PRL **102,** 185501 (2009) PHYSICAL REVIEW LETTERS week ending 8 MAY 2009

Superhard Semiconducting Optically Transparent High Pressure Phase of Boron

E. Yu. Zarechnaya,[1] L. Dubrovinsky,[1] N. Dubrovinskaia,[2,3] Y. Filinchuk,[4] D. Chernyshov,[4] V. Dmitriev,[4] N. Miyajima,[1] A. El Goresy,[1] H. F. Braun,[5] S. Van Smaalen,[3] I. Kantor,[6] A. Kantor,[6] V. Prakapenka,[6] M. Hanfland,[7] A. S. Mikhaylushkin,[8] I. A. Abrikosov,[8] and S. I. Simak[8]

[1]*Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany*
[2]*Mineralphysik, Institut für Geowissenschaften, Universität Heidelberg, 69120 Heidelberg, Germany*
[3]*Lehrstuhl für Kristallographie, Physikalisches Institut, Universität Bayreuth, 95440 Bayreuth, Germany*
[4]*Swiss-Norwegian Beam lines at ESRF, 38043 Gernoble, France*
[5]*Experimentalphysik V, Physikalisches Institut, Universität Bayreuth, 95440 Bayreuth, Germany*
[6]*GeoSoilEnviroCARS, University of Chicago, 5640 South Ellis, Chicago, Illinois 60637, USA*
[7]*ESRF, Boîte Postale 220, 38043 Grenoble, France*
[8]*Department of Physics, Chemistry and Biology, Linköping University, SE-581 33 Linköping, Sweden*
(Received 16 January 2009; published 7 May 2009)

An orthorhombic (space group *Pnnm*) boron phase was synthesized at pressures above 9 GPa and high temperature, and it was demonstrated to be stable at least up to 30 GPa. The structure, determined by single-crystal x-ray diffraction, consists of B_{12} icosahedra and B_2 dumbbells. The charge density distribution obtained from experimental data and *ab initio* calculations suggests covalent chemical bonding in this phase. Strong covalent interatomic interactions explain the low compressibility value (bulk modulus is $K_{300} = 227$ GPa) and high hardness of high-pressure boron (Vickers hardness $H_V = 58$ GPa), after diamond the second hardest elemental material.

DOI: 10.1103/PhysRevLett.102.185501 PACS numbers: 61.66.−f, 61.50.Ks, 62.20.D−, 62.50.−p

Pure boron is one of the most enigmatic elements. Boron's three valence electrons are too localized to make it metallic but insufficient in number to form a simple covalent structure. As a compromise, boron atoms form quasimolecular B_{12} icosahedra that become building blocks of boron and boron-rich crystalline phases [1]. Several dozens of possible crystalline boron phases have been proposed in the literature, but most of them proved to be borides or to be stabilized by a small amount of impurities. Only α- (high-temperature form, rhombohedral, 12 atoms per a unit cell) and β-boron (rhombohedral, structure is not fully understood and consists of 105 or 108 atoms in the unit cell) are established as pure boron crystalline forms [2–4]. The existence of "tetragonal boron" as a modification of pure elemental boron or as a boron-rich nitride or carbide has been a subject of controversy [5,6]. In addition, elemental boron exists in amorphous forms of different purity prepared by various techniques [7,8]. On compression of a β-boron single crystal at room temperature to 100 GPa, amorphization was observed [9]. Energy-dispersive x-ray powder diffraction experiments in laser-heated diamond anvil cells (DACs) suggest that β-boron is stable up to 30 GPa and 3500 K, and above these conditions a phase transition to the tetragonal "T-192" structure occurs [10]. Resistivity measurements demonstrate metallization of boron and the occurrence of a superconducting state at about 160 GPa [11]. However, the crystal structure of metallic boron is not known. Theoretical studies predict the transformation of α-boron into a phase with the α-Ga structure, accompanied by an insulator-metal transition [12].

In 1965, Wentorf [13] 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 [14,15]. The structure of a high-pressure boron phase was solved from powder x-ray diffraction data [15] and found theoretically [14,16]. The high-pressure boron form has orthorhombic symmetry, and its unit cell contains 28 atoms, so we designate it as B_{28}. Here we report the results of single-crystal x-ray diffraction studies of B_{28} which, along with the results of our theoretical *ab initio* calculations, allow us to unambiguously conclude that the nature of chemical bonding in this phase is covalent. Additionally, we demonstrate that B_{28} is a wide band gap semiconductor, is superhard, has low compressibility, and is stable at least to 30 GPa at high temperatures.

Although polycrystalline B_{28} is known [13] and has just attracted substantial attention [14–16], so far single crystals of this phase were not synthesized. Using a large-volume press, at 20 GPa and 1700 K we have grown elongated prismatic dark-red crystals with sizes of about $6 \times 6 \times 25\ \mu m^3$. The crystals are mixed with platinum boride (PtB), which appeared due to a reaction of boron with a platinum capsule (see Ref. [17], methods). We confirmed the purity of B_{28} crystals by chemical analysis, collected single-crystal x-ray diffraction data (Ref. [17], single-crystal diffraction), and refined the crystal structure (Table I). There is remarkable agreement between structural parameters (Table I) obtained from single-crystal and powder x-ray diffraction data and those from our *ab initio* calculations [18]. The *bc* projection [Fig. 1(a)] shows that

TABLE I. Crystal structure data of orthorhombic B_{28} (space group *Pnnm*, $Z = 28$) at ambient conditions, obtained from powder and single-crystal x-ray diffraction data and from *ab initio* calculations.

	Powder diffraction [15]	Single-crystal diffraction	*Ab initio* calculations
a, Å	5.0563(4)	5.0576(4)	5.04
b, Å	5.6126(5)	5.6245(8)	5.61
c, Å	6.9710(7)	6.9884(10)	6.92
V, Å^3	197.83(4)	198.80(4)	196.0
B1 8 h	0.162(2), 0.599(2), 0.794(9)	0.1539(3), 0.5938(2), 0.7924(2)	0.15, 0.59, 0.79
B2 4 g	0.645(2), 0.725(2), 0.5	0.6469(4), 0.7284(4), 1/2	0.65, 0.73, 0.5
B3 4 g	0.335(2), 0.505(2), 0.0	0.3362(4), 0.5076(4), 0	0.34, 0.51, 0.0
B4 8 h	0.837(2), 0.719(1), 0.870(1)	0.8391(3), 0.7189(3), 0.8737(2)	0.84, 0.72, 0.87
B5 4 g	0.669(2), 0.986(2), 0.0	0.6690(4), 0.9823(4), 0	0.67, 0.98, 0.0
R factors	$wRp = 6.5\%$, $Rp = 5.5\%$	$R_1 = 3.73\%$, $wR_2 = 11.5\%$	

the structure is built of B_{12} icosahedra and B_2 dumbbells linked together, thus forming a three-dimensional network. According to single-crystal x-ray diffraction data, the distances B-B within a B_{12} icosahedron [1.766(3)–1.880(3) Å] are slightly longer than those within a dumbbell [1.721(4) Å]. The shortest distances in the structure are those between atoms linking (i) two icosahedra—1.659(4) Å, (ii) an icosahedron and a dumbbell—1.669(3) Å, and (iii) two boron atoms within the dumbbell—1.721(4) Å. Chemical bonds within B_2 dumbbells and B_{12} icosahedra, as well as between an icosahedron and a dumbbell, are strongly covalent, as is evident from the presence of residual electron density peaks (0.53 and 0.40 $e/\text{Å}^3$, respectively) in the difference Fourier maps. Enhanced electron densities of similar magnitudes have been obtained in the same bonding regions using the maximum entropy method [19] applied to the single-crystal x-ray diffraction data, thus confirming the strong covalent bonding character of these contacts.

Ab initio calculations also suggest strong charge density redistributions due to interactions of the boron atoms constituting the B_{28} phase which lead to an increase of the charge density around the lines connecting boron atoms, i.e., to formation of covalent or polar covalent bonds. Also, the calculated electronic density of states projected onto B_2 dumbbells and B_{12} icosahedra (Fig. 2) shows very strong hybridization, typical for the predominantly covalent bonds. Moreover, the calculated electron localization function [20,21] between the boron atoms [Fig. 1(b)] has a high value (about 0.9 at its maximum in the dumbbells-icosahedra bond), a characteristic feature of strong covalent bonding. Oganov *et al.* [16] reported results of theoretical studies on the orthorhombic B_{28} high-pressure phase suggesting that the material is an ionic boron boride $(B_2)^{\delta+}(B_{12})^{\delta-}$. Our experimental single-crystal structural data and theoretical results do not confirm this model.

Calculated from structural data, the density of the B_{28} phase is 2.54(1) g/cm^3, which is about 1% higher than densities of known (α-, β-, "tetragonal") boron modifications [1–4]. This is not surprising, because only B_{28} contains additional B atoms in an intericosahedral space (although in β-boron there are probably interstitial defect atoms). The increased density of B_{28} indicates that it may be stable at high pressure. Figure 3 summarizes the results of the multianvil quenched and *in situ* DAC experiments dedicated to studies of the relative stability of β-boron and B_{28}. At pressures below ~8.5 GPa, only β-boron was

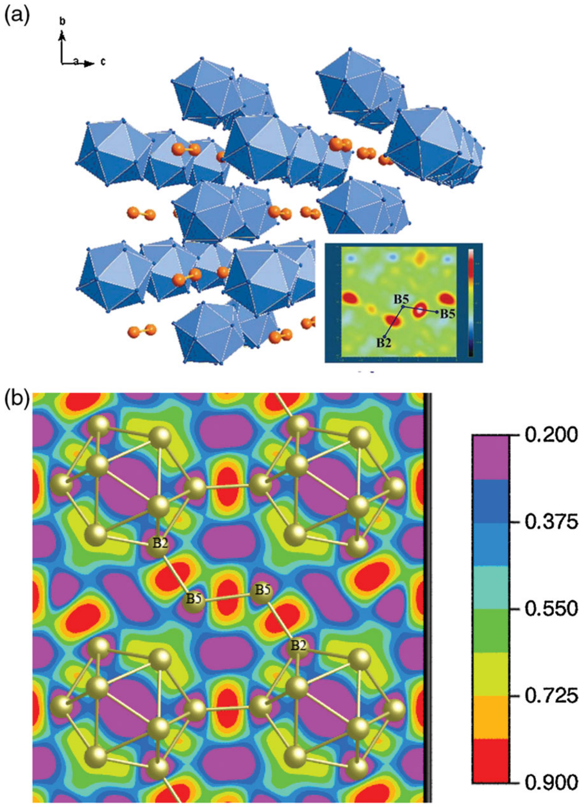

FIG. 1 (color). (a) The structure of B_{28} shown in the *bc* projection. The inset shows difference electron density plots around the atoms B5 (dumbbell) and B2 and B5 (dumbbell-icosahedron contact) extracted from experimental single-crystal x-ray diffraction data. The maximum electron density is centered in the middle of the bond, suggesting covalent bonding between the B_2 dumbbell and the B_{12} icosahedron. (b) The calculated electron localization function in the plane through the dumbbell and dumbbell-icosahedra contacts.

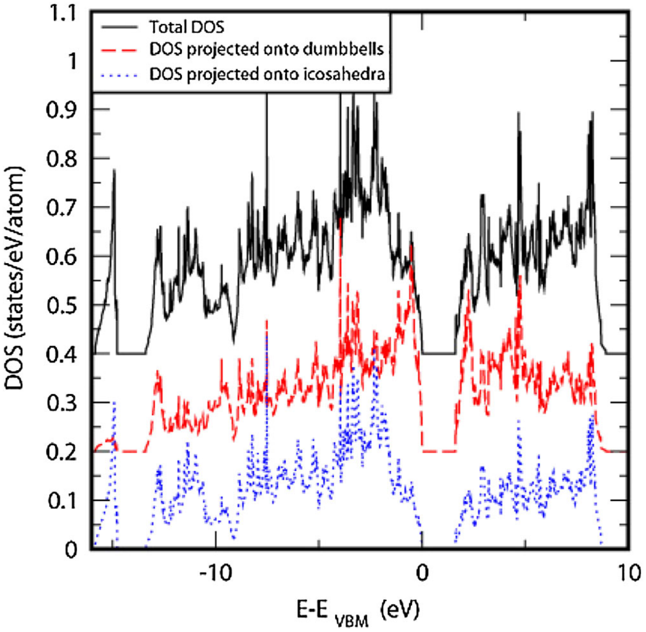

FIG. 2 (color online). Calculated total density of states (solid black line) as well as local density of states at boron atoms in the dumbbells (B_2) (dashed red line) and at boron atoms in the icosahedra (B_{12}) (dotted blue line). The energy is given with respect to the valence band maximum (VBM). For clarity, the three graphs are shifted with respect to each other by a constant shift.

observed in good agreement with previous reports [4,13,15]. At higher pressures we observed a formation of the orthorhombic phase found in both quenched products and *in situ* experiments by means of Raman spectroscopy and x-ray diffraction. If the B_{28} phase synthesized in a DAC at pressures above 10 GPa is reheated by a laser at pressures below 7 GPa, it completely transforms back to β-boron thus confirming reversibility of the phase transition (Fig. 3). In agreement with experiment, *ab initio* calculations suggest that orthorhombic boron is more stable than α-boron at pressures above about 20 GPa, and on further compression it might transform into the α-Ga-type phase at about 88 GPa.

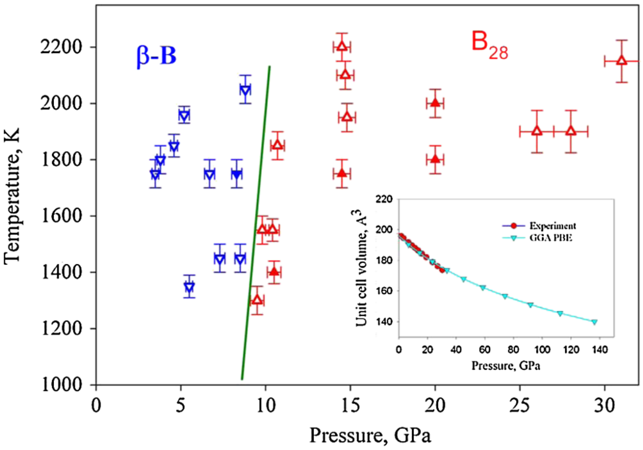

FIG. 3 (color online). Phase relations between β-boron (blue inverse triangles) and B_{28} (red triangles) based on the results of the multianvil quenched (solid symbols) and *in situ* DAC (open symbols) experiments. The line is a tentative phase boundary between β-boron and the orthorhombic phase. The inset shows the experimental [$K_{300} = 227(2)$ GPa, $K' = 2.2(2)$, $V_0 = 197.44(2)$ A^3] and calculated [$K_0 = 221.7(7)$ GPa, $K' = 3.6(3)$, $V_0 = 195.97$ A^3] pressure dependence of the molar volume of the orthorhombic B_{28} boron phase.

The higher density and strong covalent bonding in B_{28} suggest that it could be less compressible than other known boron phases. The compression experiment (inset in Fig. 3) up to ~30 GPa in a DAC with Ne as a pressure transmitting medium and a powder of B_{28} presynthesized in a multianvil press gave values of the bulk modulus of $K_{300} = 227(2)$ GPa and its pressure derivative $K' = 2.2(2)$ [the molar volume was fixed at the value of $V = 197.44(3)$ Å^3/unit cell measured at ambient conditions]. *Ab initio* simulations (Fig. 3, inset) give $K_0 = 221.7(7)$ GPa, $K' = 3.6(3)$, and $V_0 = 195.97(6)$ A^3. The value of K' we obtained experimentally is notably lower but in accordance with the data of Sanz, Loubeyre, and Mezouar [9] for β-boron. The values of the bulk moduli reported in literature for α- and β-boron are in the range of 185–213 GPa [9,10,22] that is lower than the value we obtain for the B_{28} phase. The experimental data are too limited to discuss a mechanism of compressibility, but both high-pressure x-ray powder diffraction and theoretical calculations show (Ref. [17], Fig. S1) that the least compressible direction is the *a* axis, along which there are shortest contacts (and stronger covalent bonding) between B_{12} icosahedra and B_2 dumbbells, while compression along *b* and *c* axes (normal to the channels hosting B_2 dumbbells) is easier.

In a thin section, both polycrystalline samples and B_{28} single crystals are transparent and have a red color (Fig. 4). The optical absorption edge of the orthorhombic boron phase, measured by the near-infrared and optical absorption spectroscopy, is equal to 2.1 eV (Ref. [17], methods). As usual, the first-principles calculations underestimate the band gap, so the obtained theoretical value of 1.7 eV (see Fig. 2) is in reasonable agreement with experiment. Assuming that the optical absorption is due to excitations across the band gap, we can apply an empirical rule that an indirect edge is generally well approximated by a linear relationship between the square root of the adsorption coefficient and phonon energy [23]. Although this is true in a narrow region (about 0.2 eV) above the absorption edge, the optical spectra (Fig. 4) are too noisy to draw any firm conclusion regarding the nature (direct or indirect) of the band gap. However, theoretical calculations predict an indirect band gap (Ref. [17], Fig. S2).

Pure orthorhombic B_{28} is a poor electrical conductor with a resistivity of the order of 10^6 Ω cm at ambient conditions. With increasing temperature, the resistivity decreases indicating semiconducting behavior (Ref. [17],

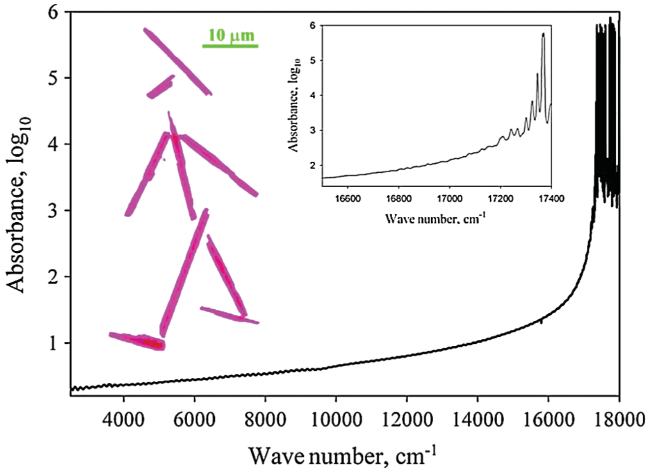

FIG. 4 (color). Absorbance of the orthorhombic B_{28} phase as determined by the near-infrared and optical absorption spectroscopy for a doubly polished slice of the sample with a thickness of 10 μm. The inset on the right gives an enlarged view of the near-edge spectrum. The inset on the left shows a microphotograph of single crystals of B_{28} in transmitted light.

Fig. S3). The activation energy [1.9(2) eV] is in reasonable agreement with the value of the band gap energy determined from optical spectroscopy measurements.

Boron is known as a hard material (with the Vickers hardness reported as high as 25–30 GPa [24] for β-boron). We measured the Vickers microhardness of the orthorhombic boron phase in an asymptotic-hardness region (load up to 10 N) as recommended for hard and brittle materials and as described in our previous publications [25,26]. We found that samples with submicron grain sizes synthesized at 14 GPa and 1700 K in an indium medium have a hardness of 58(5) GPa (Ref. [17], Fig. S4). This value is in the range of polycrystalline cBN [24] that makes B_{28} the second hardest elemental solid after diamond.

Our study demonstrates that the orthorhombic high-pressure high-temperature boron phase, synthesized above 9 GPa, has a new structure type, consists of covalently bonded B_{12} icosahedra and B_2 dumbbells, and combines unusual properties—it is a wide band gap semiconductor that is superhard, optically transparent, and thermally stable (above 1000 K in air). We have proved the possibility to grow single crystals of this phase, which opens perspectives for applications of the new material in electronics and optics.

Financial support from the Swedish Research Council (VR), the MS2E Strategic Research Centre, and the Göran Gustafsson Foundation for Research in Natural Sciences and Medicine is gratefully acknowledged. Calculations were performed at Swedish National Infrastructure for Computing (SNIC). Work at Bayreuth was supported by Deutsche Forschungsgemeinschaft (DFG) through the DFG Priority Program No. 1236 and Elite Network Bayern.

[1] K.C. Buschveck, *Boron Compounds, Elemental Boron and Boron Carbides 13, Gmelin Handbook of Inorganic Chemistry* (Springer-Verlag, Berlin, 1981).
[2] G. Will and B. Kiefer, Z. Anorg. Allg. Chem. **627**, 2100 (2001).
[3] G. Will and K. Ploog, Nature (London) **251**, 406 (1974).
[4] V.V. Brazhkin, T. Taniguichi, M. Akaishi, and S.V. Popova, J. Mater. Res. **19**, 1643 (2004).
[5] R. Naslain, in *Boron and Refractory Borides*, edited by V.I. Matkovich (Springer-Verlag, Berlin, 1977).
[6] J.L. Hoard, D.B. Sullenger, C.H.L. Kennard, and R.E. Highes, J. Solid State Chem. **1**, 268 (1970).
[7] K. Katada, Jpn. J. Appl. Phys. **5**, 582 (1966).
[8] J.S. Gillespie, J. Am. Chem. Soc. **88**, 2423 (1966).
[9] D.N. Sanz, P. Loubeyre, and M. Mezouar, Phys. Rev. Lett. **89**, 245501 (2002).
[10] Y. Ma, Ch.T. Prewitt, G. Zou, Ho-kwang Mao, and R.J. Hemley, Phys. Rev. B **67**, 174116 (2003).
[11] M.I. Eremets, V.V. Struzhkin, Ho-kwang Mao, and R.J. Hemley, Science **293**, 272 (2001).
[12] U. Häussermann, S.I. Simak, R. Ahuja, and B. Johansson, Phys. Rev. Lett. **90**, 065701 (2003).
[13] R.H. Wentorf, Science **147**, 49 (1965).
[14] V.L. Solozhenko, O.O. Kurakevych, and A.R. Oganov, J. Superhard Mater. **30**, 428 (2008).
[15] E.Yu. Zarechnaya, L. Dubrovinsky, N. Dubrovinskaia, N. Miyajima, Y. Filinchuk, D. Chernyshov, and V. Dmitriev, Sci. Tech. Adv. Mater. **9**, 044209 (2008).
[16] During the review process of our manuscript, the following paper appeared: A.R. Oganov *et al.*, Nature (London) **457**, 863 (2009).
[17] See EPAPS Document No. E-PRLTAO-102-018921 for additional information on experimental and theoretical methods and results. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.
[18] *Ab initio* simulations were performed using the projector augmented waves method as implemented in the VASP package; see G. Kresse and J. Furthmuller, Phys. Rev. B **54**, 11 169 (1996). We used generalized gradient approximations, up to $12 \times 12 \times 12$ k-points mesh. The energy cutoff was set to 600 eV.
[19] S. van Smaalen, L. Palatinus, and M. Schneider, Acta Crystallogr. Sect. A **59**, 459 (2003).
[20] A.D. Becke and K.E. Edgecombe, J. Chem. Phys. **92**, 5397 (1990).
[21] A. Savin *et al.*, Angew. Chem., Int. Ed. Engl. **31**, 187 (1992).
[22] R.J. Nelmes *et al.*, Phys. Rev. B **47**, 7668 (1993).
[23] R. Zallen and M.P. Moret, Solid State Commun. **137**, 154 (2006).
[24] L.I. Berger, *Semiconductor Materials* (CRC Press, Boca Raton, FL, 1996), p. 472.
[25] V.V. Brazhkin, N. Dubrovinskaia, M. Nicol, N. Novikov, R. Riedel, V. Solozhenko, and Y. Zhao, Nature Mater. **3**, 576 (2004).
[26] N. Dubrovinskaia, V. Solozhenko, N. Miyajima, V. Dmitriev, O. Kurakevych, and L. Dubrovinsky, Appl. Phys. Lett. **90**, 101912 (2007).