

On the Structural Effect of the Insertion of Carbon Atoms in B₁₂ Icosahedra

Helmut WERHEIT*), Udo KUHLMANN*), and Torsten LUNDSTRÖM†)

Solid State Physics Laboratory, University of Duisburg, Lotharstr. 1 - 21, D 47048 Duisburg, Germany)*

Institute of Chemistry, Uppsala University, S 75121 Uppsala, Sweden†)

X-ray diffraction of β -rhombohedral boron doped with up to 1 at.% carbon and a model calculation of the anisotropic distortion of the single icosahedron were carried out. The carbon atoms substitute for boron in the polar sites of the B₁₂ icosahedra. The carbon atom is shifted by 0.115 Å (6.5%) towards the center of the icosahedron. In boron carbide the distortion of the unit cell of boron carbide $\parallel c$ exceeds that of the icosahedron by far, while for the a axis the distortions are similar and twice that of the distortion in β -rhombohedral boron. The effect of chainless elementary cells on the distortion is evident; the effect of an electron-phonon interaction seems possible.

KEYWORDS: β -rhombohedral boron, boron carbide, icosahedra, crystal structure, carbon-doping

1. Introduction

The icosahedra are responsible for the basic properties of the boron-rich solids. The icosahedra are not regular but distorted in consequence of the static Jahn-Teller effect, which modifies the electronic properties by splitting the orbitals determining the uppermost valence bands^{1,2,3}.

By electron diffraction on gaseous 1,12-Dicarbido-dodecarborane with two carbon atoms on opposite sites in the icosahedron Bohn and Bohn⁴) showed that the diameter of the icosahedron between the diametrically arranged carbon atoms is about 10% shorter than between opposite boron atoms. Based on the meanwhile disproved model of bipolarons in boron carbide Howard et al.⁵) calculated that the carbon atom is shifted towards the center of the icosahedron by 0.09 Å (5.3%). Abbot and Beckel⁶) calculated a radius reduction by 10%.

According to⁴⁻⁶) not more than one carbon atom can substitute for boron in one icosahedron. Below, the anisotropic shrinkage of the B₁₂ icosahedra is estimated from the anisotropic modifications of the unit cell parameters of β -rhombohedral boron and boron carbide.

2. Results

2.1 B₁₂ icosahedron

In D_{3d} symmetry the icosahedra (approximately assumed to be regular) have three five-fold rotation axes determined by the polar atoms of the icosahedron. These axes form angles of $\varphi_p = 37.4$ degrees with the c axis e.g. in β -rhombohedral boron and boron carbide. Three five-fold rotation axes determined by the equatorial atoms inclined by 10.5 degrees against the plane formed by the a and b axes of the structures, and they form angles of $\varphi_e = 79.5$ degrees with the c axis. Hence anisotropic changes of the crystal axes are expected to give evidence of the preferential substitution of polar or equatorial sites of the icosahedra. We ignore distortions of the icosahedra of other kind, e.g. by the static Jahn-Teller effect¹⁻³) and assume movements of neighbored atoms to be of secondary order in agreement with the phonon spectra.

Replacing the icosahedron approximately by a sphere, the effect of this distortion on the c axis is proportional to $\cos \varphi$, and the effect on the a axis proportional to $\sin \varphi$. Since only one atom of the polar triangle is substituted, the

effective change of the diameter, which coincides with the c axis is related to the shift ΔR of the substituted atom by

$$(\Delta c)_{p(icos)} = \Delta R \frac{\cos \varphi_1}{3}$$

For the effect on the a axis averaged according to the threefold symmetry one gets

$$(\Delta a)_{p(icos)} = \Delta R \frac{\sin \varphi_1}{3}$$

and an improved model (see 7)) leads to

$$(\Delta a)_{p(icos)} = \Delta R (\sin \varphi / 3) \cdot \cos 15.2^\circ \cdot \cos 20.85^\circ$$

Accordingly the relation $\Delta c / \Delta a$ determined by the anisotropic effect on the crystallographic parameters for the substitution on a polar site ($\varphi_1 = 37.4^\circ$) yields:

$$(\Delta c / \Delta a)_{p(icos)} = 1.31 \text{ (improved model 1.45).}$$

For the substitution of an equatorial site in the icosahedron ($\varphi_2 = 79.5^\circ$), one gets

$$\begin{aligned} (\Delta c)_{e(icos)} &= \Delta R \cdot \cos \varphi_2 / 3 \\ (\Delta a)_{e(icos)} &= \Delta R \cdot 1/2 \cdot \sin \varphi_2 / 3 \end{aligned}$$

and for the improved approximation

$$(\Delta a)_{e(icos)} = \Delta R \cdot 1/2 \cdot \sin \varphi_2 / 3 \cdot \cos 15.2^\circ \cdot \cos 20.85^\circ$$

Hence for the substitution of carbon for boron on an equatorial site ($\varphi_2 = 79.5^\circ$) one gets:

$$(\Delta c / \Delta a)_{e(icos)} = 0.37 \text{ (improved model 0.41).}$$

If hypothetically all 12 sites of the icosahedron are substituted for by carbon, the total distortion would be isotropic ($\Delta c / \Delta a = 1$). The deviation of 16%, and 7% respectively for the improved model only allows to use these values to check the experimentally determined unit cell parameters of β -rhombohedral boron and boron carbide.

2.2 β -rhombohedral boron

In the crystal structure of β -rhombohedral boron the effect of the distortion of the single icosahedron on the unit cell parameters depends on the position of the icosahedra in the elementary cell and the distribution of the carbon atoms

on the different sites within the icosahedra. The results of many model calculations⁷⁾ were compared with the experimentally measured change of the unit cell parameters obtained by X-ray diffraction. From Ref. 8 (figure 1) one gets for 1% carbon content:

$$\begin{aligned}\Delta c &= -0.016(5) \\ \Delta a &= -0.0105(15) \\ (\Delta c/\Delta a)_{\beta\text{-rh. B (exp.)}} &= 1.52\end{aligned}$$

The best agreement by far is based on the assumption that carbon atoms substitute for boron in the polar sites of the four B₁₂ icosahedra only, and yields

$$(\Delta c/\Delta a)_{p(\beta\text{-rh. B/B}_{12})} = 1.31 \text{ (improved model 1.45)}$$

and confirms this carbon distribution in β -rhombohedral boron. Within the accuracy of the model calculation estimate the averaged shift ΔR of a carbon atom towards the center of an icosahedron of β -rhombohedral boron is estimated:

$$\begin{aligned}\Delta R &= 0.115(6) \text{ \AA} \\ \Delta R/R &= 0.067(3)\end{aligned}$$

2.3 Boron Carbide

The structure of boron carbide contains only one B₁₂ icosahedron at the vertex of the unit cell. Therefore the distortions of the icosahedron can be immediately compared with the change of the unit cell parameters experimentally determined^{9,10)}. It is necessary to restrict these consideration to the range close to the carbon-rich limit, where the parameters depend linearly on the carbon content and are to be related to an exchange of 43% B₁₂ by B₁₁C icosahedra^{11,12)}. Of course this is far from the weak perturbation in β -rhombohedral boron.

The relation obtained from these data

$$(\Delta c/\Delta a)_{\text{boron carbide (exp.)}} = 4.38$$

shows, that in boron carbide, too, the distortion parallel to the crystallographic *c* axis is prevailing, hence on the first view suggesting that the polar sites of the icosahedra in boron carbide are preferably substituted as well. Contrary to β -rhombohedral boron, $\Delta c/\Delta a$ exceeds the value expected for the carbon insertion in the icosahedron by far. However, according to the crystallographic data the size of the icosahedron in boron carbide changes only weakly within the part of the homogeneity range considered^{13,14)} and this is in accordance with the small shifts of the IR and the Raman active intraicosahedral phonon frequencies¹⁵⁾. Hence it is obvious that the major part of the anisotropic change of the unit cell parameters in boron carbide is induced from outside the icosahedra. Of course, therefore it is not possible to derive ΔR from the unit cell parameters of boron carbide reliably.

The value of $(\Delta c)_{\text{icos.}}$ is approximately the same for β -rhombohedral boron and boron carbide⁷⁾, and accordingly we take this for indication that the substitution of carbon for boron in the icosahedra of boron carbide takes place at the polar sites as well. Then the large distortion parallel to the *a*

axis must have other reasons outside the icosahedra and may be caused e.g. by the exchange of CBC by CBB chains and in particular by the unit cells without chains at all.

For a more detailed discussion of the different effects on the anisotropical change of the unit cell parameters and on the icosahedra in boron carbide see 7).

Acknowledgements

The authors are grateful to Dr. K.A. Schwetz, ESK, to Dr. D. Fister and H. Neisius, H.C. Starck, for providing specimens, and to Mrs. A.-S. Ullström, Uppsala University, for assistance with syntheses. Parts of the investigations were supported by the Ministry of Research and Technology of the FRG (contract Nr. 317-4003-0328845A). Thanks are also due to the Swedish Natural Science Research Council for financial support.

References

- 1) R. Franz, H. Werheit, *Europhys. Lett.* **9**, 145 (1989).
- 2) H. Werheit, in: R. Freer (editor) *The Physics and Chemistry of Carbides, Nitrides and Borides*, Kluwer Acad. Publ. Dordrecht (1990) p. 677.
- 3) R. Franz, H. Werheit, *AIP Conf. Proc.* **231**, 29 (1990).
- 4) R.K. Bohn and M.D. Bohn, *Inorg. Chem.* **10**, 350 (1971).
- 5) I.A. Howard, C.L. Beckel, D. Emin, *Phys. Rev.* **B 35**, 2929 (1987). I.A. Howard, C.L. Beckel, D. Emin, *Phys. Rev.* **B 35**, 9265 (1987). I.A. Howard, C.L. Beckel, D. Emin, in D. Emin, T.L. Aselage, C. Wood (editors) *Novel Refractory Semiconductors*, MRS Symp. Proc. Vol. 97 (1987), p. 39.
- 6) P.A. Abbott, C.L. Beckel, *Vibrational Analysis of B₄C*. In D. Emin, T. Aselage, A.C. Switendick, B. Morosin, and C.L. Beckel editors) *Boron-Rich Solids*, *AIP Conf. Proc.* **231**, 345 (1990).
- 7) H. Werheit, U. Kuhlmann, T. Lundström, to be published in *J. Alloys Comp.*
- 8) H. Werheit, U. Kuhlmann, M. Laux, T. Lundström, this conference.
- 9) M. Boucacourt, F. Thevenot, *J. Less-Common Met.* **82**, 227 (1981).
- 10) T.L. Aselage, D.R. Tallant, J.H. Gieske, S.B. van Deusen, R.C. Tissot, *Preparation and Properties of Icosahedral Borides*. In R. Freer (editor) *The Physics and Chemistry of Carbides, Nitrides and Borides*, Kluwer Acad. Publ. Dordrecht (1990) p. 97.
- 11) U. Kuhlmann, H. Werheit, *Solid State Comm.* **83**, 849 (1992).
- 12) U. Kuhlmann, H. Werheit, K.A. Schwetz, *J. Alloys Comp.* **189**, 249 (1992).
- 13) T.L. Aselage, D. Emin, *Structural Model of the Boron Carbide Solid Solution*. In sec 19), p. 177.
- 14) A. Kirfel, A. Gupta, G. Will, *Acta Cryst.* **B35**, 1052 (1979).
- 15) U. Kuhlmann, H. Werheit, in preparation.