substance: boron compounds, general properties
property: structural properties of dodecaborides with B_{12} cubo-octahedra

Dodecaborides of the lanthanides Tb, Dy, Ho, Er, Tm, Yb, Lu have been obtained. Additionally a number of alloys of these dodecaborides with dodecaborides of other elements is known. Some of these alloying dodecaborides are not synthetized in pure form [72S, 81S, 77S3].

Structure

The crystalline structure can be described in two ways

a) Metal atoms and cubooctahedral B_{12} units are arranged in a cubic face-centered lattice (Fig. 1a).

b) B_{24} cages surround the metal atoms which are arranged in a cubic lattice (Fig. 1b) [72S, 75S, 76C, 77M, 81S, 77S1, 77S2].

lattice parameters: Fig. 2

The structure ("UB_{12} type") may be described in terms of a modified fcc unit cell with the metal atoms in the center of regular B_{12} cubo-octahedra having B atoms at each of their 24 vertices. An alternative description is a modified NaCl-type structure formed by metal atoms and B_{12} cubo-octahedra [68M, 77S3, 79C]. Structure in Fig. 3 [86S].

This structure may be also considered as composed of two sublattices, boron clusters and RE atoms. The links within and between the B_{12} cubooctahedra are strong covalent bonds and therefore responsible for the high melting temperatures and the rigidity [77S3, 85E].
Theoretical studies of the electronic structure indicate that two valence electrons of each rare earth atom compensate the electron deficiency in the boron sublattice, thus realizing the maximum stability [55L, 60L]. This charge transfer is responsible for the ionic bonding between the boron clusters and the RE atoms. Despite its approximate character, this model seems to make the electronic properties of these compounds qualitatively explicable: Dodecaborides with divalent metals are expected to be semiconductors or insulators, those with trivalent metals to be metals [86K, 85H, 90H, 95H].

Rare earth dodecaborides exhibit a variety of physical properties that predominantly result from the nature of the RE ions with their partly occupied 4f-shell. LuB_{12} is superconducting below 0.4 K [85E, 95B]. YB_{12} is an intermediate valent system showing features of van Vleck paramagnetism [85K, 98O]. LnB_{12} (Ln = Tb, Dy, Ho, Er, Tm) are antiferromagnetic [68M, 79M, 93B, 95M, 95P] with a maximum Néel temperature of 23 K for TbB_{12} [81M]. Preparation of single crystals by zone melting [91P].

Representatives of the dodecaborides:

YB_{12}	79M
GdB_{12}	79M
TbB_{12}	79M
DyB_{12}	91P
HoB_{12}	91P
ErB_{12}	91P
TmB_{12}	91P
YbB_{12}	91P
LuB_{12}	91P
UB_{12}	91P

Physical properties

Systematic investigations on the semiconductor properties are not known. But the distinct coloring of most of the dodecaborides (see [72S, 81S]) indicate band gaps up to some eV.

For transport properties, see [71G, 71O1, 71O2, 71P, 72O].

Review papers

Preparation and physical properties of rare earth hexaborides and dodecaborides [86K].

On the physical properties of intermediate valent hexa- and dodecaborides [87W].

Cluster energy levels of the B_6 octahedron compared with the B_{12} icosahedron and the B_{12} cubo-octahedron [86B]

Octahedron (B_6)			Icosahedron (B_{12})			Cubo-octahedron (B_{12})		
Energy [eV]	Degeneracy	Symmetry	Energy [eV]	Degeneracy	Symmetry	Energy [eV]	Degeneracy	Symmetry
						10.0	2	e_g
						9.6	3	f_{2u}
						7.2	3	f_{2g}
			13.9	3	t_{2u}	6.2	3	f_{1u}
			12.7	5	v_g	4.4	3	f_{1g}
13.3	2	e_g	9.5	3	t_{1u}	3.0	2	e_u
10.5	3	t_{1u}	5.8	3	t_{1g}	2.6	1	a_{2g}
2.4	3	t_{1g}	3.5	5	v_u	0.6	3	f_{2u}
–0.6	3	t_{2u}	1.1	4	u_g	–2.1	3	f_{1g}
–5.0	3	t_{1u}	–3.8	5	v_g	–4.1	2	e_g
–6.6	2	e_g	–4.7	3	t_{2u}	–4.1	3	f_{2g}
–7.1	3	t_{2g}	–4.8	3	t_{1u}	–4.7	3	f_{1u}
–7.5	1	a_{1g}	–6.6	4	u_u	–5.6	3	f_{2u}
–11.5	3	t_{1u}	–8.1	1	s_g	–6.1	3	f_{1u}
–20.2	1	a_{1g}	–10.4	5	v_g	–7.9	1	a_{1g}
			–14.9	3	t_{1u}	–8.9	1	a_{2u}
			–23.2	1	s_g	–9.7	2	e_g
						–10.6	3	f_{2g}
						–14.2	3	f_{1u}
						–20.7	1	a_{1g}

Low-temperature physical properties of REE dodecaborides [99S].

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Fig. 1.

Lanthanide dodecaborides. a) Structure model; metal atoms and cubo-octahedral B_{12} units arranged in a NaCl–like cubic face-centered lattice. b) Structure model; metal atoms arranged in a cubic lattice, each metal atom surrounded by a B_{24} cage [72S, 81S].

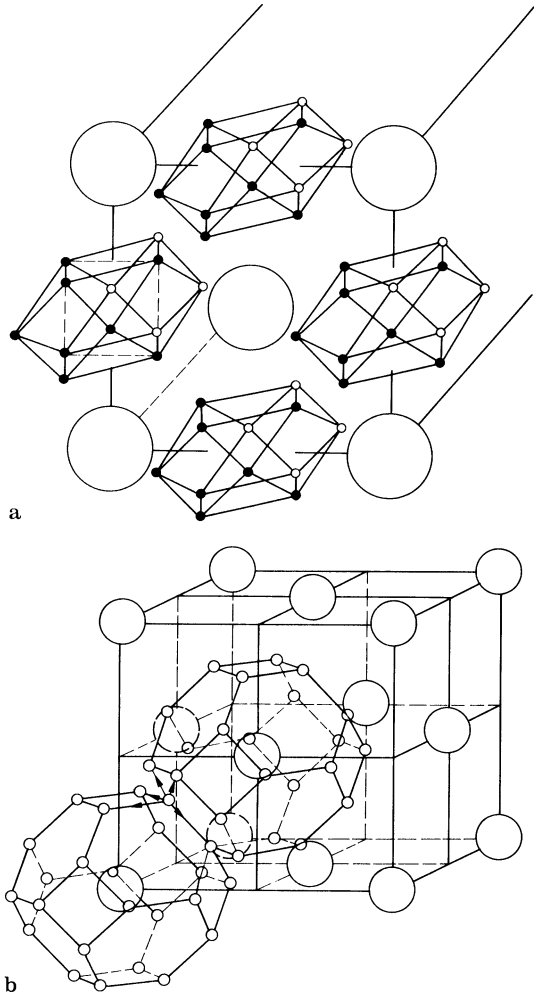

Fig. 2.

Lattice parameters of the dodecaboride phases vs. the atomic radii of the Me atoms, R_M [72S].

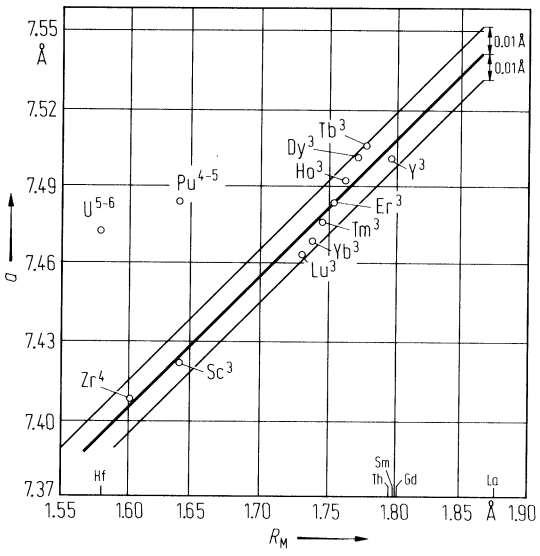

Fig. 3.

Metal dodecaborides MB_{12}. Unit cell [86S].