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## **Linköping University Post Print**

N.B.: When citing this work, cite the original article.

**Original Publication:** 

http://www.aps.org/

Postprint available at: Linköping University Electronic Press http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-69916

Eyvas Isaev, Sergey Simak, Arkady Mikhaylushkin, Yu. Kh. Vekilov, E. Yu. Zarechnaya, L. Dubrovinsky, N. Dubrovinskaia, M. Merlini, M. Hanfland and Igor Abrikosov, Impact of lattice vibrations on equation of state of the hardest boron phase, 2011, Physical Review B. Condensed Matter and Materials Physics, (83), 13, 132106. http://dx.doi.org/10.1103/PhysRevB.83.132106 Copyright: American Physical Society

## Impact of lattice vibrations on equation of state of the hardest boron phase

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(Received 22 December 2010; revised manuscript received 1 February 2011; published 21 April 2011)

An accurate equation of state (EOS) is determined for the high-pressure orthorhombic phase of boron,  $B_{28}$ , experimentally as well as from *ab initio* calculations. The unique feature of our experiment is that it is carried out on the single crystal of  $B_{28}$ . In theory, we take into consideration the lattice vibrations, often neglected in first-principles simulations. We show that the phonon contribution has a profound effect on the EOS of  $B_{28}$ , giving rise to anomalously low values of the pressure derivative of the bulk modulus and greatly improving the agreement between theory and experiment.

DOI: 10.1103/PhysRevB.83.132106

PACS number(s): 63.20.D-, 64.30.Jk

Boron is a unique element of the Periodic Table with very unusual structural and physical properties. It is situated at the borderline between metallic and nonmetallic elements. At ambient conditions, boron is a semiconducting element and exhibits unique crystal structures based on icosahedral entities, which are linked together in a variety of ways. A general theory of the structural behavior of boron and other elements in the 13th group of the Periodic Table under pressure, following from the tendency to optimize the sp hybridization, has been developed in Ref. 1, where a phase transformation into the  $\alpha$ -Ga structure accompanied by a nonmetal-metal transition at a pressure of about 74 GPa has been predicted.<sup>1</sup> Boron has been subjected to extensive high-pressure research.<sup>2-5</sup> In particular, the lattice dynamics and superconductivity of different boron phases were studied in Refs. 6-10. Recently, another highpressure phase of boron has attracted substantial attention. In fact, already in 1965, Wentorf<sup>11</sup> reported the synthesis of a new boron form at pressures above 10 GPa and temperatures above 1500 °C. The existence of this material was not confirmed until recently.<sup>12-14</sup> High-pressure boron has orthorhombic symmetry, and its unit cell contains 28 atoms (B<sub>28</sub>). The properties of  $B_{28}$  are rather remarkable. It is a wide-band-gap semiconductor that is superhard and has low compressibility. Indeed, the measured Vickers microhardness 58(5) GPa of the orthorhombic boron phase in an asymptotic-hardness region (load up to 10 N) is in the range of polycrystalline cubic boron nitride and makes B28 the second hardest elemental solid after diamond.15

An experimental equation of state (EOS) for the  $B_{28}$  phase has been obtained in Refs. 15 and 16. The results of *ab initio* calculations of the EOS have also been reported.<sup>14,15,17</sup> While there is generally a reasonable agreement among these results, which are summarized in Table I, certain inconsistencies should be pointed out. In particular, theoretical volumes obtained by different groups agree very well with each other, but they *underestimate* the experimental values by about 2%, despite the use in the calculations of

the generalized gradient approximation (GGA), which usually overestimates cell volumes. Also, theoretical values of B' for B<sub>28</sub> considerably overestimate the experimental results, which are quite low in the orthorhombic phase of B. Here we would like to emphasize that there are certain concerns regarding both the theoretical and experimental results on the EOS of B<sub>28</sub> reported in the literature. For instance, one could note that Le Godec *et al.*<sup>16</sup> did not report the equilibrium volume,  $V_0$ , measured in the same experiment, which is essential for an accurate EOS determination. Moreover, the diffraction pattern shown in Ref. 16 contains numerous unidentified reflections, suggesting that the samples may not be pure, and the samples were not annealed on compression. At the same time, all theoretical EOS's were obtained from the static total energy calculations, and therefore do not include any effects of the lattice vibrations.

In this paper, we report the results of a combined theoretical and experimental study of the EOS of  $B_{28}$ . The unique feature of our experiment is that it is carried out on the single crystal of  $B_{28}$  compressed to about 40 GPa in a helium pressure-transmitting medium. Our theoretical simulations explicitly account for the lattice vibrations and show that the lattice dynamics has a profound and qualitative influence on the theoretically calculated EOS of B. We calculate the phonon-dispersion relations in the orthorhombic phase of boron at ambient as well as at high pressures, and we show that adding vibrational energies improves considerably the agreement between experimental and theoretical volumes, increases the calculated bulk modulus, and strongly weakens its variation with pressure in the low-pressure interval.

Single crystals and polycrystalline aggregates of  $B_{28}$  were grown as described in our previous publications.<sup>18</sup> In two different runs, the sample was clamped between diamond anvils with culets of 300 or 250  $\mu$ m in diameter. Steel gaskets were indented to a thickness of about 50  $\mu$ m, and holes with a diameter of 100 or 80  $\mu$ m were drilled in the center. As a pressure-transmitting medium, He was loaded at 1.4 kbar. A

	Volume (Å <sup>3</sup> )	Bulk modulus (GPa)	B'	
Experiment	198.8(4) <sup>a</sup> , 198.476 <sup>b</sup> , 197.577 <sup>c</sup> , 197.44(3) <sup>d</sup>	227(.2) <sup>a</sup> , 237(.5) <sup>e</sup>	2.2(2) <sup>a</sup> , 2.7(3) <sup>e</sup>	
Theory	195.97(6) <sup>a</sup> , 195.873 <sup>b</sup> , 195.66 <sup>f</sup>	221.7(7) <sup>a</sup> , 222 <sup>f</sup>	$3.6(3)^{a}, 3.67^{f}$	

TABLE I. Summary of experimental and incordical results on the ground-state parameters of D <sub>28</sub> from the incrature	TABLE I. Summary	of experimental and	theoretical results on the	ground-state paran	neters of $B_{28}$ from the literature.
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<sup>a</sup>Reference 15. <sup>b</sup>Reference 14. <sup>c</sup>Reference 12.

<sup>d</sup>Reference 13.

<sup>e</sup>Reference 16.

<sup>f</sup>Reference 17.

crystal of ~7  $\mu$ m × 7  $\mu$ m × 30  $\mu$ m size was selected from the bulk and measured at ID09a at the European Synchrotron Radiation Facility (ESRF). Diffraction data were collected at 293 K using the MAR555 detector, a 0.4143 Å wavelength, and a crystal-to-detector distance of 399 mm. A total of 120 frames in the omega scanning range  $-30 \pm 30$  deg were collected (0.5 deg scanning step size) with an exposure time of 1 s. At least 60 independent reflections were collected for each pressure point. The data have been processed with Crystalis software [Oxford Diffraction (2006) Crystalis RED, version 1.171.31.8, Oxford Diffraction Ltd., Abingdon, Oxfordshire].

The static total energy calculations were performed in the framework of the density functional theory.<sup>19</sup> To calculate the phonon-dispersion relations in  $B_{28}$ , we used the linearresponse method implemented in the quantum ESPRESSO code.<sup>20</sup> Electron-ion interactions were described by means of the ultrasoft pseudopotential<sup>21</sup> with the valence electron configuration  $2s^2 2p^1$ , and the exchange-correlation effects have been treated in the framework of the GGA.<sup>22</sup> Electron wave functions were expanded over plane waves with a kinetic energy up to 30 Ry, and plane waves with a kinetic energy up to 450 Ry were used to describe the augmented charge. Integration over the Brillouin zone (BZ) was performed using an  $8 \times 6 \times 4$  k-mesh grid, the self-consistent threshold was accepted as  $10^{-10}$  Ry, and for phonon calculations it was  $10^{-16}$  Ry. Atomic positions and the cell volume were optimized by means of a damped Wentzcovitch algorithm.<sup>23</sup> Residual forces acting on individual atoms were less than  $2 \times 10^{-4}$  Ry/a.u. Phonon-dispersion relations and density of states (DOS) were calculated using a real-space force-constant matrix obtained via fast Fourier transformation of eight dynamical matrices. Phonon DOS and zero-point vibration energies were calculated using the quasiharmonic (QHA)  $code^{24}$  and about 300 k points in the BZ. Then the Helmholtz free energy was calculated as

$$F(V,T) = E_{\text{tot}}(V,T=0) + \sum_{nk} \left( \frac{1}{2} \hbar \omega_{nk} + k_B T \ln[1 - \exp(\hbar \omega_{nk}/k_B T)] \right)$$

to find temperature-dependent cell volumes. The reliability of the method has been well established, e.g., in studies of the phase transitions in FeH (Ref. 25) or the stability of  $\alpha$  and  $\beta$  phases of boron.<sup>26</sup>

A volume correction due to the zero-point motion contribution to the free energy,  $F(0) = (1/2) \sum_{nk} \hbar \omega_{nk}$ , in the low-temperature limit is  $\Delta V = (1/2B) \sum_{nk} \hbar \omega_{nk} \gamma_{nk}$ , where  $\Delta V$  is the correction to the equilibrium volume  $V_0$ ,  $\gamma_{nk}$  is the mode Grüneisen parameter,  $\omega_{nk}$  stands for a mode frequency at a given k point in the irreducible Brillouin zone, and B is the bulk modulus at zero pressure. Using an averaged value for the Grüneisen parameter  $\gamma$ , we obtain  $\Delta V = \gamma F(0)/B$ . We have calculated the Grüneisen parameter via the relation  $\Theta(V)/\Theta(V_0) = (V_0/V)^{\gamma}$  and averaging the mode Grüneisen parameter  $\gamma_{nk}$  over the Brillouin zone,

$$\gamma = \frac{\sum_{nk} \gamma_{nk} C_V(n,k)}{\sum_{nk} C_V(n,k)},$$

where

$$C_V(n,k) = k_B \left(\frac{\hbar\omega_{n,k}}{2k_BT}\right)^2 / \sinh^2 \left(\frac{\hbar\omega_{n,k}}{2k_BT}\right)$$

is the mode specific heat.  $\Theta(V)$  and  $\Theta(V_0)$  are the Debye temperature at volume V and  $V_0$ , respectively.

The zero-pressure unit-cell volume [198.1(3) Å<sup>3</sup>] of the single crystal of B<sub>28</sub> measured in diamond anvil cells within an uncertainty of measurements coincides with the value reported by Zarechnaya *et al.*<sup>15</sup> [198.8(4) Å<sup>3</sup>], and it is reasonably close to all other experimental values summarized in Table I. Fitting of the pressure-volume (*P-V*) data with the Birch-Murnaghan EOS (Ref. 27) gives values of B(300 K) = 237(5) GPa and B' = 2.5(2), confirming results obtained earlier in powder x-ray diffraction experiments in a neon pressure medium.<sup>15</sup> It means that a relatively low B' value of the B<sub>28</sub> phase is robust and confirmed by independent measurements.

We now turn to our theoretical results. To establish a consistency between our approach and earlier theoretical calculations, <sup>14,15,17</sup> we first determined the ground-state parameters of the B<sub>28</sub> phase from the static total energy calculations using the volume-energy set (with relaxed atomic positions at a given volume) in the pressure range up to 40 GPa. The equilibrium volume  $V_0$  was found to be 195.43 Å<sup>3</sup>, the bulk modulus (*B*) 225 GPa, and its pressure derivative (*B'*) 3.26. They compare well to earlier theoretical results (see Table I).

Calculated phonon-dispersion relations for  $B_{28}$  reveal its dynamical stability at all volumes considered in this study, corresponding to the pressure range up to 40 GPa. This is illustrated in Fig. 1 by the phonon spectra calculated at the static theoretical equilibrium volume, 195.43 Å<sup>3</sup> [Fig. 1(a)] and at a volume of 169.74 Å<sup>3</sup> [corresponding to pressure ~40 GPa, Fig. 1(b)]. Both calculations do not show any softening of acoustic modes. Our calculated phonon-dispersion relations for  $B_{28}$  at ambient conditions are in good agreement



FIG. 1. (Color online) Phonon-dispersion relations (left panels) and phonon density of states (right panels) in  $B_{28}$  calculated at static theoretical equilibrium volumes, 195.43 Å<sup>3</sup> (a) and 169.74 Å<sup>3</sup> (b), corresponding to pressure ~40 GPa.

with those provided in the supplementary information for Ref. 14. The main difference between our phonon DOS and the one from Ref. 14 is the lack of a small gap around 1100 cm<sup>-1</sup> in our calculations and a more smooth phonon DOS in Ref. 14, which likely comes from different integration methods used. Certain peculiarities can be observed in the behavior of the phonon spectrum. In particular, one should note almost constant lower-lying modes along the *X*-*S*-*Y* direction [Fig. 1(a)]. Phonon modes with frequencies around 850 and 920 cm<sup>-1</sup> are almost dispersionless. The highest three optical modes are Einstein-like ones and the last mode is related to bond-stretching vibrations of two *B*3-type (Wyckoff position 4g, see Table I in Ref. 15) boron atoms located on the fivefold rotation axis of an icosahedra shell.

The calculated phonon DOS was used to obtain the contribution from the lattice vibration to the Helmholtz free energy, which in turn allowed us to obtain the theoretical EOS of  $B_{28}$  including the zero-point motion and finite-temperature effects.<sup>24</sup> This is compared to our new experimental data in Fig. 2, where the EOS from the static total energy calculations and experimental data from the literature are also presented for completeness. One can see that at any pressure, theoretical volumes obtained by means of the static total energy calculations are lower than the experimental ones. However, the disagreement is almost completely eliminated if the phonon contribution to the free energy is included. In particular, the calculated equilibrium volume obtained from the free energy at temperature 300 K, 197.54 Å<sup>3</sup>, is in excellent agreement with the experimental value 198.1(3) Å<sup>3</sup>. We note here that most of



FIG. 2. (Color online) Equation of state of  $B_{28}$  for pressures up to 40 GPa. Theoretical results are obtained from free energies at 300 K (red solid line) and at 0 K including the effect of lattice vibrations (black dashed line). Experimental results of this work (green squares) are obtained on single crystals. Also shown are theoretical results from static total energy calculations (dark-green dashed-dotted line), experimental data for powder in Ne from Ref. 15 (red circles), as well as experiment on polycrystalline samples from Ref. 16 (blue diamonds).

the effect comes from the inclusion of the zero-point motion (see Fig. 2). This is a remarkable result, as it is often assumed that this contribution can be safely neglected in theoretical calculations of the EOS. Here we demonstrate that in light elements like boron, this common belief is clearly incorrect. We note also that an incorrectly defined theoretical volume would yield a pressure error of about several GPa on the theoretical EOS.

We have also made a theoretical estimation to justify the validity of results obtained in our direct first-principles conclusions. For this purpose, a volume correction due to the zero-point motion contribution to the free energy was found using the averaged Grüneisen parameter  $\gamma$  by means of the Debye theory and integrating mode Grüneisen parameters  $\gamma_{nk}$ over the Brillouin zone. The averaged value of the Grüneisen parameter, obtained by both methods, turned out to be 1.01, i.e., the Debye model works fine for  $B_{28}$  at low temperatures (from the phonon calculations, we found the Debye temperature for  $B_{28}$  to be 1250 K). We note that the linear dependence of the zero-point motion contribution to the free energy on the cell volume, used in Ref. 28, is incorrect, as this would mean a negative value of the Grüneisen parameter. Using the calculated Grüneisen parameter ( $\gamma = 1.01$ ), the zero-point vibration energy at P = 0 GPa (~0.245 Ry/cell), and the bulk modulus from static total energy calculations (225 GPa), we obtain the volume correction,  $\Delta V \approx 2.6 \text{ Å}^3$ , that in combination with static volume 195.43  $\text{\AA}^3$  gives 198.03  $Å^3$ , in exciting agreement with our single-crystal experiment as well as with results of our direct ab initio calculations.

To illuminate the qualitative influence of the lattice vibrations on the EOS of  $B_{28}$ , we note that the EOS in the considered pressure range is anomalously linear (though a small deviation from the linear behavior does occur). This is in full accordance with our experimental results, also shown in Fig. 2. On the contrary, the EOS from the static total energy calculations in the same pressure range shows more conventional behavior with considerable deviations from the linear dependence. Consequently, the peculiar behavior of the EOS is reflected in the bulk modulus and its pressure derivative B' for  $B_{28}$ . The calculated bulk modulus, 241 GPa, is slightly larger than the value 227 GPa from Ref. 15, and it agrees quite well with the experimental value of 237.5 GPa obtained in this work and by Le Godec et al.<sup>16</sup> More importantly, it increases upon the inclusion of the lattice vibrations in the simulations. Moreover, in agreement with the anomalously linear behavior of the EOS, the calculated B', 2.34, decreases greatly in comparison with the value 3.26 obtained in static calculations, and attains very good agreement with the experimental value 2.5 obtained for the single crystal of  $B_{28}$  in this work, as well as with the value 2.2 obtained earlier in Ref. 15. In addition, we have calculated B' using different forms of the EOS, the Murnaghan, the natural strain, and the universal EOS, as they are implemented in the EOS code of the Elk project.<sup>29</sup> We have found that the results are very similar, within  $\sim 10\%$ , to B' values 3.26 and 2.34 for the static EOS and the EOS at 300 K, respectively, obtained using the third-order Birch-Murnaghan fitting.<sup>27</sup> Therefore, the reduction of B' upon the inclusion of lattice vibrations in the simulations is a real physical effect, which does not depend on the form of EOS used to fit the data. We would like to note that the observed anomalous pressure-volume relation for the  $B_{28}$  phase in the low-pressure interval indicates that any experimental investigation of this phase of boron should have a good sampling of experimental points between 0 and 40 GPa.

In summary, we have performed accurate measurements and *ab initio* calculations of the EOS for the B<sub>28</sub> phase up to 40 GPa including the effect of lattice vibrations, and we determined its ground-state parameters (volume, bulk modulus, and its pressure derivative). Considering the free energy rather than the static total energy in our theory substantially improves agreement with experiment. In particular, properly accounting for the phonon contribution, we obtain a higher value for the theoretical equilibrium volume and we observe anomalously linear pressure-volume relations in our calculations. This leads to a substantially reduced value of B' in the low-pressure range (<40 GPa) and resolves the disagreement between earlier theoretical calculations and experiment. We conclude that the ground-state parameters of  $B_{28}$  are strongly affected by atomic vibrations, an effect that is often neglected in theoretical simulations. In general, our results indicate that vibrational effects should be included in theoretical calculations of the EOS for solids, at least in cases of light elements.

We are grateful to A. Polian, whose question stimulated this study. The Swedish Research Council (VR), the Swedish Foundation for Strategic Research (SSF) MS<sup>2</sup>E Strategic Research Center, and the Göran Gustafsson Foundation for Research in Natural Sciences and Medicine are acknowledged for financial support. E.I.I. also thanks RFBR. Calculations were performed at the Swedish National Infrastructure for Computing (SNIC).

- <sup>1</sup>U. Haussermann, S. I. Simak, R. Ahuja, and B. Johansson, Phys. Rev. Lett. **90**, 065701 (2003).
- <sup>2</sup>D. N. Sanz, P. Loubeyre, and M. Mezouar, Phys. Rev. Lett. **89**, 245501 (2002).
- <sup>3</sup>B. Siberchicot, Phys. Rev. B 79, 224101 (2009).
- <sup>4</sup>Y. Ma, C. T. Prewitt, G. Zou, H.-k. Mao, and R. J. Hemley, Phys. Rev. B **67**, 174116 (2003).
- <sup>5</sup>A. Polian, J. C. Chevrin, P. Munsch, and M. Gauthier, J. Phys.: Conf. Ser. **121**, 042017 (2008).
- <sup>6</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>7</sup>M. I. Eremets, V. V. Struzhkin, H.-k. Mao, and R. J. Hemley, Science 293, 272 (2001).
- <sup>8</sup>M. Calandra, N. Vast, and F. Mauri, Phys. Rev. B 69, 224505 (2004).
- <sup>9</sup>D. A. Papaconstantopoulos and M. J. Mehl, Phys. Rev. B **65**, 172510 (2002).
- <sup>10</sup>Y. Ma, J. S. Tse, D. D. Klug, and R. Ahuja, Phys. Rev. B **70**, 214107 (2004).
- <sup>11</sup>R. H. Wentorf, Science **147**, 49 (1965).
- <sup>12</sup>V. L. Solozhenko, O. O. Kurakevych, and A. R. Oganov, J. Superhard Mater. **30**, 428 (2008).
- <sup>13</sup>E. Yu. Zarechnaya *et al.* Sci. Tech. Adv. Mater. **9**, 044209 (2008).

- <sup>14</sup>A. R. Oganov *et al.*, Nature (London) **457** 863 (2009). See also supplementary information for the paper.
- <sup>15</sup>E. Yu. Zarechnaya et al. Phys. Rev. Lett. 102, 185501 (2009).
- <sup>16</sup>Y. Le Godec *et al.* Solid State Commun. **149**, 1356 (2009).
- <sup>17</sup>C. Jiang, Zh. Lin, J. Zhang, and Y. Zhao, Appl. Phys. Lett. **94**, 191906 (2009).
- <sup>18</sup>E. Yu. Zarechnaya, N. Dubrovinskaia, L. Dubrovinsky, Y. Filinchuk, D. Chernyshov, and V. Dmitriev, J. Cryst. Growth **312**, 3388 (2010).
- <sup>19</sup>P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W. Kohn and L. J. Sham, *ibid*. **140**, A1133 (1965).
- <sup>20</sup>P. Giannozzi et al. J. Phys. Condens. Matter 21, 395502 (2009).
- <sup>21</sup>D. Vanderbilt, Phys. Rev. B **41**, R7892 (1990).
- <sup>22</sup>J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
- <sup>23</sup>R. M. Wentzcovich, Phys. Rev. B 44, 2358 (1991).
- <sup>24</sup>E.I. Isaev, QHA project, [http://qe-forge.org/qha].
- <sup>25</sup>E. I. Isaev, N. V. Skorodumova, R. Ahuja, Yu. K. Vekilov, and B. Johansson, Proc. Natl. Acad. Sci. USA **104**, 9168 (2007).
- <sup>26</sup>M. J. van Setten, M. A. Uijttewaal, G. A. de Wijs, and R. A. de Groot, J. Am. Chem. Soc. **129**, 2458 (2007).
- <sup>27</sup>F. Birch, Phys. Rev. **71**, 809 (1947).
- <sup>28</sup>J. Y. Zhang et al. J. Phys. Condens. Matter **19**, 425218 (2007).
- <sup>29</sup>Elk project, [http://elk.sourceforge.net].