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SUPERCONDUCTING BORIDES

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ABSTRACT

A number of superconductors are found among binary and ternary boride compounds. The highest T_c 's are often found near a limiting composition for the compound's stability. Ternary borides have been a fertile area for exploring the interaction between superconductivity and magnetism, and appear to be the area in which further aspects of boride superconductivity will be pursued.

INTRODUCTION

Among the large number of known boron containing metallic conductors, only a small number have been reported to be superconductors. There is no reason to think that boron is particularly unfavorable for the occurrence of superconductivity, but neither is there reason to regard boron as particularly favorable for its occurrence either. What a survey of the boron containing superconductors shows indeed is the capricious character of superconductivity, depending sensitively on details of interatomic interactions of which we have little a priori knowledge. The variety of behavior shown by the boride superconductors does give us a broad vantage point from which to view many of the important and interesting questions concerning superconductivity.

The focus in the field of superconductivity has shifted considerably in recent years with the discovery of materials with $T_c > 100K$. Less effort is now spent looking for superconductors with T_c in the 10K range, and the compilation of superconductors kept by Roberts¹ is no longer maintained. In what follows, the superconductivity of compounds in which boron is an essential constituent will be surveyed, ignoring most cases where a small amount of boron has been substituted for some other element. It is worth keeping in mind that in many cases a given material has been checked for superconductivity only to 1.5K, and occasionally only to 4K.

BINARY BORIDES

A. Rare Earths

The binary borides formed by some, and in some cases all, of the rare earths (including Y in the category) have the formulae RB_2 , R_2B_5 , RB_4 , RB_6 , and RB_{12} . In this set of compounds, superconductors have only been found in the cubic RB_6 and RB_{12}

structures. These are listed in Table 1. The Sc,Th, and Zr superconductors forming in these structures are included.

The hexaboride structure is particularly simple: it can be thought of as a CsCl arrangement of metal atoms and B_6 octahedra. The B_6 octahedron acts chemically as a doubly negative anion², and the alkaline earths in this structure are in fact semiconductors. For the trivalent rare earths we naively expect, therefore, one conduction electron per unit cell, and band structure calculations and de Haas-van Alphen experiments³ show this to be the case. This structure is formed by the rare earths La through Dy, including Y and Th. The structure appears not to be formed by the heavier rare earths because of their small size (Yb is divalent in YbB_6). LaB_6 and ThB_6 become superconducting at .122K⁴ and .74K⁵, respectively. YB_6 , on the other hand, becomes superconducting at 5.7K.⁵ What is interesting here is that Y is essentially the smallest radius metal atom that can form this structure, and it had the highest T_c , a situation that one notices often in the systematics of superconducting compounds. Splat cooling samples of YB_6 raises T_c to 8.4K, a further indication of incipient structural problems coupling to the superconducting properties.⁶ The contrast between the electrical resistivity of LaB_6 and YB_6 is also interesting, the latter showing the saturating resistivity characteristic of strong electron-phonon coupling⁷, in contrast to the temperature dependence characteristic of s-p metals exhibited by LaB_6 . We note that the other rare earth hexaborides all order magnetically at low temperature, and the strength of the f-electron coupling to the conduction electrons precludes superconductivity in these hexaborides.⁸

The dodecaboride structure is formed by the smaller rare earths, as well as by U, Sc, and Zr. Considerations of the boron bonding requirements in these dodecaborides has led to the suggestion that the B_{12} entity, like the B_6 octahedron, requires two electron to achieve a closed shell configuration.⁹ Among the dodecarbides, only ZrB_{12} , LuB_{12} , ScB_{12} and YB_{12} are superconducting (Table 1). YB_{12} is like YB_6 right at one limit-here the upper limit of size stability of the lattice, ZrB_{12} at the lower limit. YB_{12} forms at a Y stoichiometry of $Y_{.92}$. ZrB_{12} was found to have a very sharp superconducting transition, allowing a determination of the isotope effect on T_c for both Zr and B. For Zr, the effect was found to be $\alpha = d \log T_c / d \log m = -.32 \pm .02$,¹⁰ while for B it was much smaller, $\alpha = -.09 \pm .05$.¹¹ We note that $\alpha \approx 0$ for elemental Zr. The very small isotope effect for B in ZrB_{12} suggests that the boron network in the compound serves as a kind of inert background against which the Zr-derived superconductivity occurs. A further interesting fact about ZrB_{12} is that Pr atoms substituted for Zr act as Kondo impurities, apparently the only clear instance of such behavior known for Pr.⁸

B. Transition Metal Borides

The known binary transition metal boride superconductors are surprisingly few in number (Table 2). Two superconductors have been found in the B1(NaCl)-structure, ZrB and HfB. The orthorhombic B₁(δ -CrB) also has two superconductors, NbB and TaB. The hexagonal D1O₂(Th₇Fe₃)-structure has one known boride superconductor, Ru₇B₃.

In the widely occurring C32(AlB₂)-structure, superconductors based on NbB₂ and MoB₂ are known. For both compounds, the stoichiometric composition is not superconducting. Rather, T_c is found to be a maximum near B_{2.5}.¹² This was interpreted as being an indication of a new Matthias rule-type maximum in T_c for electron concentration per atom e/a $\approx$ 3.7. Adding Zr to MoB_{2.5} raised T_c to 11.2K in splat cooled samples. No really convincing explanation for the Matthias e/a rules has ever been given. It seems likely that the systematics follows from rigid band aspects of transition metal alloying phenomena, and the variation of T_c seen in MoB₂ and NbB₂ is a manifestation of these rigid band effects.

The other known binary boride transition metal superconductors are found in the C16(CuAl₂)-structure: Mo₂B and W₂B. A careful isotope effect study was carried out in both these compounds.¹³ In Mo₂B, the results were: $\alpha(\text{Mo}) = -.42 \pm .02$, $\alpha(\text{B}) = .004 \pm .016$. Correspondingly in W₂B, $\alpha(\text{W}) = -.52 \pm .05$, $\alpha(\text{B}) = -.09 \pm .016$. The results here are reminiscent of those seen above in ZrB_{1.2}: a sizeable effect on the transition metal, here close to the classical BCS value of -.5, and a much reduced value on the B. These results emphasize the dominant effect of the transition metal on the superconducting properties of the materials.

C. Impurity Effects

In a number of cases B-impurities in non-boride materials have been used to raise T_c. Such effects are not part of our main concern here. Two substitution effects will be noted here however, the first because it illustrates a way in which materials are occasionally very sensitive to impurities, and the second for its unusual character.

The composition Re₂B has been reported superconducting with T_c = 4.6K.¹⁴ Crystallographic compilations show no compound at this stoichiometry. The T_c of Re is known, however, to be extremely sensitive to shear. The superconductivity of the boride seems likely due to strained elemental Re.

A second example of an unusual effect of boron impurities producing sizeable effect is found with the heavy Fermion

superconductor UBe_{13} . Substitution of B to make $\text{UBe}_{12.97}\text{B}_{0.03}$ causes little or no shift in T_c , perhaps not very surprising. What is surprising that the borided sample appears to have a substantially increased low temperature electronic specific heat ($\approx 20\%$) and a much larger $\Delta C/\gamma T_c = 2.5$, from 1.5 in the unborided sample.¹⁵ The boron addition here corresponds to one boron per every seven formula units, yet the effects are extraordinary large.

TERNARY BORIDES

A. Introduction

The orthorhombic compound Mo_2BC has $T_c = 7.1\text{K}$. Other than this compound, all other reported ternary boride superconductors are rare earth or rare earth related ones, i.e. formed by rare earths or by Sc, Y, U, or Th. The superconducting rare earth boride structures can be categorized into two groupings, depending on whether or not any of the rare earth members with local 4f-moments which form from the structure become superconducting.

B. Superconducting and Magnetic Rare Earth Ternaries

Great attention has focused on the ternary boride structures having members in which superconductivity and magnetism coexist or in which superconductivity is destroyed by magnetic order occurring below the superconducting T_c . This interest, of course, derives from pair breaking effects of localized moments, and it is remarkable that materials have been found which can support simultaneously superconductivity and magnetic order. These matters are dealt with in this conference by M. B. Maple. Suffice it to say here that there is so far only one known boride crystal structure which allows this, the tetragonal, CeCo_4B_4 -structure. The superconductors are found in rare earth RRh_4B_4 and the meta-stable RIr_4B_4 phases which have this crystal structure at ambient temperature (Table 3).

C. Superconducting But Not Magnetic Rare Earth Ternaries

Several ternary boride phases have been found in which a non-magnetic rare earth forms a superconductor (Table 3). In particular, superconductivity is found in the body centered tetragonal LuRu_4B_4 -structure for $R = \text{Sc}, \text{Y}$ and Lu . La does not form in this structure but in the NdCo_4B_4 -structure. There are no known superconductors with this last structure. It is interesting that ScRu_4B_4 forms in the LuRu_4B_4 -structure metastably while at the same time having the highest T_c in the structure, 7.2K.

Superconductivity is also found in the CeCo_3B_2 and closely related YO_3B_2 phases. These are derivatives of the CaCu_3 -structure, involving different substitutions for the 3-fold

and 2-fold Cu positions. It is interesting that the Ce compound with the highest magnetic ordering temperature, CeRh_3B_2 ($T_m = 105\text{K}$), has the CeCo_3B_2 -structure. $\text{La}_{0.9}\text{Ru}_3\text{B}_2$ forms the CeCo_3B_2 -structure and is not superconducting. $\text{LaRu}_{2.7}\text{B}_2$ forms the YOs_3B_2 -structure and is superconducting at 4.0K . This last structure is orthorhombic with lattice parameters related to the hexagonal parameters of CeCo_3B_2 by the approximate relations $a \approx a_h$, $b \approx \sqrt{3}b_h$ and $c \approx 6c_h$. Another closely related structure at this stoichiometry adopted by a number of rare earth boride ternaries is the monoclinic ErIr_3B_2 -structure.¹⁶ No superconductors are known with this structure.

Five superconductors are known in the orthorhombic LuRuB_2 -structure, with the prototype LuRuB_2 having the highest T_c , 10.0K .¹⁷ Only rare earths without 4f-local moments form superconductors in this structure.

CONCLUDING REMARKS

The most promising area for new boride superconductors lies among the ternary compounds. Since the discovery of high T_c oxide superconductivity there has been very little exploratory work done in this region, a region in which there is every reason to believe that there remain many interesting superconductors to be discovered. The particularly interesting physics associated with the interplay between superconductivity and magnetism can also be expected to be found in further and new ramifications in this class of materials. The idiosyncratic chemistry of boron leads to many unique structures, and new structures are a good place to look for new properties of matter.

TABLE I

Rare Earth Related Binary Borides

Compound	T_c (K)	Structure	Ref.
LaB ₆	.122	CaB ₆	4
ThB ₆	.74	CaB ₆	5
YB ₆	5.7, 8.4	CaB ₆	5, 6
YB _{1/2}	4.7*	UB _{1/2}	5
LuB _{1/2}	.48	UB _{1/2}	5
ScB _{1/2}	.39	UB _{1/2}	5
ZrB _{1/2}	6.03	UB _{1/2}	5

* Possibly due to second phase YB₆

TABLE 2

Transition Metal Binary Borides

Compound	T_c (K)	Structure	Ref.
HfB	3.1	NaCl	18
ZrB	3.4	NaCl	19
NbB	8.25	δ -CrB	20
TaB	4.0	δ -CrB	20
MoB _{2.5}	7.45	AlB ₂	12
NbB _{2.5}	6.4	AlB ₂	12
Mo ₂ B	5.86	CuAl ₂	13
W ₂ B	3.18	CuAl ₂	13
Ru ₇ B ₃	2.58	Th ₇ Fe ₃	21

TABLE 3

Ternary Borides

Compound Mo ₂ BC	T _c (K) 7.1	Structure Ortho	Ref. 12
YRh ₄ B ₄	11.34	CeCo ₄ B ₄	22
LuRh ₄ B ₄	11.76	CeCo ₄ B ₄	22
ThRh ₄ B ₄	4.34	CeCo ₄ B ₄	22
NdRh ₄ B ₄	5.4	CeCo ₄ B ₄	22
SmRh ₄ B ₄	2.72	CeCo ₄ B ₄	22
ErRh ₄ B ₄	8.7	CeCo ₄ B ₄	22
TmRh ₄ B ₄	9.5	CeCo ₄ B ₄	22
HoIr ₄ B ₄	2.12	CeCo ₄ B ₄	23
ErIr ₄ B ₄	2.34	CeCo ₄ B ₄	23
TmIr ₄ B ₄	1.75	CeCo ₄ B ₄	23
LaRh ₃ B ₄	2.82	CeCo ₃ B ₂	24
LaIr ₃ B ₂	1.65	CeCo ₃ B ₂	24
ThIr ₃ B ₂	2.09	CeCo ₃ B ₂	24
CeRu ₃ B ₂	1.10	CeCo ₃ B ₂	26
LaRu _{2.7} B ₂	4.0	YOs ₃ B ₂	23
YOs ₃ B ₂	6.00	YOs ₃ B ₂	23
ThOs ₃ B ₂	3.46	YOs ₃ B ₂	23
CeOs ₃ B ₂	3.34	YOs ₃ B ₂ (?)	25
YRuB ₂	7.8	LuRuB ₂	17
LuRuB ₂	9.99	LuRuB ₂	17
ScOsB ₂	1.34	LuRuB ₂	17
YOsB ₂	2.22	LuRuB ₂	17
LuOsB ₂	2.66	LuRuB ₂	17

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