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3rd Edition

Otfried Madelung

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C Further elements

11 Group III elements

11.0 Crystal structure and electronic structure of boron

The different modifications of elementary boron and the related boron-rich borides exhibit complex structures, which are essentially composed of nearly regular B_{12} icosahedra and of structural elements consisting of fragments or condensed systems of icosahedra. These structure elements are bonded directly to one another or via single boron or foreign atoms thus forming rigid comparably open three-dimensional frameworks with a large variety of structures. In the open structures of all the icosahedral boron-rich solids there are voids of sufficient size to accommodate foreign atoms. This interstitial doping is very important to modify the semiconductor properties of these solids. Only the rhombohedral phases of boron show semiconducting properties.

structure of α-rhombohedral boron

α-rhombohedral boron is the low-temperature modification of elementary boron. It can be prepared at temperatures below about 1200°C only. At this temperature an irreversible transformation to β-rhombohedral boron takes place via three metastable phases. The structure may be considered as a slightly deformed cubic close packing of icosahedra. Space group: $R\bar{3}m$, 12 atoms per unit cell (Fig. 11.0.1)

structure of β-rhombohedral boron

β-rhombohedral boron is the high-temperature, thermodynamically stable crystalline modification of elementary boron. Its unit cell (Fig. 11.0.2) consists of essentially 105 atoms (106.5 atoms, if some additional sites with very low occupation densities are taken into account. The structure formula $(B_{12})_4(B_{28})_2B$ exhibits four icosahedra, one of which is positioned at the vertex, three on the edge centers of the unit cell (both sites are crystallographically inequivalent) and two B_{28} units, which consist of three condensed icosahedra, each, arranged symmetrically to a centered single atom on the main diagonal of the unit cell, which diagonal is parallel to the crystallographic c-axis.

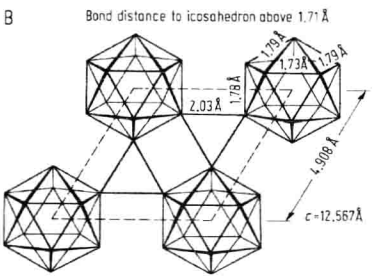


Fig. 11.0.1. B_{12} icosahedra at the corners of the unit cell of α-rhombohedral boron viewed from above.

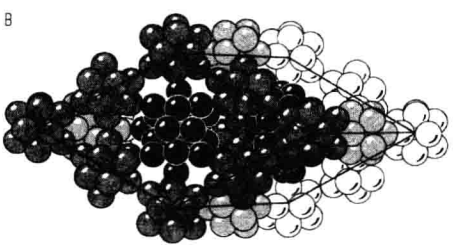


Fig. 11.0.2. Model of the unit cell of β-rhombohedral boron

Fig. 11.0.3 shows the band structure of α-B, Fig. 11.0.4 its Brillouin zone. An energy band scheme for β-B is shown in Fig. 11.0.5.

For details see the following section.

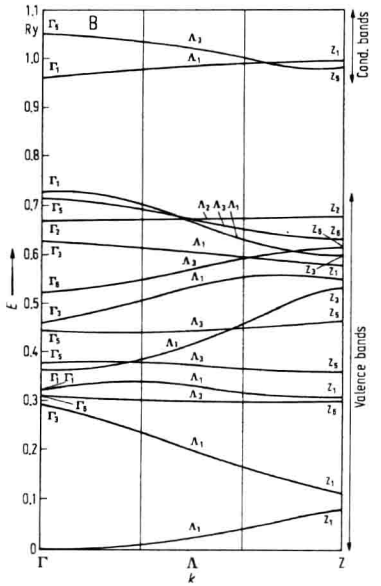


Fig. 11.0.3. Energy band structure along the Γ – Z axis of α-boron.

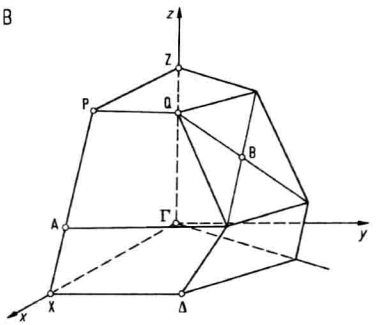


Fig. 11.0.4. Irreduzible part of the Brillouin zone of α-rhombohedral boron.

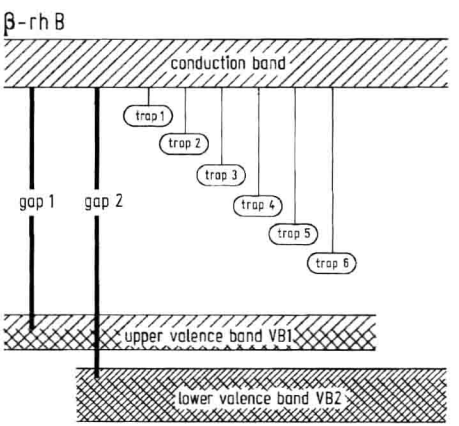


Fig. 11.0.5. β-rhombohedral boron. Widely accepted energy band scheme. The vertical lines indicate the allowed optical transitions between different levels.

11.1 Physical properties of boron

Electronic properties

General remarks

The boron-rich semiconductors with icosahedral structure elements are characterized by largely common features of electronic properties:

a) The semiconducting icosahedral boron-rich solids are not in accordance with the general rule, which holds for crystals with simple periodic structures, that atoms with odd electron numbers are metallic in the condensed state.

b) The band gaps of the boron-rich solids do not depend essentially on the crystal structure.

c) In many cases of icosahedral boron-rich solids a split-off valence band about 0.19 eV above the valence band edge has been found.

d) Icosahedral boron-rich solids are p-type semiconductors. Overcompensation to n-type demands donor densities of the order of 10^{20} cm^{-3}.

e) The electronic transport is composed of band-type conduction and hopping side by side. Depending on temperature or chemical composition the share of both contributions varies.

As essential for the fundamental electronic properties of the icosahedral boron-rich solids the Jahn-Teller effect is assumed, by which the icosahedra are distorted and the electronic levels are split in consequence of the symmetry reduction. This splitting leads to a separation of occupied and unoccupied electronic levels of the isolated icosahedra, and in the solids to a largely unoccupied split-off valence band (see for example β-rhombohedral boron Fig. 11.0.5, p.398). Electronic transport is assumed to take place as a superposition of classical band-type conductivity in the valence band and hopping conductivity within the split-off valence band or by a kind of hopping-like transport in the main valence band due to holes, whose motion is strongly impeded by multiple trapping in occupied states of the split-off valence band.

α-rhombohedral boron

band structure: Fig. 11.0.3 (p.398), Brillouin zone: Fig. 11.0.4 (p.398).

energy gap

E_g	0.73(2) eV	$T = 300$ K	deep level to band (optical absorption)
	1.49(2) eV		deep level to band or
	1.63(2) eV		indirect allowed interband (optical absorption)
	2.055(2) eV		indirect allowed interband (optical absorption)

reduced effective mass

$2m_r/m_0$	0.029		absorption
	0.034		

***g*–factor**

g	2.0036	$T = 77$ K	ESR

β-rhombohedral boron

The actual energy band scheme of pure β-rhombohedral boron (Fig. 11.0.5, p.398) consists of the lower valence band, the split-off valence band (attributed to the Jahn-Teller effect), one conduction band and six equidistant intrinsic electron trapping levels (attributed to the interaction between electrons and specific intraicosahedral phonons) .

energy gap

$E_{g,ind}$	1.32(1) eV	T = 0 K (extrapolated)	$E \parallel c$, opt. absorption, single crystal
	1.29(1) eV	T = 0 K (extrapolated)	$E \perp c$
	1.50 eV	T = 300 K	$E \parallel c$
	1.46 eV		$E \perp c$

temperature dependence of the energy gap

empirical approximation by $E_g(T) = E_g(0) - \alpha T^2$

parameters of the empirically temperature dependence of the energy gap (*Fig. 11.1.1 (CD)*)

α	$3.4(2)\cdot10^{-7}$ K^{-2}eV	$E \parallel c$	for gap 1.32 eV
		$E \parallel c$	for gap 1.50 eV
	$7.8(2)\cdot10^{-7}$ K^{-2}eV	$E \perp c$	for gap 1.29 eV
		$E \perp c$	for gap 1.46 eV

effective masses

m_n	$\approx 4.5\ m_0$	from energy dependence of work
m_p	$\approx 1.8\ m_0$	function
m_n/m_p	≈ 2.5	

Lattice properties

α-rhombohedral boron

lattice parameters

rhombohedral description

a	5.057(3) Å	T = 300 K	precession and Weißenberg method
α	58.06(5)°		

bulk modulus

B	224(15) GPa	T = 300K	single crystal X-ray technique

optical phonons

Group theory gives: IR: 4 A_{2u}, 6 E_u; Raman: 4 A_{1g}, 5 E_g.

phonon wavenumbers, phonon cut-off

$\bar{\nu}$	300 cm^{-1}		acoustic phonon cut-off
	920 cm^{-1}	T = 300 K	one-phonon cut-off

IR-active one-phonon processes

$\bar{\nu}$	548 cm^{-1}	$T = 300$ K	powder absorption
	705 cm^{-1}		
	806 cm^{-1}		
	920 cm^{-1}		
	1080 cm^{-1}?		
	1200 cm^{-1}?		

phonon dispersion curves: *Fig. 11.1.2 (CD)*

β-rhombohedral boron

lattice parameters

rhombohedral description

a	10.145(15) Å	$T = 300$ K	precession and Weißenberg method
α	65°17(8)'		

bulk modulus

B	185(7) GPa	$T = 300$K	neutron powder diffraction

linear thermal expansion coefficient

α_{av}	$6.47 \cdot 10^{-6}$ K^{-1}	$T = 10...1028$ K	average coefficient
α_a	$0.98 \cdot 10^{-6}$ K^{-1}		X-ray diffraction
α_c	$1.82 \cdot 10^{-6}$ K^{-1}		

optical phonons

ir modes: theor. 31 A_{2u}, 52 E_u, exp. 33 A_{2u} 30 E_u. Raman active modes: theor. 31 A_{1g}, 52 E_g, exp. 35 + 5 (uncertain).

phonon wavenumbers, phonon cut-off

$\bar{\nu}$	130 cm^{-1}		acoustic phonon cut-off
	1275 cm^{-1}	$T = 300$ K	one-phonon cut-off
	2200 cm^{-1}	$T = 300$ K	two-phonon cut-off

elastic constants

calculation for α-rhombohedral boron compared with experimental data for β-rhombohedral boron

(c_{ik} in GPa)	α-rhombohedral B Theory (different models)			β-rhombohedral B Theory	Exp.
	(I)	(II)	(III)		
c_{11}	389.5	314.5	323.9	448.38	467
c_{33}	455.1	327.4	333.7	588.90	473
c_{44}	123.1	.0	33.4		198
c_{12}	129.8	130.1	122.4	110.42	241

elastic constants (continued)

c_{13}	123.1	160.8	158.6	41.10	?
c_{14}	− 9.2	.0	− 5.8		15.1
c_{15}				24.49	

Young's modulus

E	up to $48.26 \cdot 10^{10}$ Pa	$T = 300$ K	questionable if β-rhombohedral B

compressibility

κ	$1.8 \cdot 10^{-7}$ bar^{-1}	$T = 300$ K	questionable if β-rhombohedral B

melting temperature

T_m	2365 K		

Debye temperature

Θ_D	1305 K	$T = 400$ K	α-rhombohedral boron
	1430 K	$T = 0$ K	derived
	1540 K	$T = 4...20$ K	β-rhombohedral boron, from heat capacity

heat capacity

C_p	10.21 J mol^{-1} K^{-1}	$T = 298.15$ K	α-rhombohedral boron
	2.879 J mol^{-1} K^{-1}	$T = 300$ K	β-rhombohedral boron

density

d	2.45...2.46 g cm^{-3}	$T = 296$ K	α-rhombohedral boron
	2.326 g cm^{-3}	$T = 293$ K	β-rhombobedral boron, bulk

Transport properties

α-rhombohedral boron

electrical conductivity

σ	$10^{-3}...3.10^{-2}$ (Ωcm)$^{-1}$	T =300 K	extrinsic. see *Fig. 11.1.3 (CD)*

mobility

μ	120 cm^2 (Vs)$^{-1}$	$T = 300$ K	Hall effect

Temperature dependence of the hole mobility: $\mu_H \propto T^{-1.75}$, *Fig. 11.1.4 (CD)*

β-rhombohedral boron

The transport properties of β-rhombohedral boron have not been clarified definitely. They are mainly affected by levels of high concentration in the band gap.

dc conductivity

σ	$10^{-7}...10^{-6}$ (Ωcm)$^{-1}$	T =300 K	intrinsic (see *Fig. 11.1.5 (CD)*)
	up to 20 (Ωcm)$^{-1}$	T =300 K	extrinsic

carrier mobility

μ	$10^{-5}...3 \cdot 10^{2}$ cm^2/Vs	$T = 300$ K	obtained by different methods on samples of
	$10^{-1}...10^{-7}$ cm^2/Vs	$T = 77$ K	different origin and purity
			(see *Fig. 11.1.6 (CD)*)

thermal conductivity

κ	0.01 W cm^{-1} K^{-1}		α-rhombohedral boron

Optical properties

α-rhombohedral boron

optical spectra: absorption: *Fig. 11.1.7 (CD).*

dielectric constant

ε_0	6.5	$T = 300$K	from electron energy-loss

Dielectric function in the range of fundamental absorption derived from the electron energy loss spectrum in *Fig. 11.1.8 (CD).*

β-rhombohedral boron

optical spectra: optical constants of β-rhombohedral boron: *Fig. 11.1.9 (CD).*

dielectric constant

$\varepsilon(0)$	10.6(2)	$T = 300$ K, static	polycrystalline sample
$\varepsilon(\infty)$	9.12(15)		$E \perp c$
	8.41(15)		$E \parallel c$

12 Group V elements

12.0 Crystal structure and electronic structure

12.0.1 Crystal structure and Brillouin zones

Phosphorus:

Phosphorus shows a structural variety exceeded only by sulfur and possibly boron. The most common allotropes are: white, red and black phosphorus and some amorphous forms.

Black phosphorus is the most stable form of the allotropic modifications under standard conditions. It crystallizes in a layered structure with orthorhombic symmetry (Fig. 12.0.1, Brillouin zone: Fig. 12.0.2). The space group is $D_{2h}^{18}(=V_h^{18})$–Bmab. The unit cell of black phosphorus contains eight atoms at the position ± $(0, v, u)$, ± $(1/2, -v, u+1/2)$, ± $(1/2, v+1/2, u)$ and ± $(0, 1/2-v, u+1/2)$. Within the layers, each atom forms three covalent bonds essentially made of 3p orbitals. The layers are connected by weak van der Waals forces.

White phosphorus consists of tetrahedral P_4 molecules. The crystalline α (cubic) and β (hexagonal) modifications have not been fully characterized and are probably rotationally disordered plastic crystal phases.

Red phosphorus is not a single allotrope, but a term used to describe a variety of different forms, which are more or less red in color. The most common form of red phosphorus is amorphous red phosphorus, but powders of tetragonal, triclinic or cubic red phosphorus are also known.

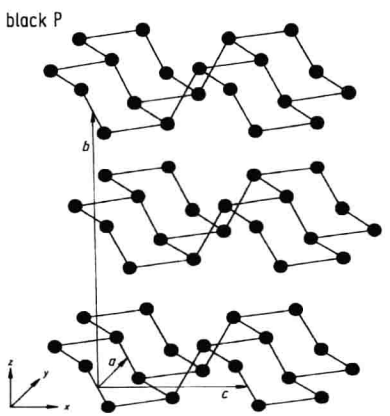


Fig. 12.0.1. Perspective view of the black phosphorus structure

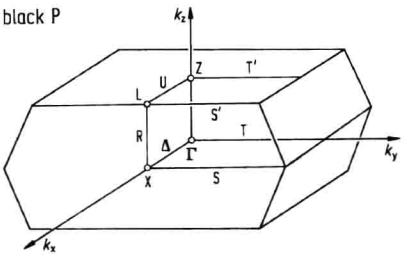


Fig. 12.0.2. Brillouin zone of black phosphorus

Arsenic:

There are three crystalline modifications and some amorphous forms of arsenic under normal conditions.

Grey (α, ordinary) arsenic is the most stable form of arsenic under normal conditions. It is crystallized in a rhombohedral structure (A7-type; Fig. 12.0.3, Brillouin zone: Fig. 12.0.4). The space group is $R\bar{3}m$ - D_{3d}^5.

Orthorhombic (ε, arsenolamprite) arsenic has a similar structure like black phosphorus, but its structure can not be derived by a simple scaling of the bond length from black P. The unit cell contains eight atoms (Fig. 12.0.5) at the positions ± $(0,u,v)$, ± $(1/2,u+1/2,v)$, ± $(1/2,u,v+1/2)$ and ± $(0,u+1/2,1/2-v)$. The structure consists of double layers separated by 5.50 Å.

Yellow arsenic shows a cubic symmetry and presumably consists of As_4 molecules. This allotrope is only metastable and decomposes easily to grey arsenic. Structural data are not available, since X-ray radiation destroys this modification.

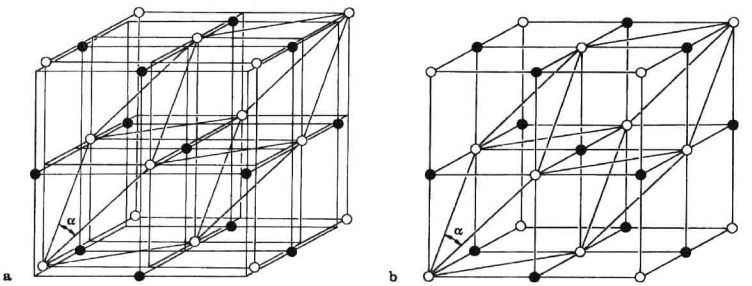
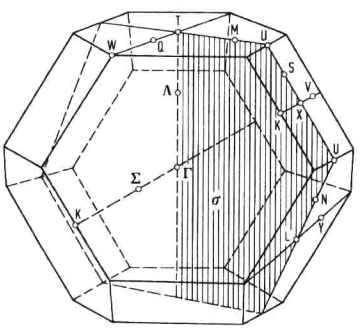
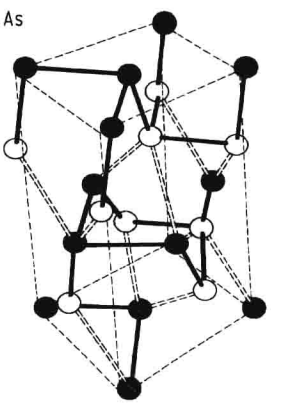


Fig. 12.0.3. Crystal structure of grey arsenic (a) and the cubic NaCl structure (b) from which it can be derived. The open and solid circles represent the two sublattices.



Left:
Fig. 12.0.4. Brillouin zone of grey arsenic showing points, lines and planes of symmetry.

Right:
Fig. 12.0.5. The unit cell of orthorhombic arsenic.



Antimony:

Three allotropes of antimony under normal conditions are known: metallic, black and explosive antimony.

α- (gray, ordinary) antimony is the most stable form of antimony under normal conditions. It crystallizes in a rhombohedral structure (A7 -type) like arsenic. The space group is $R\bar{3}m$ - D_{3d}^5.

Black antimony is strong reactive on air and has an amorphous structure. Under vacuum, it transforms easily to crystalline metallic antimony during heating.

Explosive antimony is only metastable and transforms fiercely in metallic antimony during mechanical stress or heating. Explosive antimony is probably not an allotropic form, but a mixed polymer.

Bismuth:

α-bismuth is the only stable form of bulk bismuth under normal conditions. It crystallizes in a rhombohedral A7-type structure, like arsenic and antimony. The space group is $R\bar{3}m$ - D_{3d}^5. The primitive cell contains two atoms at the positions (u,u,u) and $-(u,u,u)$.

12.0.2 Electronic structure

Figs. 12.0.6...12.0.9 show the band structure of phosphorus, arsenic, antimony and bismuth.

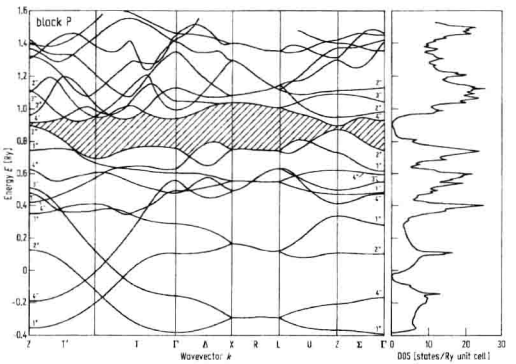


Fig. 12.0.6. Band structure of black phosphorus

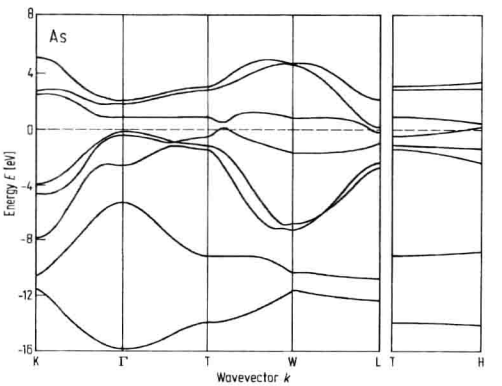


Fig. 12.0.7. Band structure of grey arsenic.