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Compounds Based on Octahedral B₆ Units: Hexaborides and Tetraborides

J. ETOURNEAU, J.-P. MERCURIO, and P. HAGENMULLER

Atoms in a three-dimensional boron lattice have a five-fold coordination when situated in the vertex positions of a B₆ octahedron: they share four bonds with atoms of the same octahedron and the fifth one points outwards along one of the A₄ axes of the octahedron. The presence of this fifth bond is responsible for the occurrence of the three-dimensional structure. Only two families of boron-rich borides have structures based on the B₆ octahedron: the CaB₆-type hexaborides and the ThB₄-type tetraborides.

MOISSAN and WILLIAMS (1897) reported the discovery of CaB₆-type cubic hexaborides. Later ANDRIEUX (1929) proposed a general synthesis method for these compounds, by fused-salt electrolysis. Then Von STACKELBERG and NEUMANN (1932) determined the approximate structure, which was later refined (ALLARD, 1932; PAULING and WEINBAUM, 1934; BLUM and BERTAUT, 1954).

Fused salt electrolysis had also allowed ANDRIEUX (1929) to prepare UB₄ uranium tetraboride. Later BREWER and SAWYER (1950) prepared CeB₄, ThB₄ and UB₄ isotopes; BERTAUT and BLUM (1949) fixed the positions of the metal atoms in the UB₄ lattice. ZALKIN and TEMPLETON (1950) established a complete model of the crystal structure using a ThB₄ single crystal.

1. Crystal Structure

a) CaB₆-Type Hexaborides

Elements that form hexaborides of a CaB₆-type are potassium, alkaline earths, yttrium and the larger lanthanides, as well as thorium and some actinides (NASLAIN and ETOURNEAU, 1966; EICK and MULFORD, 1969; McDONALD and STUART, 1960). The crystal structure of these compounds with cubic symmetry (Pm3m, O_h¹) is represented in Figure 1. It is characterized by a three-dimensional skeleton of B₆ boron octahedra, the interstices of which are filled by metal atoms.

Theoretical studies have shown that in the absence of an inserted metal the covalent boron sublattice is electron-deficient, and that electron transfer from the metal sublattice to that of boron is required (EBERHARDT et al., 1954; LIPSCOMB and BRITTON, 1960). The existence of thermodynamically stable KB₆, Na_xTh_{1-x}B₆ and Na_xBa_{1-x}B₆ phase indicates that the number of transferred electrons is at least 1 (BLUM and BERTAUT, 1954; NASLAIN and ETOURNEAU, 1966).

According to different investigators, the structural parameters differ quite noticeably, which suggests the existence of homogeneity ranges. Many studies have been undertaken concerning the non-stoichiometry of MB₆ hexaborides: all of them lead to deviations from stoichiometry through cation defects. The reported results are summed up in Table 1.

Fig. 1. Structure of CaB_6

Table 1.

M	x	Parameters ($\text{\AA}$)	Reference
K	1.00	4.232	NASLAIN and ETOURNEAU (1966)
Ca	1.00	4.1520	ETOURNEAU (1970)
Sr	1.00	4.1981	ETOURNEAU (1970)
Ba	1.00	4.2706	JOHNSON and DAANE (1961)
Y	1.00	4.103	JOHNSON and DAANE (1961)
La	1.00	4.1561	JOHNSON and DAANE (1961)
Ce	0.77	4.1561	JOHNSON and DAANE (1961)
	1.00	4.1396	YAJIMA and NIIHARA (1971)
Pr	0.70	4.1414	YAJIMA and NIIHARA (1971)
	1.00	4.1329	YAJIMA and NIIHARA (1971)
Nd	0.69	4.1355	YAJIMA and NIIHARA (1971)
	1.00	4.1265	MERCURIO (1974)
Sm	1.00	4.1304	MERCURIO (1974)
	0.68	4.1278	NIIHARA (1971)
Eu	1.00	4.1780	SCHWETZ and LIPP (1973)
	0.90	4.1843	SCHWETZ and LIPP (1973)
Gd	1.00	4.1065	YAJIMA and NIIHARA (1971)
	0.70	4.1113	YAJIMA and NIIHARA (1971)
Tb	1.00	4.1008	YAJIMA and NIIHARA (1971)
	0.75	4.1052	YAJIMA and NIIHARA (1971)
Dy	1.00	4.0969	SPEAR (1974)
		4.1008	
Yb	1.00	4.1478	ETOURNEAU et al. (1970)
Th	1.00	4.1104	ETOURNEAU et al. (1971)
	0.78	4.1125	ETOURNEAU et al. (1971)
Np	-	4.1129	EICK and MULFORD (1969)
Pu	-	4.115	McDONALD et al. (1960)
		4.140	
Am	-	4.1154	EICK and MULFORD (1969)

b) ThB_4 -Type Tetraborides

Elements likely to form tetraborides of a ThB_4 type are yttrium, lanthanides except europium, as well as some actinides: thorium, uranium, neptunium, plutonium and americium (BERTAUT and BLUM, 1949; ZALKIN and TEMPLETON, 1953).

The crystal structure of the phases with tetragonal symmetry ($P4/\text{mbm}$, D_{4h}^2) can be described as follows: the boron covalent sublattice is formed by chains of B_6 octahedra, developing along the c-axis, and by pairs of B_2 atoms, bonding the octahedra in the xOy plane (Fig. 2). The resulting three-dimensional skeleton contains tunnels parallel to the c-axis that are filled by metal atoms (ZALKIN and TEMPLETON, 1953).

Because of the many common features of CaB_6 and ThB_4 -type structures (covalent skeleton, B_6 octahedra, existence of boron "cages" ...), deviations from stoichiometry can be expected for tetraborides. The few studies made in this field concern only parameter values (EICK and MULFORD, 1969; JOHNSON and DAANE, 1961). Their results are too contradictory to allow a precise evaluation of the limits of possible homogeneity ranges. However it can reasonably be assumed that deviations from stoichiometry must take place on the deficit side of the metal.

2. Preparation

Since boron readily combines with most metals and reduces refractory oxides at high temperatures, different methods can be utilized to prepare borides. Since fused salt electrolysis is only of historical interest for hexaboride and tetraboride synthesis, we shall describe only general methods such as direct synthesis from elements and reduction of oxides by boron at high temperatures. Special attention will be given to methods of crystal growth.

Fig. 2. Structure of ThB_4 .

a) Direct Synthesis from Elements

The choice of the specific experimental technique is determined by the degree of volatility of the metal to be used.

a) Direct Synthesis in the Presence of a Vapor Phase

This technique is utilized when the metals involved have high vapor pressures at the temperatures required for synthesis. This is the case for potassium, alkaline earths, samarium, europium, thulium and ytterbium. The utilization of these relatively volatile metals requires sealed containers, that resist the corrosive action of boron and of metal gases under pressure (ETOURNEAU, 1970b).

B) Direct Synthesis Involving Metals with Low Volatility

The reactions are generally carried out in vacuum or an argon atmosphere. To facilitate solid-state diffusion, the boron and the metal (often as a finely divided hydride) are shaped into tablets under high pressure (about 15 kb).

b) Indirect Synthesis

The principle of this method is the reduction, at high temperatures, of metal oxides by boron. As a general rule, the reduction reaction can be described as follows:

where the nature of the volatile boron oxide is not well defined.

Oxide-boron mixtures pressed into cylindrical tablets under high pressure, are treated either by arc-melting, or by high-frequency induction heating in tantalum, molybdenum or tungsten crucibles (ETOURNEAU, 1970b). The elimination of oxygen in boron oxide generally requires that the reactions be carried out in vacuum.

Boron-carbon mixtures or B_4C boron carbide make it possible to reduce metal oxides at lower temperatures. However their utilization presents one drawback, that of a risk of contamination by carbon. Consequently the preferred method of synthesis involves only boron itself as the reducing agent, since it is the only element that can provide materials that are well characterized and of high purity.

c) Single Crystal Growth

Several crystal growing methods have been utilized in the preparation of tetraboride and hexaboride single crystals.

a) Chemical Transport

RABENAU, KAUER and KLOTZ obtained lanthanum hexaboride crystals ($0.15 \times 0.15 \times 2 \text{ mm}^3$) by chemical transport in the presence of bromine. The reaction was carried out in a sealed ceramic (SiO_2 and Al_2O_3) flask with a thermal gradient between 1105 and 1095°C (KLOTZ, 1965). NIEMYSKI and KIERZEK-PECOLD used a $BCl_3 + H_2$ mixture as a transport agent that reacted with lanthanum oxide. Here the temperatures of both the cold and the hot sources were much higher (1000 and 1450°C). The edges of the crystals obtained were about one millimeter in length (NIEMYSKI and KIERZEK-PECOLD, 1968).

B) Melting with a Metal Excess

These reactions are carried out in open or sealed containers, according to the volatility of the metals involved. JOHNSON and DAANE, and later DEACON and HISCOCKS obtained prismatic LaB_4 needles 5 to 8 mm long as well as small SrB_6 single crystals (0.2 mm approximately) by slow cooling (16°C/h) from 1700°C (JOHNSON and DAANE, 1961; DEACON and HISCOCKS, 1971).

FISK et al. (1972) prepared single crystals of tetraborides of the first members of the rare earths (La to Nd) by this method.

γ) Zone-Melting

Zone-melting is an appropriate method for crystallization of congruent-melting compounds.

JOHNSON and DAANE (1963) obtained large yttrium tetraboride crystals (6 mm diameter and 10 cm long, approximately).

CURTIS and GRAFFENBERGER (1966), followed by NIEMYSKI and KIERZEK-PECOLD (1968) prepared, with a floating zone technique, lanthanum hexaboride single crystals from 4 to 10 mm long and with 3 mm^2 in cross section, approximately.

δ) Utilization of a Metal Flux

Aluminum is generally used as the metal flux. The method consists in heating up to 1550°C in an argon atmosphere a boron + metal mixture (in stoichiometric proportions) in the presence of a large excess of aluminum, then to let the molten mass cool down to 1000°C within 10 min, and finally to stop abruptly the heating.

FISK et al. (1972) thus obtained single crystals of tetraborides of the heavy rare-earths (from Sm to Lu, except Eu). With the same technique, STURGEON et al. (1974) prepared samarium hexaboride single crystals as well as (Eu, Sm) B_6 -crystals a few millimeters in length.

d) Conclusion

A review of the methods of hexaboride and tetraboride preparation shows that indirect synthesis by borothermal reduction of oxides appears to be the most satisfactory and easiest method to apply when large quantities of borides are needed. It also makes it possible to obtain $\text{M}_x\text{M}'_{1-x}\text{B}_6$ (or $\text{M}_x\text{M}'_{1-x}\text{B}_4$) solid solutions with perfectly defined compositions.

However a detailed study of the physical properties of these materials - already quite developed concerning polycrystalline samples - more and more often requires single crystals. Consequently the previously described crystal growth techniques will have to be refined in order to fulfill the more and more demanding requirements of single crystal studies.

3. Thermal Stability

A study of the thermal stability of materials over a large temperature range provides a most helpful guide in the determination of ideal preparation conditions, for polycrystalline samples as well as for single crystals.

a) Experimental Results

The thermal behavior of hexaborides and tetraborides can be described with the help of reaction mechanisms involving either congruent melting or dissociation through preferential evaporation of metal or boron (ETOURNEAU, et al., 1972a, b).

a) Hexaborides

There are four classes of compounds from the point of view of stability:

- a) $M = \text{La, Ce, Pr, Nd, Sm or Am}$:

$\text{MB}_6 \rightarrow \text{congruent melting.}$

- b) $M = \text{K, Ca, Sr, Ba or Eu}$:

$\text{MB}_6 \rightarrow \text{M}^\times + 6\text{B}$ (boron residue)

- c) $M = \text{Y, Gd, Tb, Dy or Th}$:

$\text{MB}_6 \rightarrow \text{MB}_4 + 2\text{B}^\times$

- d) $M = \text{Yb}$:

$2\text{MB}_6 \rightarrow \text{MB}_{12} + \text{M}^\times$

β) Tetraborides

There are two classes of compounds:

- a) $M = \text{Y, Gd, Tb, Dy, Ho, Er, Tm, Lu, U or Pu}$:

$\text{MB}_4 \rightarrow \text{congruent melting}$

- b) $M = \text{La, Ce, Pr, Nd, Sm or Yb}$:

$\text{MB}_4 \rightarrow \text{MB}_6 + \text{M}$

b) Discussion

a) Relative Stability of Hexaborides

The interpretation of thermal behavior of hexaborides is based on two factors: the saturation vapor pressure of the metal, an increase of which increases the dissociation, and the stability of the B-B bonds within the boron sublattice, the strength of the B-B bonds decreasing as the size of the cubic lattice parameter increases.

The great stability of hexaborides from lanthanum to neodymium can be explained by the progressive contraction of the lattice, which compensates for the increasing volatility of the metal. Samarium hexaboride, thermally very stable, is the limiting case with regard to volatility of metal which is high, but the lattice parameter is still relatively small, since it is intermediate between those of CeB_6 and PrB_6 (Figs. 3 and 4).

The thermal behavior of EuB_6 and YbB_6 is a result of the high volatility of the metals, and also of the great dilatation of the unit cell and consequently of the fragility of the B-B bonds. The exceptional volatility of ytterbium explains the fact that YbB_6 is less stable than LaB_6 , although their unit cells have very nearly the same size.

The dissociation of YB_6 , GdB_6 , TbB_6 and DyB_6 hexaborides into tetraborides with loss of boron at 1550°C , is a consequence of the volatility of boron at this temperature, and also of the very high stability of the corresponding tetraborides.

Fig. 3. Lattice parameters of rare-earth hexaborides

Fig. 4. Saturation vapor pressures of rare-earths at 1800 K

The interpretation proposed for the LnB_6 phases can be extended to alkaline-earth and potassium hexaborides. These dissociate through metal evaporation, yielding a β -rhomboedral boron residue, at the melting-point in the case of CaB_6 , SrB_6 and BaB_6 , and at 750°C in the case of KB_6 (ETOURNEAU, 1970b; NASLAIN and ETOURNEAU, 1966).

For a given volume of the unit cell, the most stable hexaborides will be that which corresponds to the least volatile metal: LaB_6 is then more stable than CaB_6 , in spite of their identical parameters.

On the other hand, for comparable metal vapor pressure, the most stable hexaboride will be that which has the smallest unit cell: SmB_6 is indeed more stable than BaB_6 , which has a larger unit cell.

The fact that europium and strontium have comparable volatilities and also B-B bonds of identical strength accounts for the similar thermal behavior of EuB_6 and SrB_6 .

In the same way one can explain the easy dissociation of KB_6 ($a_{\text{KB}_6} = 4.232 \text{ \AA}$, $p_K^{1700^\circ\text{K}} = 27 \text{ bar}$).

β) Relative Stability of Tetraborides

The temperatures at which dissociation of tetraborides (under 10^{-6} torr) begins are the following:

LaB_4 : 1850°C ; CeB_4 : 2200°C ; PrB_4 : 1950°C ; NdB_4 : 1850°C ;
 SmB_4 : 1650°C .

Thus, while the thermal stability increases from LaB_4 to CeB_4 , there is a monotonic decrease with increasing atomic number from CeB_4 to SmB_4 .

PADERNO and POKRZYWNICKI (1967a) showed, by studies of magnetic properties, that the inserted rare earth ion for GdB_4 , DyB_4 , HoB_4 , ErB_4 and TmB_4 was in +III oxidation state. Figure 5 shows that this is also the case for the other tetraborides except of CeB_4 and YbB_4 . The abnormal volume contraction for CeB_4 unit cell observed by many authors, can certainly be explained by the presence (at least partially) of Ce^{4+} ions (GSCHNEIDNER, 1961). On the other hand, the dilatation of YbB_4 could be the result of the presence of Yb^{2+} ions (FISK et al., 1972).

The trend in thermal stability observed for LaB_4 , CeB_4 , PrB_4 , NdB_4 and SmB_4 is explainable by the counteracting effects of increasing metal volatility and decreasing unit cell volume. The first effect accounts for the lesser stability of LaB_4 relative to SmB_4 and the second for the maximum at CeB_4 .

For comparable metal volatilities, the tendency to dissociate decreases with shortening of B-B distances. The high thermal stability of YB_4 , GdB_4 , TbB_4 , DyB_4 , HoB_4 and ErB_4 is the result of the combination of both a relatively low metal volatility and a small unit cell volume.

Fig. 5. Elementary volume of rare-earth tetraborides and ionic radii of rare-earth tetraborides in the +III oxidation state

EuB_4 and YbB_4 are difficult to obtain because of the high vapor pressure of europium and ytterbium. However this factor is not sufficient to explain why EuB_4 has never been prepared to date: an equally important factor could be the large unit cell that would result for a +III oxidation state, by analogy with YbB_4 .

c) Structural Observations

A basis for comparison of the CaB_6 and ThB_4 structure types is the dimension of the site available for the metal atoms within the boron sublattice. Table 2 gives the extrema of the radii of these sites, calculated from average B-M distances, assuming the atomic radius of boron ($r_B = 0.88 \text{ \AA}$) does not significantly vary from one structure to another (NASLAIN, et al., 1973). It also shows the extrema for metal and ion radii of the elements that might form hexaborides and tetraborides (SHANNON and PREWITT, 1969). The site for metal occupancy for the hexaborides is noticeably larger than for tetraborides, as can be predicted from their respective coordinations (24 in MB_6 phases, 16+2 in MB_4 phases).

Table 2.

Structure type	Radii of metal sites ($\text{\AA}$)	r_M ($\text{\AA}$)	$r_{M^{3+}}$ ($\text{\AA}$)
MB_6	2.26 - 2.14	2.23 - 1.75	1.28 - 0.92
MB_4	1.99 - 1.87	1.95 - 1.68	1.14 - 0.85

The available sites in hexaborides will then accommodate atoms larger than those in tetraborides. This is one of the reasons why large atoms such as Ca, Sr, Ba, Eu, and Yb can form hexaborides, whereas the small rare earths (Ho, Er, Tm, Lu) cannot.

The metal sites in tetraborides by contrast accommodate smaller atoms: this explains the great thermal stability of tetraborides of the heaviest trivalent rare earths (Gd to Lu). As in the rare earth series only europium - whose radius is large for the divalent state ($r_{\text{Eu}^{2+}} = 1.12 \text{ \AA}$) - does not form any tetraborides, and because of the questionable existence of CaB_4 , we consider the size of the calcium ion ($r_{\text{Ca}^{2+}} = 0.99 \text{ \AA}$) as the upper limit for insertion of a metal ion into the boron sublattice. The fact that cerium is, at least partially, in a +IV oxidation state in CeB_4 and in a +III oxidation state in CeB_6 , is in agreement with this conclusion.

4. Physical Properties

This section is concerned mainly with the study of electrical and magnetic properties of the ThB_4 -type tetraborides and of the hexaborides.

a) Hexaborides

Since the publication in 1950 of the first physical data concerning CaB_6 -type hexaborides, many band structure models have been proposed based on theoretical considerations, generally involving a LCAO-type approximation for atomic orbitals of boron (LONGUET-HIGGINS and ROBERTS, 1954; YAMAZAKI, 1957; FLODMARK, 1960; PADERNO et al., 1970).

The calculations made by LONGUET-HIGGINS and ROBERTS (1954) led to a model consisting of four bonding orbitals, which could contain 20 electrons per MB_6 group, separated from four anti-bonding orbitals by a forbidden band. For a $M^{II}B_6$ divalent element hexaboride, the 18 electrons donated by 6 boron atoms and the two valence electrons of the metal atom completely fill the bonding orbitals: thus $M^{II}B_6$ is an insulator or a semiconductor. For CaB_6 the calculated width of the forbidden band was 4.4 eV, but YAMAZAKI (1957) obtained a value of 1.5 eV. If the metal atom yields more than two electrons, the extra electrons partially fill an anti-bonding band and the hexaboride becomes metallic.

In FLODMARK's Calculations the wave functions relative to the 3s, 3p and even 3d boron orbitals were included (FLODMARK, 1960). The band occurring from the new orbital combinations and those obtained from solely 2s and 2p orbitals are different: in the new energy diagram, totally occupied bonding bands can accommodate 12 electrons and partially occupied conduction bands the remaining electrons. CaB_6 -type hexaborides would then be, according to this model, compounds of a metallic character, whatever the number of electrons provided by the metal.

Both methods of calculation lead to the same conclusion that for a metal in a +III or +IV oxidation state, the corresponding boride is metallic. They differ markedly, however, in their predictions for hexaborides containing divalent elements.

It is in order, however, to question the significance of either model, since they both lead to contradictions with certain experimental facts, for example CaB_6 and SrB_6 are all semiconductors contrary to the predictions of FLODMARK'S model.

The LONGUET-HIGGINS and ROBERTS model has shortcomings regarding its predictions for hexaborides containing less than two electrons per metal site. The model requires that the metal donates at least two electrons and that the number of electrons per MB_6 group be 20. But BERTAUT and BLUM have shown the existence of sodium substitutions in BaB_6 and ThB_6 corresponding to the formulas $Na_{0.43}B_{0.57}B_6$ and $Na_{0.77}Th_{0.23}B_6$, where the number of electrons per group was respectively 19.57 and 19.69 (BLUM and BERTAUT, 1954). This difference is still greater in KB_6 prepared by NASLAIN and ETOURNEAU (1966), where only 19 electrons are available. The existence and the stability of KB_6 of the former ternary hexaborides show that their lattices are stable in the case of an electron concentration below two per inserted atom.

It was not possible to test the validity of the proposed models and possibly to make necessary modifications until significant progress had been made in the preparation of high purity poly- or single crystalline materials that were thoroughly characterized.

a) Transport Properties

$M^{III}B_6$ and $M^{IV}B_6$ hexaborides ($M = Y, La, Ce, Pr, Nd, Gd, Tb, Dy$ and Th)

These hexaborides have a metal-type conductivity, the value of which, at room temperature, is in the range of 10^4 to $10^5 \Omega^{-1}cm^{-1}$ (ETOURNEAU et al., 1970a; LAFFERTY, 1951; SAMSONOV et al., 1963; AUSKERN and ARONSON, 1968). The Hall effect measurements show that the number of conduction electrons is close to one per metal atom for trivalent hexaborides and to two per thorium atom for ThB_6 (JOHNSON and DAANE, 1963; SAMSONOV et al., 1963; AUSKERN and ARONSON, 1968). The thermoelectric power has a value of a few μVK^{-1} at room temperature, con-

firming the metallic character of these compounds (SAMSONOV et al., 1963; ETOURNEAU et al., 1970).

We must also note that studies on electronic specific heat at low temperatures have led ETOURNEAU et al. (1970) to find that the density of states at the Fermi level is not zero, but of the same order of magnitude as for the metallic rare earths.

$M^{II}B_6$ Hexaborides ($M = Ca, Sr, Ba, Eu$ and Yb)

The high value of the lattice parameter of EuB_6 and YbB_6 compared to those of hexaborides of the other rare earths, as well as magnetic studies and Mössbauer resonance studies have shown that, among these compounds, europium and ytterbium were in a +II oxidation state (POST et al., 1956; PADERNO et al., 1967; COHEN, 1968).

By measuring electrical conductivity on single crystals, JOHNSON and DAANE (1963) established that CaB_6 , SrB_6 and BaB_6 were semiconductors with activation energies of 0.40, 0.38 and 0.12 eV respectively. SAMSONOV et al. (1963) reported, from Hall effects measurements, conduction electron concentrations below 0.1 per metal atom for CaB_6 , SrB_6 , BaB_6 , EuB_6 and YbB_6 . Recently FISK (1969) confirmed the semiconductor behavior of EuB_6 and YbB_6 ($\Delta E = 0.38$ eV for EuB_6), as well as MERCURIO et al. (1973) ($\Delta E = 0.30$ for EuB_6 and 0.14 eV for YbB_6), by measurements on sintered bars (Fig. 6) (GOODENOUGH et al., 1973).

For all hexaborides containing a metal in the +II oxidation state, the thermoelectric power is high in absolute value (MERCURIO et al., 1973; GOODENOUGH et al., 1973). Measurements of specific heat with electron state densities at the Fermi level close to zero for YbB_6 , CaB_6 and SrB_6 have confirmed the semiconductor nature of the $M^{II}B_6$ hexaborides (ETOURNEAU et al., 1970a).

Fig. 6. Electrical conductivity of EuB_6 and YbB_6 , plotted vs reciprocal temperature

$M_{1-x}^{II}M_x^{III}B_6$ Ternary Hexaborides

These compounds are interesting because of the simultaneous presence of elements in +II and +III oxidation states. By measuring electrical conductivity and thermoelectric power as a function of x , one can follow the development of their properties from semiconductor ($M^{II}B_6$) to metallic ($M^{III}B_6$) behavior. In the case of $La_xEu_{1-x}B_6$ solid solutions, a sudden transition from a semiconductor to a metal has been observed (MERCURIO et al., 1974). The semiconductor character of EuB_6 disappears as soon as $x = 0.01$, while the metallic character grows as $x \rightarrow 1$ (Fig. 7). The Seebeck coefficient variation is high for small values of x , but quickly reaches a value near to that obtained for LaB_6 when x increases (Fig. 8).

Thus, the substitution of europium by La^{3+} ions - in small quantities - annihilates the semiconductor character of EuB_6 , since the occurrence of electrons donated by lanthanum to the conduction band creates a metallic-type conductivity.

Samarium Hexaboride

For SrB_6 although the unit cell dilation is much less than for EuB_6 and YbB_6 , it is still sufficient for samarium hexaboride to be considered as an intermediate compound between the $M^{II}B_6$ and $M^{III}B_6$ types (Fig. 3).

Electrical conductivity measurements carried out on polycrystalline samples as well as on single crystals, show that SrB_6 behaves as a semiconductor with a very low activation energy at low temperatures: $\Delta E \approx 5 \cdot 10^{-3}$ eV (Fig. 11) (STURGEON et al., 1974; MENTH et al., 1969; FALICOV and KIMBALL, 1969; COHEN et al., 1970; GEBALLE et al., 1970; NICKERSON et al., 1971). The thermal variations of the Hall coefficient

Fig. 7. Resistivity of $La_xEu_{1-x}B_6$ solid solutions as a function of temperature

Fig. 8. Thermoelectric power of $\text{La}_x\text{Eu}_{1-x}\text{B}_6$ solid solutions as a function of temperature

and of the thermoelectric power seem to correspond first to localized electron conduction and then to highly mobile carriers with rising temperature. It appears that $4f^6 \rightarrow 4f^5 5d^1$ transition takes place. The d-electrons are initially localized by disordered potentials (Anderson localization) at the bottom of the conduction band, they become progressively delocalized as higher energy levels are occupied.

Energy Diagrams

The models described above are appropriate only to CaB_6 , taking simply into account the atomic orbitals of boron. To extend these models to the whole family of CaB_6 -type hexaborides and particularly to rare-earth hexaborides, one must consider not only the $\text{B}_6\sigma$ bonding band and $\text{B}_6\sigma^*$ anti-bonding bands, but also the participation of the rare-earth 5d and 6s orbitals.

$M^{III}\text{B}_6$ Hexaborides. Two of the three valence electrons of the metal are donated to the boron skeleton and fill the $\text{B}_6\sigma$ bonding bands, the third one occupies a conduction band. It is reasonable to consider that the conduction electrons occupy a 5d-6s band originating from the rare-earths and not an anti-bonding $\text{B}_6\sigma^*$ band which would disturb the stability of the boron framework. This pattern can be extended to actinide hexaborides, involving 6d and 7s orbitals.

$M^{II}\text{B}_6$ Hexaborides. This concerns mostly europium and ytterbium hexaborides. For EuB_6 it can be assumed that the $\text{Eu}^{2+}: 4f^7$ level is situated in the forbidden band (as for EuO). Europium vacancies would introduce holes in the $4f^7$ configuration. These holes are small polarons, i.e. Eu^{3+} ions trapped by electrostatic forces on a site near-neighbor to the vacancy. The density of these acceptor sites is N_A ; the negative value of the Seebeck coefficient indicates that electron donor sites are also present actually with a $N_D > N_A$ density. These are rare earths in a state of substitutional impurity, represented in Figure 9 by the

Fig. 9. Energy diagram for EuB_6

$5d^1$ donor levels of $\text{Ln}^{2+}: 4f^{n-1}5d^1$ centers. When the density of impurity atoms is sufficient, a narrow $5d^1$ impurity band is formed: since $N_D - N_A < N_D$, the Fermi level drops down to this narrow $5d^1$ band.

Figure 6 shows that in the case of EuB_6 and YbB_6 , the electrical conductivity, in a temperature range of 77 to 300 K approximately, occurs only because of electrons moving within the impurity band excited in the conduction band. Only at very high temperatures the excitations of electrons situated in $4f^7$ (EuB_6) or in $4f^{14}$ (YbB_6) levels have to be taken into consideration. The linear variation with temperature of the Seebeck coefficient shows, however, that the Fermi level remains located in the $5d^1$ band, even at the highest temperatures. Accordingly, the 0.30 and 0.14 eV values do not represent an intrinsic forbidden gap for $4f^7$ or $4f^{14}$ electrons.

In the case of $\text{La}_x\text{Eu}_{1-x}\text{B}_6$ solid solutions, the mobility - and consequently the conductivity - increases with x , because the Eu^{2+} ions, whose number is decreasing, behave as high electron-scattering centers. For low values of x ($x \leq 0.03$) the electron mobility increases very quickly with x : indeed, the conduction takes place inside a narrow lanthanum impurity band which widens with x and progressively overlaps the bottom of the $5d-6s$ conduction band of europium as the number of lanthanum atoms increases.

A transition from semiconductor to metal appears between $x = 0$ and $x = 0.01$. For higher values of x , the Fermi level is higher than E_C , the energy at which the electrons are no longer correlated. This transition has a less noticeable influence on the thermoelectric power. The curves of Figure 8 can be interpreted by the presence of chemical composition inhomogeneities which would give rise to microphases, one corresponding to a polaron conduction, the other to an impurity band conduction. As long as the impurity band ranges are isolated, the material is a semiconductor, but when they become continuous, the conduction is metallic (MERCURIO et al., 1974).

Samarium Hexaboride. Since the rare-earth hexaborides in a +III oxidation state are metallic, the semiconductor character of SmB_6 seems to exclude the presence of $\text{Sm}^{3+}: 4f^5$ ions. However, when samarium is in +II oxidation state, the Sm^{2+} ions can have both configurations $4f^65d^0$ and $4f^55d^1$, the former being obviously more stable than the latter

because of the strong tendency of the rare earths to complete their 4f subshell. COHEN et al. (1970) showed by Mössbauer absorption measurements that both configurations coexist in SmB_6 .

The very weak measured activation energy ($5 \cdot 10^{-3}$ eV) makes it plausible that the energy level diagram is similar to that of EuB_6 and that localized $5d^1$ levels could be situated in the lower part of the 5d6s conduction band (MERCURIO, 1974). The maximal energy E_c of this zone would constitute a separation limit between localized and non-localized states, according to Anderson localization (Fig. 10).

At low temperatures (<50 K) strong electron-electron and electron-lattice correlations take place within the $5d^1$ localized levels. With rising temperature the thermal excitation allows electrons to pass progressively from these $5d^1$ localized states to more and more delocalized states within a real conduction band $\text{Sm}^{2+} : 5d6s$: the change in the slope of the $\ln \sigma = f(1/T)$ curve and the rapid decrease of $|\alpha|$ between 100 and 200 K can be explained by a progressive increase in conduction by highly mobile carriers, i.e. by the transition to a metallic state (Figs. 11, 12).

The presence of electrons in the hybrid 5d6s band reinforces their overlapping, which leads to a decrease in Sm-Sm distances. The variation of the lattice parameter of SmB_6 with temperature could be the result of the competition between this overlapping phenomenon and the normal lattice dilatation with temperature, which becomes predominant above 70 - 80 K (Fig. 13).

β) Magnetic Properties

Hexaborides of Non Magnetic Ions (Ca^{2+} , Sr^{2+} , Ba^{2+} , La^{3+} , Th^{4+})

These are diamagnetic, since their magnetic susceptibility is mostly caused by boron atoms. In the case of YbB_6 : ($\text{Yb}^{2+} : 4f^{14}5d^0$) the observed weak paramagnetism may be due to presence of impurities in very low concentrations (ETOURNEAU et al., 1970; ETOURNEAU, 1970; RABENAU et al., 1967).

Hexaborides of Magnetic Rare-Earths ($\text{M}^{\text{III}}\text{B}_6$)

These hexaborides become antiferromagnetic at low temperatures (MERCURIO, 1974; LEE and BELL, 1972; LEE et al., 1970; COLES and GRIFFITHS, 1961; BENOIT, 1955; PADERNO et al., 1969). While the effective moments calculated from experimental data in the paramagnetic range are close to the theoretical values obtained for free trivalent ions, there exists,

Fig. 10. Energy diagram for SmB_6

Fig. 11. Electrical conductivity of SmB_6

Fig. 12. Thermoelectric power of SmB_6

however, a large difference between the values of T_N and $|\theta_p|$, except for DyB_6 . It seems that this difference is caused by deviations with respect to the straight lines that represent the behavior of the free ions of the $\chi^{-1} = f(T)$ curves, when $T < 100$ K (Fig. 14). Since M^{II}B_6 -type hexaborides are metals, it is reasonable to expect interaction of the local moments with the conduction electrons. This interaction

Fig. 13. Lattice parameters of some hexaborides as a function of temperature. The parameter values have been related to the CeB_6 parameter at room temperature

Fig. 14. Reciprocal magnetic susceptibility of rare-earth hexaborides.

is of the form $H_{\text{int.}} = 2J_{sf}\vec{S}\vec{s}$, where J_{sf} is the exchange integral between a magnetic ion characterized by a $\vec{S}$ spin caused by 4f electrons and the conduction electrons carrying the $\vec{s}$ spin. J_{sf} polarizes the s electrons locally around the paramagnetic ion. Through the conduction electrons this local polarization gives rise to a large-distance interaction between localized moments. This phenomenon called Ruderman-

Kittel-Kasuya-Yosida interaction provides at least a qualitative understanding of the antiferromagnetism of the rare-earth hexaborides in the +III oxidation state (RUDERMAN and KITTEL, 1954; KASUYA, 1956; YOSIDA, 1957).

Europium Hexaboride and $\text{La}_x\text{Eu}_{1-x}\text{B}_6$ Solid Solutions

EuB_6 orders ferromagnetically for $T < 13$ K, the Curie temperature varying from 8 to 13 K according to different investigators. The Curie constant determined in the paramagnetic range corresponds to the $4f^7$ ($^8\text{S}_{7/2}$) configuration of the Eu^{2+} free ion in its ground state (MERCURIO et al., 1974; GEBALLE et al., 1968; BACHMANN et al., 1970; HACKER et al., 1971).

FISK (1969) explained the ferromagnetism of EuB_6 by a modification of the RKKY interaction studied by BLOEMBERGEN and ROWLAND (1955) for semiconductors. According to these authors, the moments could be coupled through the valence band electrons. Their calculations, established with the aid of some simplifying assumptions lead to an exchange function that varies with the distance between inserted atoms; in the case of EuB_6 the interaction would be ferromagnetic.

In the case of $\text{La}_x\text{Eu}_{1-x}\text{B}_6$ solid solutions, the paramagnetic Curie temperature increases at the beginning, up to 20 K for $x = 0.03$, and then decreases to -10 K for $x = 0.50$, after having passed through a zero value for $x = 0.33$. It starts increasing again for $0.50 < x < 0.75$ and vanishes for $x \geq 0.75$ (Fig.15).

For small values of x ($x \leq 0.05$) we saw that supplementary electrons were localized on $5d^1$ impurity levels, and then formed a narrow impurity band when x increased. These electrons interact with the localized spins of Eu^{2+} ions, giving a RKKY-type interaction. As long as x remains small, and consequently as long as the dilution of moment carriers is negligible, this interaction, which has a ferromagnetic nature, tends to reinforce the coupling between Eu^{2+} ions. A consequence is the remarkable increase of the paramagnetic Curie temperature (Fig. 15).

For compositions corresponding to $0.05 < x < 0.33$, there seems to be a noticeable difference between T_C and $|\theta_p|$, indicating that long-range antiferromagnetic interactions compete with ferromagnetic interactions.

Another increase of x ($0.33 \leq x \leq 0.75$) involves an increase of the average distance between Eu^{2+} ions; the RKKY interaction then becomes highly antiferromagnetic, which gives a negative paramagnetic Curie temperature; the long-range antiferromagnetic interactions become dominant.

For $x > 0.75$, the dilution of the magnetic moments in the lanthanum hexaborides lattice is such that the material is paramagnetic at all temperatures.

The previous analysis is confirmed by the study of $\text{Sr}_x\text{Eu}_{1-x}\text{B}_6$ phases for $x \leq 0.2$: the substitution of Eu^{2+} ions by Sr^{2+} ions essentially creates a dilution of moment carriers. Even for quite a small dilution, the paramagnetic Curie temperature slightly decreases when x increases. This result is consistent with the diminution of the paramagnetic Curie temperature with x , observed for $\text{Eu}_x\text{Yb}_{1-x}\text{B}_6$ phases (KRAUSE and SIENKO, 1973).

Fig. 15. Reciprocal magnetic susceptibility of $\text{Eu}_{1-x}\text{La}_x\text{B}_6$ phases as a function of T and paramagnetic Curie temperature as a function of x

Samarium Hexaboride

All the magnetic data show that at high temperatures the magnetic susceptibility is intermediate to those corresponding to $4f^6$ and $4f^55d^1$ configurations (MENTH et al., 1969; FALICOV and KIMBALL, 1969; MERCURIO, 1974).

The absence of magnetic order is in agreement with the simultaneous presence of both Sm^{2+} configurations: $4f^65d^0$ and $4f^55d^1$: the shape of the $\chi^{-1} = f(T)$ curve shows that at low temperatures strong correlations occur in the localized $5d^1$ levels (Fig. 16).

b) Tetraborides

The tetraboride unit cell contains 4 metal atoms and 16 boron atoms: 12 of them belong to two octahedra and the other 4 are bound by sp^2 -type bonds. For stability each octahedron requires 20 electrons per $(\text{MB}_4)_2$ group (14 for internal bonding, 6 for external bonding) and each sp^2 -type bond requires 4 electrons, i.e. a total of 56 electrons. Since 16 boron atoms provide only 48 electrons, an electron transfer from the metal sublattice to the boron one is necessary to ensure the stability of the structure (LIPSCOMB and BRITTON, 1960).

Fig. 16. Reciprocal magnetic susceptibility of SmB_6 as a function of temperature

Unlike the situation for hexaborides, there have been hardly any publications to date on the physical properties of tetraborides.

a) Transport Properties

Only the electrical properties of YB_4 , ThB_4 and SmB_4 have been studied (JOHNSON and DAANE, 1963; AUSKERN and ARONSON, 1968; STURGEON, 1973): these are compounds with a metallic character. The number of conduction electrons per metal atom, deduced from Hall effect measurements, is 2 for ThB_4 , but only 0.2 for YB_4 . This result seems, in the case of yttrium, to require an oxidation state close to +II a localization at the bottom of the conduction band of the same type as that observed for SmB_6 ; a magnetic investigation could corroborate this supposition.

β) Magnetic Properties

Tetraborides of Non-Magnetic Ions (Y^{3+} , La^{3+} , Th^{4+})

YB_4 and LaB_4 are diamagnetic, whereas ThB_4 is Pauli paramagnetic (JOHNSON and DAANE, 1963; AUSKERN and ARONSON, 1964).

Tetraborides of Magnetic Rare Earths

The NdB_4 , SmB_4 , GdB_4 , TbB_4 , DyB_4 , HoB_4 and TmB_4 phases order antiferromagnetically at low temperatures; the probable presence of two oxidation states for cerium and ytterbium in CeB_4 and YbB_4 is probably the reason for their particular magnetic behavior (no Curie-Weiss-type behavior). Only PrB_4 in the series of the rare-earth tetraborides is ferromagnetic (BUSCHOW and CREYGHTON, 1972). Just as for hexaborides, the magnetic properties of tetraborides may be interpretable on the basis of indirect RKKY interactions through conduction electrons.

However it is noteworthy that a shifting of the ordering temperature with composition has been observed in the UB_4 - DyB_4 and UB_4 - ErB_4 systems (ALI-ZADE et al., 1972). GIORGI et al. (1974) seem to have recently found a ferromagnetic ordering around 14 K in the $\text{Y}_x\text{V}_{1-x}\text{B}_4$ system for $0.62 < x < 0.70$.

5. Fields of Application

The CaB_6 -type hexaborides are well known for their mechanical and refractory properties, such as high congruent melting points and hardnesses close to that of boron (3000 kg/mm^2). They are also characterized by a great resistance to stress deformation ($5 \cdot 10^4 \text{ kg/mm}^2$). Hexaborides have a high modulus of elasticity and a high tensile strength, which suggests their use as reinforcing elements in composite materials, in the way that alumina or carbides are actually used.

Most hexaborides and especially LaB_6 are very good electrical conductors at high temperatures; furthermore, they have excellent thermionic properties: not only is the electronic emission potential quite low (2.7 eV for LaB_6), but cathodes made of lanthanum hexaboride make it possible to obtain high current densities, better than those of standard cathodes such as W, ThO_2 or activated BaO (BROERS, 1973).

This property, together with the high chemical inertia and their thermal stability, causes lanthanum hexaboride to be more and more often substituted for materials generally utilized in demontable electronic tubes with high current densities, e.g. in scanning electron microscopes, electronic masks, etc.

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