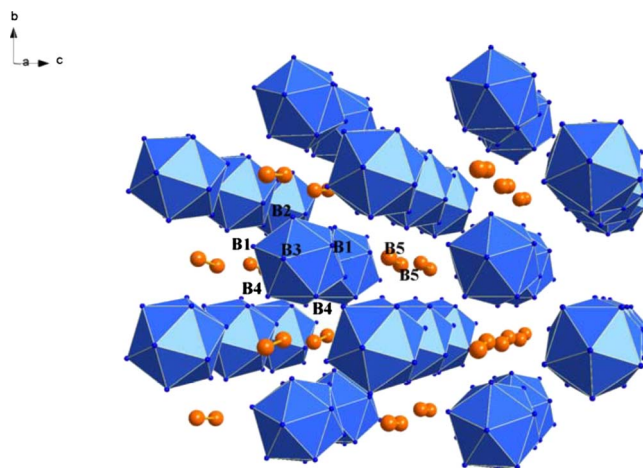


FIG. 1. (Color online) Structure of  $\gamma$ -B<sub>28</sub> (atom labels are according to Ref. 6).

(all single-crystal x-ray diffraction experiments were performed in He pressure medium). One- and double-side laser annealing of samples compressed in Ne pressure medium at pressures above 20 GPa at temperatures up to 2000 K was conducted at BGI or at ESRF.

### B. Raman spectroscopy

Raman spectroscopy studies were done on single crystals (with characteristic dimensions of  $\sim 5 \times 5 \times 25 \mu\text{m}^3$ ) and polycrystalline aggregates of the  $\text{B}_{28}$  phase. Measurements were performed with LabRam and Dilor XY (DILOR GmbH) systems with a resolution better than  $2 \text{ cm}^{-1}$ . The 632.8 nm line of a He-Ne laser and 514 nm of an Ar laser were used for an excitation with a power at the sample position of 15–50 mW. The positions of Raman peaks were determined by processing experimental data using PEAKFIT© v4.12 software.

### C. Single-crystal diffraction

Crystals with a size of about  $7 \mu\text{m} \times 7 \mu\text{m} \times 30 \mu\text{m}$  were selected and measured at ID09a at the European Synchrotron Radiation Facility (ESRF). Diffraction data were collected at 293 K using the MAR555 image plate detector, radiation with a wavelength of  $0.4143 \text{ \AA}$  and the crystal-to-detector distance of 399 mm. 120 frames in the omega scanning range of  $-30^\circ$  to  $+30^\circ$  were collected ( $0.5^\circ$  scanning step size) with exposure time of 1 s. The data were processed using the CRYSTALIS software [Oxford Diffraction (2006) CRYSTALIS RED, version 1.171.31.8. Oxford Diffraction Ltd., Abingdon, Oxfordshire]. Crystal-structure refinements on integrated intensities were carried out with JANA2006 software.

### D. *Ab initio* calculation

We performed first-principles calculations using the density-functional theory and density-functional perturbation theory formalisms as implemented in the ABINIT code.<sup>14</sup> We employed a  $6 \times 6 \times 6$  regular grid of high special  $k$  points<sup>15</sup> and a kinetic-energy cutoff of 30 Ha (1 Ha=27.2116 eV). These ensured a precision on the order of 1 mHa in energy and better than 1 GPa in pressure. The calculations were performed on the JADE machine of CINES.

## III. RESULTS

### A. Raman spectroscopy at high pressure.

The  $\gamma\text{-B}_{28}$  gives very distinct and strong Raman spectra at ambient conditions<sup>6,7,16</sup> so that the Raman spectroscopy could be the most convenient and useful technique for investigation of the high-pressure behavior of this phase. Polarized Raman spectroscopy studies<sup>16</sup> allowed assigning vibration modes of  $\gamma\text{-B}_{28}$  thus creating a basis for the present study. Some examples of Raman spectra of polycrystalline  $\gamma\text{-B}_{28}$  collected at high pressure are presented in Fig. 2(a). The pressure dependence of Raman modes [Fig. 2(b)] can be shown in terms of the mode-Grüneisen parameter, defined as  $\gamma_{\omega_i} = -\partial \ln \omega_i / \partial \ln V = -(B_0 / \omega_i) \partial \omega_i / \partial P$ , where  $\omega_i$  is the phonon frequency,  $B_0$  is the bulk modulus (227 GPa at ambient

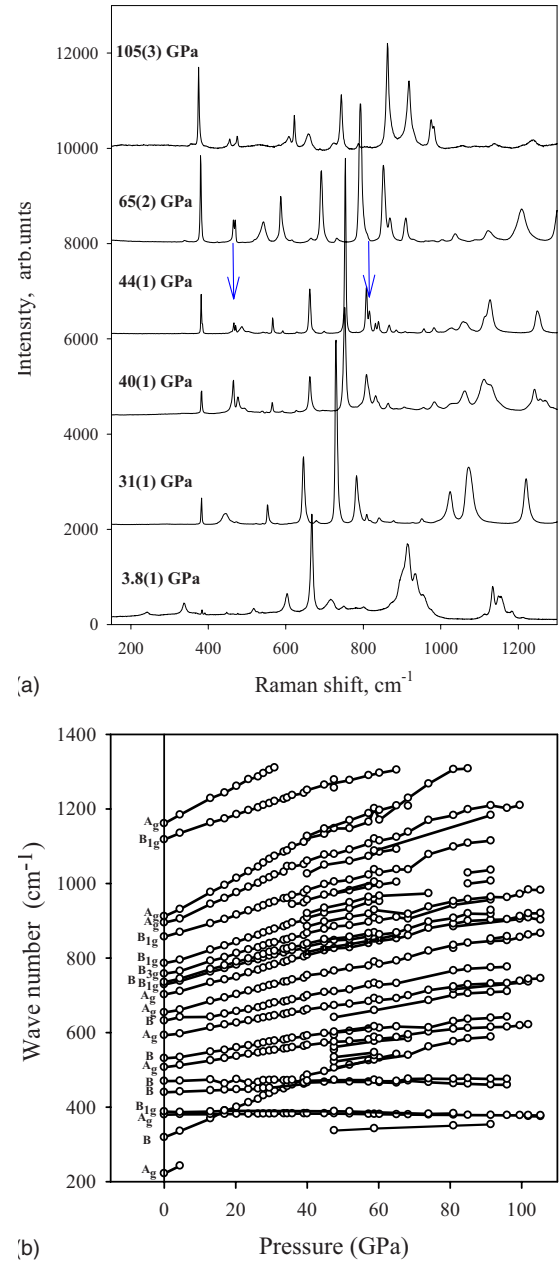


FIG. 2. (Color online) (a) Examples of Raman spectra of  $\gamma\text{-B}_{28}$  compressed in a neon pressure transmitting medium in a diamond-anvil cell. Arrows highlight some parts of the spectra which undergo rapid changes at pressure above 40 GPa. (b) Variation in the positions of Raman lines of  $\gamma\text{-B}_{28}$  as a function of pressure. Mode assignment at ambient conditions is given according to Ref. 16 [for some modes we could not assign their type ( $B_{2g}$  or  $B_{3g}$ ) so that they were labeled with the symbol “B” (Ref. 16)].

conditions<sup>7</sup>),  $V$  is the molar volume, and  $P$  is the pressure. According to the values of the mode-Grüneisen parameters, all observed Raman peaks could be divided into three groups (Table I). To the first group belongs the mode  $B_{2g}$  at  $319(3) \text{ cm}^{-1}$  for which the Grüneisen parameter (2.8) is distinctly high. According to theoretical analysis (Table II) this mode is associated with tilts (rotations) around the  $a$  axis of the  $B_{12}$  icosahedra. The second group of mode consists of weakly varying ( $\gamma=0.03\text{--}0.2$ ) narrow bands in the frequency

TABLE I. Assignment of experimental (Ref. 16) and theoretical phonon frequencies at ambient conditions with experimentally determined mode-Grüneisen parameters ( $\gamma_{\text{exp}}$ ).

Experiment				Theory	
$\omega_{\text{exp}}$ ( $\text{cm}^{-1}$ )	Assignment	$\gamma_{\text{exp}}$ below 39 GPa	$\gamma_{\text{exp}}$ above 39 GPa	$\omega_{\text{th}}$ ( $\text{cm}^{-1}$ )	Assignment
217(2)	B <sub>2g</sub> , B <sub>3g</sub>				
222(2)	A <sub>g</sub>				
319(3)	B <sub>2g</sub> , B <sub>3g</sub> <sup>a</sup>	2.76	1.04	303	B <sub>2g</sub>
380(1)	A <sub>g</sub>	0.07	-0.03	387	A <sub>g</sub>
388(2)	B <sub>1g</sub>	0.17		389	B <sub>3g</sub>
440(2)	B <sub>2g</sub> , B <sub>3g</sub>	0.20	-0.02	454	B <sub>3g</sub>
460(2)	B <sub>1g</sub> <sup>a</sup>			464/475	B <sub>3g</sub> /B <sub>1g</sub>
470(2)	B <sub>2g</sub> , B <sub>3g</sub>	0.03	-0.03	464/475	B <sub>3g</sub> /B <sub>1g</sub>
507(2)	A <sub>g</sub>	0.65	0.34	536	A <sub>g</sub>
531(2)	B <sub>2g</sub> , B <sub>3g</sub>	0.68		537	B <sub>2g</sub>
593(3)	A <sub>g</sub>	0.67	0.41	611	A <sub>g</sub>
632(2)	B <sub>2g</sub> , B <sub>3g</sub>	0.53	0.42	585/575	B <sub>2g</sub> /B <sub>3g</sub>
654(2)	A <sub>g</sub>	0.84	0.47	687	A <sub>g</sub>
686(3)	B <sub>1g</sub> , B <sub>2g</sub> , B <sub>3g</sub> <sup>a</sup>			658	B <sub>1g</sub>
702(3)	A <sub>g</sub> <sup>a</sup>	0.85	0.50	732	A <sub>g</sub>
712(3)	B <sub>2g</sub> , B <sub>3g</sub>			714/719	B <sub>3g</sub> /B <sub>2g</sub>
729(2)	B <sub>1g</sub>	0.78	0.40	726	B <sub>1g</sub>
735(2)	B <sub>1g</sub> , B <sub>2g</sub> , B <sub>3g</sub> <sup>a</sup>	0.79	0.42	735	B <sub>2g</sub>
758(2)	B <sub>3g</sub>	0.82	0.45	765	B <sub>3g</sub>
786(2)	B <sub>1g</sub>	0.87	0.54	781, 784	B <sub>1g</sub> , B <sub>1g</sub>
857(3)	B <sub>1g</sub>	0.81	0.52	862	B <sub>1g</sub>
878(2)	B <sub>1g</sub> , B <sub>3g</sub> <sup>a</sup>			884	B <sub>3g</sub>
895(2)	A <sub>g</sub>	1.05	0.55	887	A <sub>g</sub>
912(2)	A <sub>g</sub>	1.26	0.66	920	A <sub>g</sub>
929(2)	A <sub>g</sub>			970? <sup>b</sup>	A <sub>g</sub>
952(2)	B <sub>2g</sub> , B <sub>3g</sub> <sup>a</sup>			959	B <sub>2g</sub>
1095(2)	B <sub>1g</sub> , B <sub>2g</sub> , B <sub>3g</sub> <sup>a</sup>				
1118(2)	B <sub>1g</sub>	0.98	0.40	1118	B <sub>1g</sub>
1138(2)	B <sub>1g</sub>			1138	B <sub>1g</sub>
1161(2)	A <sub>g</sub>	0.42		1189	A <sub>g</sub>
1189(2)	A <sub>g</sub>			1194	A <sub>g</sub>
1218(2)	A <sub>g</sub>				

<sup>a</sup>Peaks which are visible also in forbidden scattering geometries (Ref. 16).<sup>b</sup>The “?” marks the line whose assignment is ambiguous.

range 380–470  $\text{cm}^{-1}$ . All these modes are assigned to vibrations of B<sub>12</sub> icosahedra (380, 388, and 460  $\text{cm}^{-1}$ ) or both B<sub>12</sub> icosahedra and B<sub>2</sub> dumbbells (444 and 470  $\text{cm}^{-1}$ ) along the unit-cell axes (Table II). Note that similar behavior of icosahedron and icosahedron-dumbbell vibrations were observed in  $\alpha$ -boron,<sup>17</sup> in highly ordered pnictides (B<sub>12</sub>As<sub>2</sub> and B<sub>12</sub>P<sub>2</sub>),<sup>18</sup> and boron carbide (B<sub>4</sub>C).<sup>19</sup> The Grüneisen parameters of modes observed between 507 and 1200  $\text{cm}^{-1}$  (the third group) are in the range of 0.42–1.05. These bands arise mainly from intraicosahedral vibrations, such as breathing or rocking-stretching modes. Note that apparent changes in the shape of spectra in the 800–1000  $\text{cm}^{-1}$  region on compression to about 39 GPa

(Fig. 2) are entirely due to differences in mode-Grüneisen parameters of the bands.

The observed high-pressure behavior of Raman modes can be qualitatively related to the response of the  $\gamma$ -B<sub>28</sub> structure on compression. Indeed, rotations of B<sub>12</sub> icosahedra, or of the B<sub>12</sub> icosahedra and B<sub>2</sub> dumbbells around *b* and *c* axes (Fig. 1, Table II) require changes in the length of the shortest (i.e., strongest) B-B contacts between icosahedra and/or between an icosahedron and a dumbbell<sup>7</sup>; they correspond to the modes with the smallest mode-Grüneisen parameters. The mode which is most sensitive to the volume changes is associated with the rotation of B<sub>12</sub> icosahedra

TABLE II. Calculated Raman-active modes of  $\gamma$ -B<sub>28</sub> at 0 GPa.

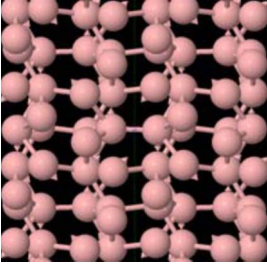
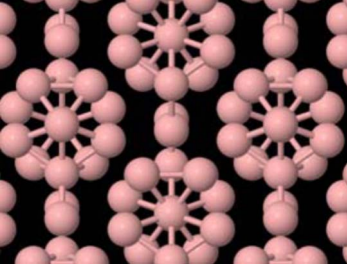
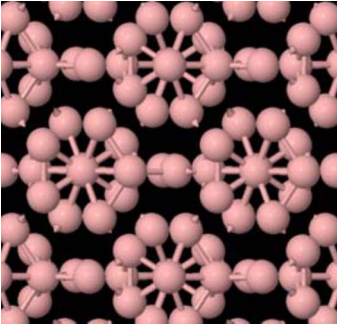
Assignment	$\omega_{\text{calc}}(\text{cm}^{-1})$	Description
<b>A<sub>g</sub></b>	<b>387</b>	The B <sub>6</sub> half-caps move up and down and the whole B <sub>12</sub> icosahedron tilts around the <i>c</i> axis 
<b>A<sub>g</sub></b>	<b>536</b>	B <sub>2</sub> dumbbells tilt around the <i>c</i> axis; slight participation of the B <sub>12</sub> icosahedra that tilt much less
<b>A<sub>g</sub></b>	<b>611</b>	Breathing mode of the B <sub>12</sub> icosahedra
<b>A<sub>g</sub></b>	<b>687</b>	Breathing mode of the B <sub>12</sub> icosahedra
<b>A<sub>g</sub></b>	<b>732</b>	Tilt of B <sub>2</sub> associated with a movement of the B atoms from the sides of the B <sub>12</sub> icosahedra, looking like a dangling bond; the B atoms from the B <sub>12</sub> that move are the furthest apart from B <sub>2</sub>
<b>A<sub>g</sub></b>	<b>770</b>	Breathing mode of the B <sub>12</sub> icosahedra
<b>A<sub>g</sub></b>	<b>811</b>	Breathing mode of the B <sub>12</sub> icosahedra; here the B atoms from the side, the ones that form a bond perpendicular to the B <sub>2</sub> -B <sub>12</sub> plane participate in the motion 
<b>A<sub>g</sub></b>	<b>887</b>	Breathing mode of the B <sub>12</sub> icosahedra
<b>A<sub>g</sub></b>	<b>920</b>	Breathing mode of the B <sub>12</sub> icosahedra 
<b>A<sub>g</sub></b>	<b>970</b>	Breathing mode of the B <sub>12</sub> icosahedra
<b>A<sub>g</sub></b>	<b>1119</b>	Tilt of the B <sub>2</sub> dumbbell associated with a displacement of the two B atoms from the B <sub>12</sub> icosahedra situated closest to the B <sub>2</sub> dumbbells along the <i>b</i> axis
<b>A<sub>g</sub></b>	<b>1194</b>	Breathing-like mode of the B <sub>12</sub> icosahedra dominated by the movement of



TABLE II. (*Continued.*)

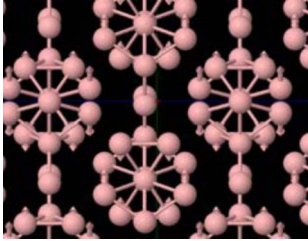
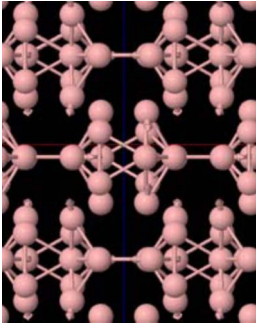
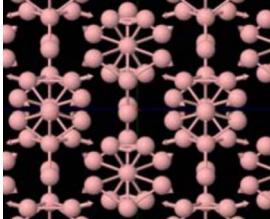
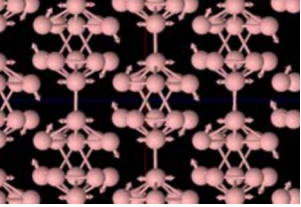
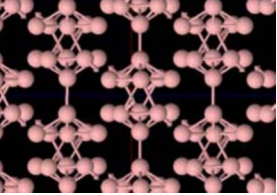
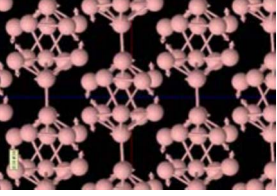
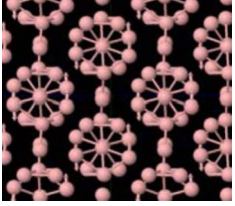
		the apex atoms (these are the only ones that really move)
$B_{1g}$	<b>475</b>	Tilts of the $B_{12}$ icosahedra around the $c$ axis
$B_{1g}$	<b>554</b>	Tilts of the $B_2$ dumbbells
$B_{1g}$	<b>658</b>	Vibration corresponding to half the $B_{12}$ icosahedra vibrating against the other half along the $b$ axis
		
$B_{1g}$	<b>726</b>	Breathing mode of the $B_{12}$ icosahedra
$B_{1g}$	<b>781</b>	Breathing mode of the $B_{12}$ icosahedra; each half-cap breathes independently
		
$B_{1g}$	<b>784</b>	Breathing mode of the $B_{12}$ icosahedra; each half-cap breathes independently; the movement has an important $a$ component, the sizes of the half-caps rotating around the $z$ axis
$B_{1g}$	<b>793</b>	Breathing mode of the $B_{12}$ icosahedra; dominated by a tilt of the B-B bond between the $B_{12}$ icosahedra, in the (010) plane
$B_{1g}$	<b>862</b>	Breathing mode of the $B_{12}$ icosahedra; $B_2$ do not participate
$B_{1g}$	<b>906</b>	Dominated by $B_2$ extension mode with some smaller participation from the breathing of $B_{12}$ icosahedra from the $B_2$ side bonds parallel to the $c$ axis
$B_{1g}$	<b>979</b>	Breathing mode of the $B_{12}$ icosahedra, with lateral extension in the (100) planes
		
$B_{1g}$	<b>1118</b>	Tilt of the $B_2$ dumbbell associated with a displacement of the two B atoms from the $B_{12}$ icosahedra situated closest to the $B_2$ dumbbells along the $b$ axis
$B_{1g}$	<b>1189</b>	Breathing-like mode of the $B_{12}$ icosahedra dominated by the movement of the apex atoms (these are the only ones that really move)
$B_{2g}$	<b>303</b>	Tilts (=rotations) of the $B_{12}$ icosahedra along the $x$ axis
$B_{2g}$	<b>454</b>	Tilts (rotations) of the $B_{12}$ icosahedra and of the $B_2$ dumbbells. The $B_{12}$ icosahedra around the $a$ axis, while the $B_2$ dumbbells have a component along the $b$ axis

TABLE II. (*Continued.*)

$B_{2g}$	537	Tilts of the $B_{12}$ icosahedra around the $b$ axis	
$B_{2g}$	585	Tilts of the $B_{12}$ icosahedra around the $a$ axis	
$B_{2g}$	719	Shear-like mode of the $B_{12}$ icosahedra; such that each half of the cage tilts around the $b$ axis producing a sheared final $B_{12}$ cage	
$B_{2g}$	735	Shear-like mode of the $B_{12}$ icosahedra; the tilt system is slightly different than from the previous mode; there are two subunits within each half that tilt in anti-phase	
$B_{2g}$	771	The apex of the $B_{12}$ atoms along the $X$ axis and the $B_2$ dumbbells vibrate around the $b$ axis	
$B_{2g}$	880	Dominated by a tilt system of the $B_{12}$ apex against the $B_2$ dumbbells	
$B_{2g}$	959	Shear mode of the $B_{12}$ icosahedra, associated with a tilt of the half-caps along the $b$ axis	
$B_{3g}$	389	Tilt mode of the $B_{12}$ icosahedra around the $b$ axis	
$B_{3g}$	403	Tilt of the $B_2$ dumbbells with a slight participation from the $B_{12}$ unit that tilt as well	
$B_{3g}$	464	Another tilt of both $B_{12}$ and $B_2$ around the $a$ axis	
$B_{3g}$	575	Shear mode of the $B_{12}$ icosahedra; half-caps vibrate against the other half with a tilt around the $b$ axis	
$B_{3g}$	714	Double shear of the $B_{12}$ icosahedra; the mode is dominated by the $B_2$ bond parallel to the $c$ axis	
$B_{3g}$	765	Breathing mode of the $B_{12}$ icosahedra	
$B_{3g}$	810	Breathing mode of the $B_{12}$ icosahedra, associated with a shear due to differential displacement in the (100) plane of the different $B$ of $B_{12}$ icosahedra	
$B_{3g}$	884	Breathing mode of the $B_{12}$ icosahedra, associated with a shear due to differential displacement along the $a$ axis of the different $B$ of $B_{12}$ icosahedra; dominated by lateral displacement of the apex atoms	
$B_{3g}$	929	Complex breathing mode of the $B_{12}$ icosahedra	

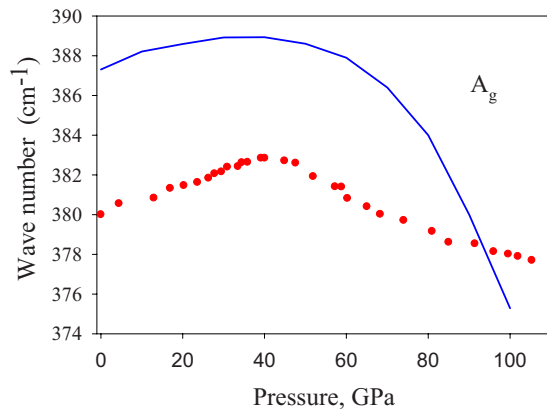


FIG. 3. (Color online) Example of the measured (dotted curve) and calculated (solid curve)  $A_g$  Raman mode as a function of pressure.

around the  $a$  axis and does not involve tension of the shortest interatomic contacts.

Most the Raman modes monotonically shift to higher wave numbers with increasing pressure up to about 35 GPa. At pressures higher than 40 GPa in all three independent experiments we observed an inflection in the modes behavior [Fig. 2(b), Table I]. Under further compression to pressures about 40–45 GPa several broaden peaks split (Fig. 2(a)). Although above  $\sim 40$  GPa we detect up to 32 Raman modes in the spectra, the total number of modes was always less than 42 allowed in orthorhombic  $\gamma$ - $B_{28}$ .<sup>16</sup> At the same pressure two modes ( $A_g$  at  $380\text{ cm}^{-1}$  and  $B_{3g}$  at  $470\text{ cm}^{-1}$ ) drastically change their behavior and become soft with Grüneisen parameters of about  $-0.03$  (Fig. 2; Table I, Fig. 3).

Phonon determination based on first-principles calculations show that the lowest six Raman modes (one  $A_g$ , one  $B_{1g}$ , two  $B_{2g}$ , and two  $B_{3g}$ ) present pressure softening in perfect agreement with the experimental observations. They are lattice modes corresponding mainly to tilts of the  $B_{12}$  icosahedra. In particular, the behavior of the lowest  $B_{2g}$  mode is relevant as it hardens up to about 50 GPa and it softens beyond that pressure.

Laser annealing at 1500–1800 K at pressures above 40 GPa does not affect the Raman spectra and the changes are fully reversible on decompression suggesting that the orthorhombic  $\gamma$ - $B_{28}$  may undergo a phase transition at high pressures. In order to test this hypothesis we have undertaken an intensive x-ray diffraction investigation of  $\gamma$ - $B_{28}$  under compression.

### B. Single-crystal x-ray diffraction at high pressure

Being the fifth element in the Periodic Table, boron is a very weak x-ray scatterer. X-ray powder-diffraction experiments on boron phases above 30 GPa are difficult<sup>7,19</sup> and could hardly provide even accurate lattice parameters. At the same time, single-crystal studies allowed investigating the behavior of lattice parameters of  $\beta$ -boron at pressure up to 100 GPa.<sup>12</sup> In three independent diamond-anvil cell (DAC) experiments we compressed single crystals of  $\gamma$ - $B_{28}$  (grown in a multianvil apparatus in metallic fluxes<sup>20</sup>) to pressures

over 65 GPa using He as a quasihydrostatic pressure transmitting medium. The collected x-ray diffraction data were sufficient in quality to refine both lattice parameters and atomic coordinates (Table III). Remarkably, the quality of the structural refinement based on the data collected in DACs was not worse than that based on the data obtained at ambient conditions (Table III), and it also proves that the crystals were in a good quasihydrostatic environment to highest pressures reached.

Up to the highest pressure reached in this study (65 GPa) all observed reflections perfectly match the  $\gamma$ - $B_{28}$  (space group  $Pnmm$ ) structure (Table III). However, the compressional behavior of the material at pressures below and above about 40 GPa is considerably different (Fig. 4). It manifests in an abrupt increase in the stiffness of the structure (more than 20% increase in the bulk modulus) and in the relative softening along the  $a$  axis in comparison with the  $c$  and especially the  $b$  axes. There is a clear change in the behavior of the  $b/a$  ratio (it decreases monotonously to about 35 GPa and increases above 40 GPa), and there is a discontinuity in “ $F$ - $f$ ” plot (normalized stress vs Eulerian strain, see insets in Fig. 4). An extrapolation of molar volumes of low-pressure and high-pressure materials to ambient conditions gives a difference of about 3% (Fig. 4).

On compression up to 40 GPa the shortest bond lengths as well as the average distances between any atom and its neighbors (“atom’s sphere radius” as defined in IVTON software<sup>22</sup>) homogeneously decrease; their compressibilities are linear with values in the  $0.019$ – $0.024\text{ GPa}^{-1}$  range (Fig. 5). The volume of the  $B_{12}$  icosahedra also decreases smoothly to 40 GPa (Fig. 6). However the bulk modulus of this polyhedron (285 GPa) is significantly higher than the bulk modulus of the bulk material (227 GPa) confirming a molecular-solidlike behavior with intericosahedral bonding weaker than intraicosahedral ones. At pressures above 40 GPa the compressibility of the spheres around the B1 and B4 atoms (Fig. 1 for designation of atoms) does not change (these two atoms are not involved into the shortest intericosahedral contacts or into the contacts of the  $B_2$  dumbbells and the  $B_{12}$  icosahedra). Contrary, the atoms involved in intraicosahedral bonding (labeled B3) or in bonding between the  $B_{12}$  icosahedra and the  $B_2$  dumbbells (labeled B2 and B5) show pronounced changes in the compressional behavior. In parallel the  $B_{12}$  icosahedra become much more incompressible, exhibiting a  $1/3$  increase in the bulk modulus (Fig. 6).

## IV. DISCUSSIONS

Both the Raman spectroscopy and the single-crystal x-ray diffraction studies reveal the existence of *two states* of  $\gamma$ - $B_{28}$  with a pronounced difference in their vibrational and compressional properties. The abrupt change in the properties occurs at pressures  $\sim 40$  GPa. However, neither the symmetry nor the structure change was detected in this pressure range. We conclude, therefore, that  $B_{28}$  undergoes an *isostructural* phase transformation.

Isostructural phase transformations are relatively exotic phenomena. They were reported for a few elements, in particular, in Ce (a well-known example of the isostructural



TABLE III. Structural parameters of the  $\gamma$ -B<sub>28</sub> phase ( $Pnnm$ ,  $Z=28$ ) as revealed by single-crystal diffraction experiments in diamond-anvil cells at high pressures.

Run	Pressure (GPa)	Lattice parameters (Å)			Atomic coordinates					$R_1(\%)$ $wR_2(\%)$	
		$a$	$b$	$c$	B1 8h	B2 4g	B3 4g	B4 8h	B5 4g		
B4_1	16.1(2)	4.9554(3)	5.5097(8)	6.8011(6)	0.1540(5)	0.6498(7)	0.3358(7)	0.8395(5)	0.6698(7)	7.57	8.07
					0.5927(7)	0.7264(11)	0.5082(9)	0.7188(7)	0.9803(10)		
					0.7902(5)	0.5	0.0	0.8731(5)	0.0		
B4_2	22.6(2)	4.9231(4)	5.4720(14)	6.7388(10)	0.1545(5)	0.6513(8)	0.3355(7)	0.8406(6)	0.6698(7)	6.39	7.12
					0.5920(7)	0.7242(11)	0.5071(10)	0.7181(6)	0.9793(10)		
					0.7898(5)	0.5	0.0	0.8731(7)	0.0		
B4_3	30.2(3)	4.8767(3)	5.4260(12)	6.6606(9)	0.1538(6)	0.6518(9)	0.3359(9)	0.8411(7)	0.6698(8)	6.92	8.18
					0.5914(8)	0.7234(13)	0.5066(11)	0.7178(9)	0.9769(12)		
					0.7895(6)	0.5	0.0	0.8733(6)	0.0		
B4_4	35.5(3)	4.8535(4)	5.4025(13)	6.6187(10)	0.1534(6)	0.6514(7)	0.3371(7)	0.8404(6)	0.6691(7)	4.68	5.21
					0.5902(7)	0.7231(10)	0.5082(9)	0.7184(7)	0.9776(9)		
					0.7885(5)	0.5	0.0	0.8723(5)	0.0		
B4_5	37.8(3)	4.8346(3)	5.3831(9)	6.5920(6)	0.1541(6)	0.6519(8)	0.3358(8)	0.8410(6)	0.6703(8)	6.02	6.92
					0.5910(8)	0.7229(12)	0.5072(10)	0.7188(8)	0.9766(11)		
					0.7884(5)	0.5	0.0	0.8724(5)	0.0		
B4_6	45.1(3)	4.8078(5)	5.3532(17)	6.5465(13)	0.1537(6)	0.6513(8)	0.3367(7)	0.8406(6)	0.6701(7)	5.46	5.62
					0.5902(8)	0.7230(11)	0.5072(9)	0.7187(7)	0.9765(10)		
					0.7878(5)	0.5	0.0	0.8719(5)	0.0		
B5_1	0.001	5.0508(2)	5.6181(4)	6.9793(5)	0.1543(4)	0.6481(6)	0.3357(5)	0.8386(4)	0.6695(5)	6.61	7.43
					0.5928(5)	0.7279(7)	0.5072(6)	0.7195(5)	0.9834(7)		
					0.7930(4)	0.5	0.0	0.8737(4)	0.0		
B5_2	5.8(1)	5.0115(5)	5.5731(10)	6.9041(12)	0.1542(4)	0.6485(6)	0.3355(5)	0.8390(4)	0.6701(5)	5.58	6.74
					0.5921(5)	0.7267(7)	0.5059(6)	0.7195(4)	0.9820(7)		
					0.7917(3)	0.5	0.0	0.8733(4)	0.0		
B5_3	9.6(2)	4.9810(2)	5.5392(3)	6.8535(4)	0.1542(5)	0.6483(6)	0.3364(6)	0.8392(4)	0.6699(6)	6.28	7.59
					0.5924(6)	0.7277(8)	0.5079(7)	0.7198(5)	0.9813(7)		
					0.7914(4)	0.5	0.0	0.8731(4)	0.0		
B5_4	14.7(2)	4.9636(2)	5.5192(4)	6.8160(5)	0.1542(6)	0.6487(8)	0.3357(7)	0.8392(5)	0.6710(7)	7.86	8.58
					0.5921(7)	0.7264(9)	0.5082(8)	0.7193(6)	0.9798(8)		
					0.7907(5)	0.5	0.0	0.8728(5)	0.0		
B5_5	15.1(2)	4.9267(2)	5.4751(4)	6.7439(6)	0.1538(6)	0.6499(9)	0.3353(8)	0.8403(6)	0.6718(8)	5.42	5.95
					0.5907(6)	0.7253(8)	0.5064(7)	0.7184(5)	0.9779(7)		
					0.7893(4)	0.5	0.0	0.8722(5)	0.0		
B5_6	21.5(2)	4.8986(4)	5.4462(9)	6.6990(11)	0.1544(4)	0.6494(7)	0.3357(6)	0.8401(4)	0.6712(6)	5.65	6.26
					0.5910(4)	0.7244(7)	0.5076(6)	0.7188(4)	0.9779(6)		
					0.7887(3)	0.5	0.0	0.8717(4)	0.0		
B5_7	26.5(2)	4.8715(3)	5.4189(6)	6.6651(7)	0.1550(11)	0.6481(18)	0.3352(14)	0.8389(10)	0.6707(16)	10.17	15.55
					0.5930(13)	0.7187(16)	0.5092(13)	0.7146(10)	0.9818(16)		
					0.7891(8)	0.5	0.0	0.8732(9)	0.0		
B5_8	31.7(3)	4.8492(5)	5.3910(10)	6.6116(13)	0.1542(5)	0.6494(7)	0.3356(7)	0.8402(5)	0.6712(7)	6.79	7.56
					0.5912(7)	0.7239(9)	0.5098(9)	0.7194(7)	0.9756(9)		
					0.7873(5)	0.5	0.0	0.8714(5)	0.0		
B5_9	36.2(3)	4.8246(6)	5.3679(12)	6.5713(11)	0.1539(4)	0.6495(6)	0.3358(6)	0.8409(4)	0.6710(6)	4.63	5.72
					0.5906(5)	0.7240(7)	0.5093(7)	0.7189(5)	0.9758(7)		
					0.7871(3)	0.5	0.0	0.8713(4)	0.0		
B5_10	41.2(3)	4.8100(2)	5.3531(5)	6.5486(5)	0.1542(5)	0.6494(7)	0.3357(7)	0.8408(5)	0.6716(7)	5.13	6.08
					0.5905(6)	0.7235(8)	0.5089(7)	0.7182(6)	0.9754(7)		
					0.7867(3)	0.5	0.0	0.8711(4)	0.0		
B5_11	45.0(3)	4.7857(3)	5.3291(7)	6.5091(7)	0.1544(6)	0.6498(8)	0.3366(7)	0.8407(5)	0.6710(7)	5.02	5.98
					0.5909(6)	0.7227(8)	0.5086(7)	0.7180(6)	0.9749(7)		
					0.7862(4)	0.5	0.0	0.8709(5)	0.0		

TABLE III. (Continued.)

Run	Pressure (GPa)	Lattice parameters (Å)			Atomic coordinates					$R_1(\%)$ $wR_2(\%)$
		$a$	$b$	$c$	B1 8h	B2 4g	B3 4g	B4 8h	B5 4g	
B5_12	51.2(4)	4.7208(5)	5.2508(12)	6.4015(14)	0.1543(11) 0.5912(12) 0.7858(9)	0.6529(17) 0.7214(14) 0.5	0.3340(13) 0.5076(13) 0.0	0.8401(10) 0.7168(11) 0.8703(8)	0.6731(14) 0.9729(12) 0.0	7.54 8.70
B5_p1	65.3(5)	4.731(3)	5.280(5)	6.4285(39)	0.1533(12) 0.5891(9) 0.7844(6)	0.6521(16) 0.7204(10) 0.5	0.3341(15) 0.5082(9) 0.0	0.8425(9) 0.7190(7) 0.8729(8)	0.6705(15) 0.9763(10) 0.0	6.94 6.91
B5_p2	55.6(5)	4.772(3)	5.318(5)	6.486(7)	0.1541(2) 0.5901(6) 0.7859(4)	0.6506(9) 0.7221(7) 0.5	0.3369(7) 0.5079(8) 0.0	0.8415(6) 0.7190(1) 0.8712(4)	0.6723(8) 0.9760(7) 0.0	5.55 5.60
B28[7]	0.001	5.0576(4)	5.6245(8)	6.9884(10)	0.1539(3) 0.5938(2) 0.7924(2)	0.6469(4) 0.7284(4) 0.5	0.3362(4) 0.5076(4) 0.0	0.8391(3) 0.7189(3) 0.8737(2)	0.6690(4) 0.9823(4) 0.0	3.73% 11.5%

transition,<sup>1</sup> see Ref. 23 for review) at high pressures, Zr and<sup>24</sup> Os.<sup>25</sup> However, established cases of the ISPhTs are related to the elements or compounds containing elements with the variable chemical valence due to fully or partially free  $d$ - or/and  $f$ -electronic shells (for example, SmS,<sup>26</sup> EuCo<sub>2</sub>P<sub>2</sub>,<sup>27</sup> rare-earth chalcogenides<sup>28</sup> and pnictides, see Ref. 29 for review), or/and materials which undergo magnetic or spin transitions, for example, MnO (Ref. 30) or YCo<sub>5</sub>.<sup>2</sup> Boron is an element of the second row of the Periodic Table and the conventional mechanisms of the ISPhT in its crystal structure are highly unlikely (indeed, theoretical calculations<sup>7,8</sup> do not indicate any significant changes in

band structure of  $\gamma$ -B<sub>28</sub> at least to 100 GPa). At the same time  $\gamma$ -B<sub>28</sub> is a quasimolecular material. The detailed single-crystal x-ray diffraction study conducted at ambient pressure<sup>7</sup> revealed the strong polar-covalent bonding with an electron density excess at B2 and B4 atoms (they belong to the B<sub>12</sub> icosahedra) and an electron density deficit at B5 atoms (which form B<sub>2</sub> dumbbells). This suggests that the ISPhT in  $\gamma$ -B<sub>28</sub> can be a result of changes in the electron density distribution between boron atoms and/or bonds or, in other words, changes in the character of chemical bonding. For compounds with the polar-covalent bonding, the splitting of the IR longitudinal- and transversal-optical (LO-TO) phonon modes can be used as a measure of the degree of the charge transfer,<sup>8,9,31</sup> which can be characterized by the generalized Lyddane-Sachs-Teller (LST) parameter  $\xi = \prod_i^n (\omega_i^{\text{LO}} / \omega_i^{\text{TO}})^2$ . Using calculated values of frequencies for all IR-active modes at different pressures (Fig. 7) we found that above 50 GPa, in strict similarity with experimental data

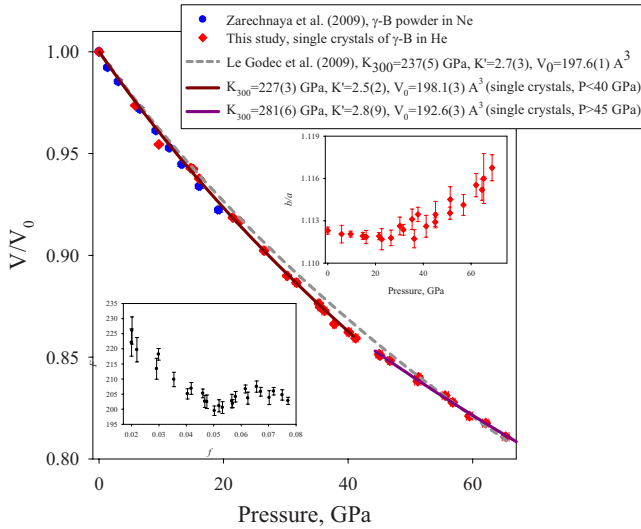


FIG. 4. (Color online) The relative unit-cell volume of  $\gamma$ -B<sub>28</sub> as a function of pressure (red diamonds—single-crystal data from this study; blue circles—powder-diffraction data (Ref. 7); lines are fits with the third-order Birch-Murnaghan (BM3) equation of state: dark red for single-crystal data below 40 GPa, dark purple for single-crystal data above 45 GPa, and dashed line as reported by Le Godec *et al.* (Ref. 21) based on powder x-ray diffraction data to 70 GPa. Insets show the variation in the ratio of the lattice parameters  $b/a$  as a function of pressure and the  $F$ - $f$  plot (normalized stress vs Eulerian strain).

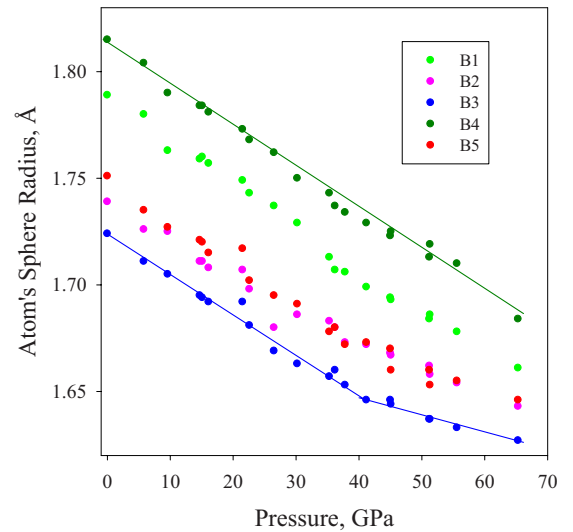


FIG. 5. (Color online) The average distance of the atom from its neighbors [“sphere radius,” as defined in IVTON software (Ref. 22)] as a function of pressure. Continuous lines for B3 and B4 atoms are guide for eyes.

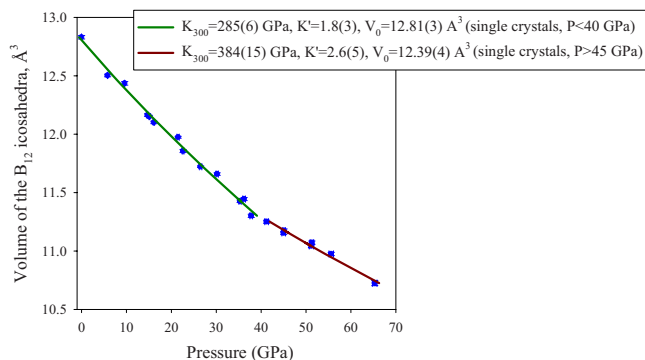


FIG. 6. (Color online) Volume of the  $B_{12}$  icosahedra as a function of pressure (blue dots). The polyhedron volumes were calculated in IVTON program (Ref. 22). Lines are fits with the BM3 equation of state: dark green for single-crystal data below 40 GPa, dark red for single-crystal data above 45 GPa.

on changes in Raman spectra and compressional behavior, the LST parameter changes its pressure dependence. This result strengthens our assignment of the isostructural phase transformation in  $\gamma$ - $B_{28}$  as due to alteration the polarity of the covalent bonding between the boron atoms in the complex quasimolecular structure.

Boron-rich carbides, nitrides, oxides, and borides of light elements with polar covalent and/or partially ionic bonding represent a large group of materials with prospective applications due to a number of unusual and potentially useful properties.<sup>9,17</sup> Our finding of the ISPhT in  $\gamma$ - $B_{28}$  suggests that the same or similar mechanism, involving rapid pressure- or chemically induced changes in chemical bond-

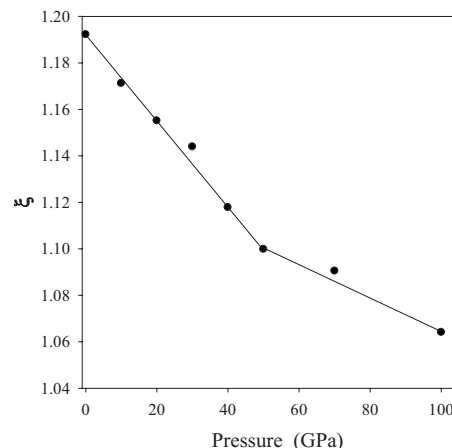


FIG. 7. The generalized Lyddane-Sachs-Teller parameter  $\xi = \Pi_i^n (\omega_i^{LO} / \omega_i^{TO})^2$  of  $\gamma$ - $B_{28}$  ( $\omega_i^{LO}$  and  $\omega_i^{TO}$  are calculated frequencies of longitudinal- and transversal-optical IR-active modes) as a function of pressure. The decrease in  $\xi$  with pressure indicates that the covalent bonding in  $\gamma$ - $B_{28}$  becomes less polar under compression.

ing, could drive isostructural transformations in other boron-rich phases as well.

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<sup>1</sup>P. W. Bridgman, Proc. Am. Acad. Arts Sci. **62**, 207 (1927).

<sup>2</sup>H. Rosner, D. Koudela, U. Schwarz, A. Handstein, M. Hanfland, I. Opahle, K. Koepernik, M. D. Kuz'min, K.-H. Müller, J. A. Mydosh, and M. Richter, Nat. Phys. **2**, 469 (2006).

<sup>3</sup>S. Lee, A. Pirogov, M. Kang, K.-H. Jang, M. Yonemura, T. Kamiyama, S.-W. Cheong, F. Gozzo, N. Shin, H. Kimura, Y. Noda, and J.-G. Park, Nature (London) **451**, 805 (2008).

<sup>4</sup>Y. W. Long, N. Hayashi, T. Saito, M. Azuma, S. Muranaka, and Y. Shimakawa, Nature (London) **458**, 60 (2009).

<sup>5</sup>A. Y. Kuznetsov, V. P. Dmitriev, O. I. Bandilet, and H.-P. Weber, Phys. Rev. B **68**, 064109 (2003).

<sup>6</sup>E. Yu. Zarechnaya, L. Dubrovinsky, N. Dubrovinskaia, N. Miyajima, Y. Filinchuk, D. Chernyshov, and V. Dmitriev, Sci. Technol. Adv. Mater. **9**, 044209 (2008).

<sup>7</sup>E. Yu. Zarechnaya, L. Dubrovinsky, N. Dubrovinskaia, Y. Filinchuk, D. Chernyshov, V. Dmitriev, N. Miyajima, A. El Goresy, H. F. Braun, S. Van Smaalen, I. Kantor, A. Kantor, V. Prakapenka, M. Hanfland, A. S. Mikhaylushkin, I. A. Abrikosov, and S. I. Simak, Phys. Rev. Lett. **102**, 185501 (2009).

<sup>8</sup>A. R. Oganov, J. Chen, C. Gatti, Y. Ma, Y. Ma, C. W. Glass, Z. Liu, T. Yu, O. O. Kurakevych, and V. L. Solozhenko, Nature

(London) **457**, 863 (2009); **460**, 292 (2009).

<sup>9</sup>B. Albert and H. Hillebrecht, Angew. Chem., Int. Ed. **48**, 8640 (2009).

<sup>10</sup>T. Ogitsu, F. Gygi, J. Reed, Y. Motome, E. Schwegler, and G. Galli, J. Am. Chem. Soc. **131**, 1903 (2009).

<sup>11</sup>R. J. Nelmes, J. S. Loveday, D. R. Allan, J. M. Besson, G. Hamel, P. Grima, and S. Hull, Phys. Rev. B **47**, 7668 (1993).

<sup>12</sup>D. N. Sanz, P. Loubeyre, and M. Mezouar, Phys. Rev. Lett. **89**, 245501 (2002).

<sup>13</sup>M. I. Eremets, V. V. Struzhkin, H.-k. Mao, and R. J. Hemley, Science **293**, 272 (2001).

<sup>14</sup>X. Gonze, G.-M. Rignanese, and R. Caracas, Z. Kristallogr. **220**, 458 (2005).

<sup>15</sup>H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13**, 5188 (1976).

<sup>16</sup>E. Yu. Zarechnaya, N. Dubrovinskaia, and L. Dubrovinsky, High Press. Res. **29**, 530 (2009).

<sup>17</sup>N. Vast, S. Baroni, G. Zerah, J. M. Besson, A. Polian, M. Grimsditch, and J. C. Chervin, Phys. Rev. Lett. **78**, 693 (1997).

<sup>18</sup>A. Polian, S. Ovsyannikov, M. Gauthier, P. Munsch, J.-C. Chervin, and G. Lemarchand, in High Pressure Crystallography: From Fundamental Phenomena to Technological Applications, edited by E. Boldyreva and P. Dera, NATO Science for Peace and Security Series B: Physics and Biophysics XIV

- (Springer, Dordrecht, Netherlands, 2010), pp. 241–250.
- <sup>19</sup>R. J. Nelmes, J. S. Loveday, R. M. Wilson, W. G. Marshall, J. M. Besson, S. Klotz, G. Hamel, T. L. Aselage, and S. Hull, *Phys. Rev. Lett.* **74**, 2268 (1995).
  - <sup>20</sup>E. Yu. Zarechnaya, N. Dubrovinskaia, L. Dubrovinsky, Y. Filinchuk, D. Chernyshov, and V. Dmitriev, *J. Cryst. Growth* **312**, 3388 (2010).
  - <sup>21</sup>Y. Le Godec, O. O. Kurakevych, P. Munsch, G. Garbarino, and V. L. Solozhenko, *Solid State Commun.* **149**, 1356 (2009).
  - <sup>22</sup>T. Balic-Žunić and I. Vicković, *J. Appl. Crystallogr.* **29**, 305 (1996).
  - <sup>23</sup>B. Johansson and S. Li, *Philos. Mag.* **89**, 1793 (2009).
  - <sup>24</sup>Y. Akahama, M. Kobayashi, and H. Kawamura, *J. Phys. Soc. Jpn.* **60**, 3211 (1991).
  - <sup>25</sup>F. Occelli, D. L. Farber, J. Badro, C. M. Aracne, D. M. Teter, M. Hanfland, B. Canny, and B. Couzinet, *Phys. Rev. Lett.* **93**, 095502 (2004).
  - <sup>26</sup>A. Chatterjee, A. K. Singh, and A. Jayaraman, *Phys. Rev. B* **6**, 2285 (1972).
  - <sup>27</sup>M. Chefki, M. M. Abd-Elmeguid, H. Micklitz, C. Huhnt, W. Schlabit, M. Reehuis, and W. Jeitschko, *Phys. Rev. Lett.* **80**, 802 (1998).
  - <sup>28</sup>R. Caracas and X. Gonze, *Phys. Rev. B* **69**, 144114 (2004).
  - <sup>29</sup>A. Svane, P. Strange, W. M. Temmerman, Z. Szotek, H. Winter, and L. Petit, *Phys. Status Solidi B* **223**, 105 (2001).
  - <sup>30</sup>C. S. Yoo, B. Maddox, J.-H. P. Klepeis, V. Iota, W. Evans, A. McMahan, M. Y. Hu, P. Chow, M. Somayazulu, D. Häusermann, R. T. Scalettar, and W. E. Pickett, *Phys. Rev. Lett.* **94**, 115502 (2005).
  - <sup>31</sup>C. Kittel, *Einführung in die Festkörperphysik*, 9th ed. (R. Oldenbourg, München, 1991).