

typical of characteristics of resolution by the detector, but is attributed to partial resolution of the $K\beta$ line and to electronic effects.

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Superconductivity and Antiferromagnetism in Boron-Rich Lattices

Abstract. *Ferromagnetism, antiferromagnetism, or superconductivity has been discovered in most hexa- and dodecaborides.*

Superconductivity, ferromagnetism, or antiferromagnetism has been found in most metallic hexa- and dodecaborides. The temperatures of superconduction and magnetic transition are given in Table 1. This is the first time that superconductivity has been discovered in boron-rich compounds.

Boron itself is nonmetallic in all elemental modifications, yet the specific resistivities of hexa- and dodecaborides at low temperatures are below those of

most transition-metal compounds. There is even a slight resemblance between the the antiferromagnetic and the superconducting transitions. At or below the Néel point, the electric resistivity drops abruptly, a feature which recently, in the case of NdB_6 , may have been mistaken for superconductivity itself (1). Antiferromagnetism and a not quite so drastic drop in resistivity have been found previously for GdB_6 by Coles (2). We have found similar behavior for all magnetic rare-earth compounds investigated except the EuB_6 (Table 1), whereas all corresponding nonmagnetic rare-earth compounds become superconducting. The nonmagnetic tetraborides, which are equally good metallic conductors, showed no superconducting transition above 0.35°K .

Specific heat data have been obtained for both YB_6 and ZrB_{12} . The expected anomalies associated with the transition into the superconducting state were observed for both compounds. The very sharp transition observed for ZrB_{12} is shown in Fig. 1. The extrapolated electronic heat capacity coefficient per mole of ZrB_{12} (13.55×10^{-4} calories mole $^{-1}$ deg $^{-2}$) is almost exactly twice that found for one mole of YB_6 . Consequently, both compounds have the same value of slightly over 1×10^{-4} calories deg $^{-2}$ per gram atom of boron.

The compounds described are, from an atomistic point of view, mostly boron. It was therefore tempting to consider the above results as indicative of the behavior of a hypothetical cubic boron lattice which is metallic. The aforementioned properties exist only when we have three-dimensional cubic arrays, which are characteristic of the hexa- and dodecaborides.

The tetraborides being tetragonal are structurally intermediate between the two-dimensional MB_2 and the three-dimensional MB_6 arrangement (3). They no longer show any superconducting transitions above 0.35°K . The absence of superconducting transitions in one- and two-dimensional lattices has been pointed out earlier for covalent borides (4) and the graphite intercalation compounds (5). The existence of superconductivity found only in the hexa- and dodecaborides again confirms the validity of the empirical result that superconductivity exists only in three-dimensional structures.

A certain formal analogy exists between these borides and the beryllides. The formulas of the latter range from MBe_{12} to MBe_{22} , M being almost any

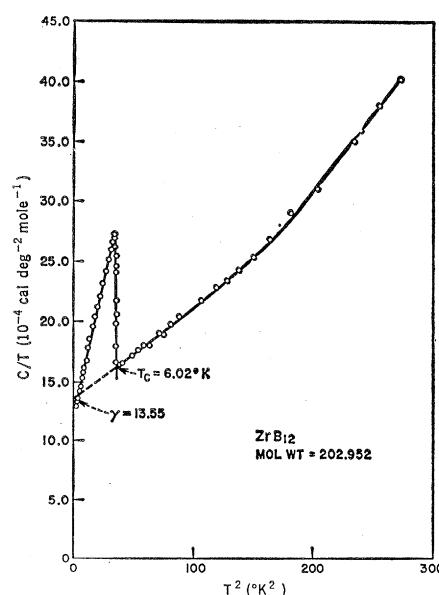


Fig. 1. Specific heat as a function of temperature for ZrB_{12} .

transition element. Most of the MBe_{22} compounds, if not all, also exhibit superconductivity (6), which might be considered typical for the body-centered cubic phase of beryllium (7). The electronic specific heat of these Be compounds is very low and in the order of 0.1×10^{-4} calories per gram atom of Be, whereas for the hexa- and dodecaborides it is an order of magnitude higher. Thus we conclude that cubic metallic boron, should it ever come into existence, would have an appreciable electronic specific heat.

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Table 1. Superconducting, antiferromagnetic, and ferromagnetic transitions of hexa- and dodecaborides. X-ray diffraction data for hexaborides sometimes showed small amounts of tetra- and dodecaborides. For T_{sc} (superconductivity), sharp transitions $\approx 0.1^\circ\text{K}$ wide were observed at 16 kc/sec unless otherwise indicated. Néel transitions identified by the abrupt decrease in resistivity as discussed in the text are given in column R; those identified by an abrupt decrease in susceptibility (measured by an inductive method at 25 cycle sec $^{-1}$) are given in column χ .

Compound	T_{sc} ($^\circ\text{K}$)	$T_{N\acute{e}el}$ ($^\circ\text{K}$)		T_{Curie} ($^\circ\text{K}$)
		R	χ	
ScB_{12}	0.39			
YB_6	6.5-7.1			
YB_{12} *	4.7			
ZrB_{12}	5.82			
LaB_6 *	5.7			
CeB_6		3.0	3.0	
PrB_6		7		
NdB_6		8.6	8.6	
EuB_6				8
GdB_6		17.6	17.5	
TbB_6		23	23	
DyB_6		21.5	21	
HoB_6		9		
HoB_{12}			6.5	
ErB_{12}			6.5	
TmB_{12}		4.2		
LuB_{12}	0.48			
ThB_6	0.74			

* Incomplete superconductive transitions indicate that not all the sample was superconducting.