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Superconducting-transition temperatures of rare-earth rhodium boride compounds, $R\mathrm{Rh}_4\mathrm{B}_4$

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It is shown that the superconducting-transition temperatures for all $R\mathrm{Rh}_4\mathrm{B}_4$ compounds, where R is a rare-earth (RE) element, can be combined and analyzed in a systematic way. The analysis utilizes an Abrikosov-Gorkov–type expression for pair breaking, with modifications for crystalline electric fields and changes of T_c due to nonmagnetic effects, to describe T_c values in concentrated systems, dilute alloys, and pseudoternary mixtures. As a result, it is seen that the exchange coupling parameter, $N(0)\mathcal{J}^2$, is larger for light RE than for heavy RE, with the increase being very large near the beginning of the rare-earth series. In view of a very similar effect in the $R\mathrm{Al}_2$ system, it is suggested such a variation is common to RE systems.

INTRODUCTION

The ternary compounds $R\mathrm{Rh}_4\mathrm{B}_4$ [where R is a rare-earth (RE) element] have been extensively studied in the last several years because of the occurrence of both superconducting and magnetic transitions which occur, sometimes coexistent, in the same material.[1,2] Such studies have greatly expanded our knowledge of the ways in which these two kinds of interactions affect one another. This extensive work has included the evaluation of a large number of magnetic and superconducting phase diagrams for pseudoternary systems,[1] measurements of extreme anisotropy in magnetic and superconducting properties,[3] an evaluation of the importance of crystalline electric field (CEF) interactions in determining the magnetic properties,[4] investigation of the modification of magnetic interaction due to superconductivity,[5] detailed studies of the way in which superconductivity yields to ferromagnetism,[6] etc. Given the vast amount of information now available, it should be possible to combine large quantities of data with an analysis that is more detailed than is generally possible. In this paper, such an analysis is provided for all the published superconducting transition temperatures (T_c) for ternary and pseudoternary $R\mathrm{Rh}_4\mathrm{B}_4$ compounds.

Information concerning the superconductivity of these systems is provided by data on concentrated alloys, pseudoternary systems, and dilute magnetic alloys. In the following we will consider all of these.

DILUTE ALLOYS

Data obtained by MacKay *et al.* measured the depression of T_c for $\mathrm{LuRh}_4\mathrm{B}_4$ by the addition of small concentrations of RE impurities.[7] Several features of this data, reproduced in Fig. 1, were noted previously. The long-dashed line in the figure connecting the values for the nonmagnetic RE impurities La and Eu in $\mathrm{LuRh}_4\mathrm{B}_4$ show a variation of the superconducting-transition temperature with the RE element which is independent of magnetic effects. In addition, large depressions in T_c are seen which peak at Gd due to magnetic depairing effects. This contribution approximately follows the de Gennes scaling rule expected in the absence of CEF effects,

$$\Delta T_c/x \sim (g_J-1)^2 J(J+1) \tag{1}$$

shown by the short-dashed curve. In view of the large CEF interactions known to be present in these materials,[4] the validity of de Gennes scaling may be questioned. Fulde and co-workers have provided an appropriate theory for superconducting alloys which properly includes CEF effects.[8] For small concentrations of magnetic impurities, they find

$$\ln\left[\frac{T_{c0}}{T_c}\right]=\frac{\pi^2 cN(0)\mathcal{J}^2(g_J-1)^2[J(J+1)]_{\mathrm{eff}}}{2k_BT_c}, \tag{2}$$

where the temperature-dependent angular momentum factor $[J(J+1)]_{\mathrm{eff}}$ is defined by

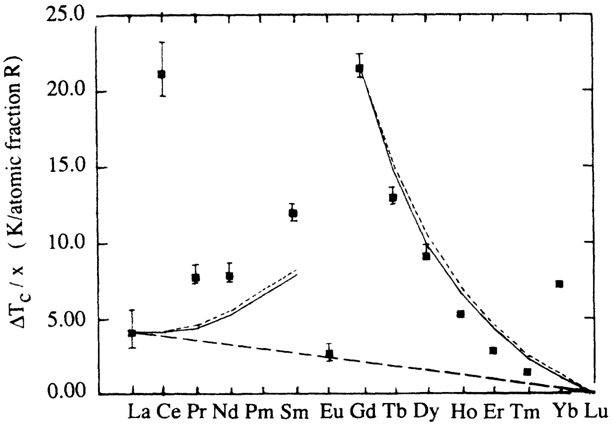

FIG. 1. Depression of superconducting-transition temperature for $R_x\mathrm{Lu}_{1-x}\mathrm{Rh}_4\mathrm{B}_4$, from Ref. 7. The short-dashed curve is based on de Gennes scaling [Eq. (1)]. The solid line shows the effect of including CEF interactions.

$$[J(J+1)]_{\rm eff}=\sum_{i,j}\frac{n_j\,|\langle i\,|\mathbf{J}\,|j\rangle\,|^2}{2}\left[1+\frac{\tanh(\delta_{ij}/2T_c)}{\delta_{ij}/2T_c}-\tanh(\delta_{ij}/2T_c)-\frac{A(\delta_{ij}/2T_c)}{\tanh(\delta_{ij}/2T_c)}+\frac{B(\delta_{ij}/2T_c)}{\tanh(\delta_{ij}/2T_c)}\right] . \qquad (3)$$

Here, i and j label CEF levels, δ_{ij} is the splitting between the ith and jth CEF levels, n_j is the normalized Boltzmann factor for the jth level, g_J is the rare-earth gyromagnetic ratio, J is the total angular momentum of the RE ion, and A and B are functions defined in Ref. 8. The magnetic impurity concentration c is given by $c=x/9$ for a compound $R_x\mathrm{Lu}_{1-x}\mathrm{Rh}_4\mathrm{B}_4$, and T_{c0} is the transition temperature for $x=0$. The exchange constant ($\mathcal{J}$), which couples the RE angular momentum (J), and the conduction-electron spin (s) is defined in accordance with the exchange Hamiltonian

$$H_{\rm ex}=-2\mathcal{J}(g_J-1)\mathbf{J}\cdot\mathbf{s} \; . \qquad (4)$$

In the limit of vanishing CEF interactions ($\delta_{ij}=0$), $[J(J+1)]_{\rm eff}=J(J+1)$, and the usual Abrikosov-Gorkov (AG) expression is obtained for the suppression of T_c by RE impurities.[9]

Using the available CEF parameters, Eqs. (2) and (3) have been evaluated at temperatures corresponding to the reported T_c to obtain $[J(J+1)]_{\rm eff}$ for all the RE ions, taking $T_{c0}=11.5$ K for $\mathrm{LuRh_4B_4}$. Using the results of those calculations to scale the value of $\Delta T_c/x$ obtained for Gd impurities to the other RE impurities gives the solid line shown in the Fig. 1. Although the CEF splittings can be as high as 400 K in these compounds, one sees that the inclusion of CEF effects causes very little deviation from free-ion behavior in this temperature region. Fulde and co-workers have pointed out that the reduction of pair breaking due to CEF interactions is not as large as one might naively expect, due to the presence of virtual transitions over energies large compared to T_c.[8] When T_c becomes sufficiently low, such reductions may become pronounced, and these effects have recently been demonstrated for the $R\mathrm{Rh_4B_4}$ compounds.[10]

One, therefore, sees that even with the inclusion of CEF interactions, substantial discrepancies still exist between the calculated values and the measured data. The Ce and Yb results are far out of line with the other materials, an effect which is presumably related to Kondo phenomena.[7] The most likely explanation for the remaining alloys is a failure of the implicit assumption that the exchange parameter $\mathcal{J}$ is independent of the RE ion. This will be discussed further below.

CONCENTRATED ALLOYS

In addition to the dilute alloy experiments discussed above, a large body of data is also available giving the superconducting- and magnetic-transition temperatures for pseudoternary alloys of the form $A_xB_{1-x}\mathrm{Rh_4B_4}$. These include the A-B systems Y-Gd,[11] Y-Er,[12] Y-Sm,[10] Lu-Ho,[13] Er-Sm,[14] Er-Ho,[15] Er-Tm,[16] and Er-Gd.[17] Johnston and Braun pointed out[18] that some of these data could be understood if one assumed that AG theory held for the concentrated alloys, since they are not *magnetically* concentrated (at best, only one atom in nine is magnetic) and the exchange interactions are relatively weak (exemplified by the low magnetic-transition temperatures). Thus plots of T_c versus $\langle (g_J-1)^2J(J+1)\rangle$, where $\langle\ \rangle$ denotes a compositional average for the RE ions in the pseudoternary alloy, gave a dependence which followed the AG theory, with some exceptions. In particular, the compounds $\mathrm{NdRh_4B_4}$ and the Er-Sm pseudoternary system showed larger pair breaking than the other compounds available at that time. CEF interactions may alter the analysis carried out by Johnston and Braun, but one should note that the discrepancies will only become worse since the inclusion of CEF interactions will always tend to give a smaller pair breaking.

In the following we will provide a complete analysis of all the presently available data in an internally consistent way, making use of as much externally provided information as possible. Direct calculations show that CEF interactions cause a large effect only for Sm and its alloys,[10] but those effects have still been included in the present analysis for all materials. For concentrated alloys, Fulde *et al.* note[8] that a good approximation to exact results is given by using the AG form

$$\ln\left[\frac{T_{c0}}{T_c}\right]=\psi\left[\frac{T_{c0}}{T_c}\rho+\frac{1}{2}\right]-\psi\left[\frac{1}{2}\right] \qquad (5)$$

with

$$\rho=\frac{cN(0)\mathcal{J}^2(g_J-1)^2[J(J+1)]_{\rm eff}}{k_BT_{c0}} \, , \qquad (6)$$

where $[J(J+1)]_{\rm eff}$ is obtained by evaluating Eq. (3) at $T=T_c$. In view of the nonmagnetic depression of T_c shown in Fig. 1, we assume that T_{c0} is dependent on the RE ion, and use Fig. 1 to provide the values tabulated in Table I. We also allow $N(0)\mathcal{J}^2$ to be dependent on the RE ion. For pseudoternary alloys $A_xB_{1-x}\mathrm{Rh_4B_4}$, an average value of Eq. (6) must be obtained. We first assume that the value of T_{c0} to be used is appropriate to the entire crystal, i.e., is not a local property, and calculate

$$\langle T_{c0}\rangle = xT_{c0}^A+(1-x)T_{c0}^B \; . \qquad (7)$$

The average value of Eq. (6) is then obtained as

$$\langle\rho\rangle=\frac{c}{\langle T_{c0}\rangle}\{N(0)\mathcal{J}^2(g_J-1)^2[J(J+1)]_{\rm eff}\}_A + \frac{(1-c)}{\langle T_{c0}\rangle}\{N(0)\mathcal{J}^2(g_J-1)^2[J(J+1)]_{\rm eff}\}_B \; . \qquad (8)$$

For each component, $[J(J+1)]_{\rm eff}$ is evaluated from Eq. (3) at the bulk transition temperature of the alloy.

We first consider the alloys where only one component is magnetic. In that case, all the parameters of Eq. (8) are known except for $N(0)\mathcal{J}^2$, so we adjust that parameter to fit the observed T_c values. For the dilute alloys,

$R_xLu_{1-x}Rh_4B_4$, the data of Fig. 1 have been used to obtain one set of $N(0)\mathcal{J}^2$ values. For pseudoternary systems where one component is nonmagnetic (Y-Er, Y-Sm, Y-Gd, and Lu-Ho), the initial depression of T_c for small impurity concentrations can be used to obtain a second set of values. Finally, another set of values can be obtained from those concentrated ($x=1$) alloys which are superconducting.[19] The results of these analyses are given in Table I. One sees considerable self-consistency among the different results. As a general trend, one sees larger values of $N(0)\mathcal{J}^2$ for the light R, becoming dramatically larger in the beginning of the series.

Using an average value of $N(0)\mathcal{J}^2$ for each rare earth obtained from the values in Table I, we can now extend the analysis to all pseudoternary alloys with no parameters remaining to be determined. Figure 2 shows the results of plotting $T_c/\langle T_{c0}\rangle$ against the quantity defined in Eq. (8). The solid line is the AG curve, Eq. (5). Error analysis is difficult because of the many different experiments which have been incorporated into the analysis, but the agreement is reasonable.

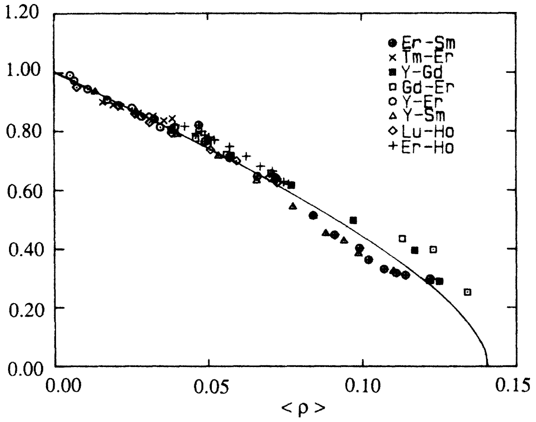

FIG. 2. Comparison of all available T_c values to an Abrikosov-Gorkov curve using the data of Table I and Eq. (8) as described in text.

DISCUSSION

The above analysis shows that all the superconducting-transition temperatures for the RRh$_4$B$_4$ systems can be discussed in terms of Abrikosov-Gorkov—type theory, with suitable modifications being made to accommodate crystal-field interactions and the variation of T_c due to nonmagnetic effects. In achieving this consolidation, one finds that the value of the exchange parameter, $N(0)\mathcal{J}^2$, varies substantially across the rare-earth series. While some variation may be expected, the very large values seen in Fig. 2 near the beginning of the series are surprising. It is therefore of interest to compare these results with previous investigations.

Maple[20] has presented a detailed analysis of EPR, NMR, spin-disorder resistivity, and T_c data to obtain $\mathcal{J}$ for the RAl$_2$ series, and those data are compared to the current ones in Fig. 3. For the RRh$_4$B$_4$ system, the values are obtained by taking the square root of the values in Table I, with the implicit assumption that N(0) does not vary significantly across the series. For both systems, the values have been normalized to 1.00 at the heavy end of the series, in order to allow a direct comparison of the RE dependence rather than of the absolute magnitudes. Within experimental scatter, one sees that the dependence of the exchange interaction on RE is identical for these two systems.

TABLE I. Values of T_{c0} and $N(0)\mathcal{J}^2$ for RRh$_4$B$_4$ systems.

R	T_{c0} (K)	$N(0)\mathcal{J}^2$ (10^{-4} eV) Dilute R in LuRh$_4$B$_4$	RRh$_4$B$_4$	$Y_xR_{1-x}Rh_4B_4$ $Lu_xR_{1-x}Rh_4B_4$
Pr	8.0	13.6	8.6	
Nd	8.3	4.64	3.06	
Sm	8.9	3.47	2.52	2.71
Gd	9.5	1.87		1.90
Tb	9.8	1.69		
Dy	10.0	1.85		
Ho	10.3	1.50		1.54
Er	10.6	1.18	1.16	1.30
Tm	10.9	1.11	1.52	
Lu	11.5			
Y	10.8			

The previous data for the RAl$_2$ system prompted a theoretical discussion by Watson *et al.*, who considered the effects of interband mixing between the $4f$ electrons and the f character of conduction electrons.[21] This is certainly dependent on the angular momentum makeup of the RE ion, and under appropriate circumstances gave a dependence similar to that shown in Fig. 3. However, detailed comparisons with specific systems have not been feasible and the arguments remain rather general. The interesting result to observe here is that the dependence of $\mathcal{J}$ on Re is virtually the same for two systems which must be considered to be very different electronically.

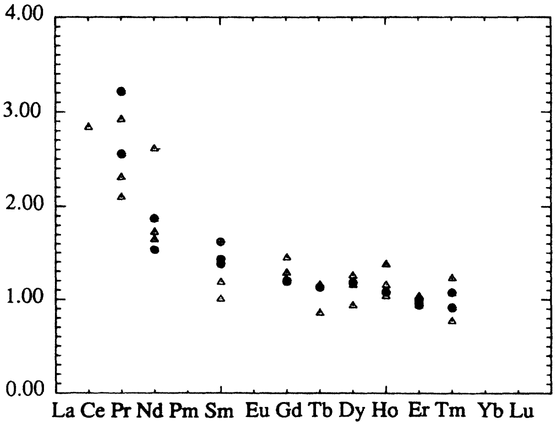

FIG. 3. Comparison of the RE dependence of the exchange constant $|\mathcal{J}|$ for the RRh$_4$B$_4$ series (●, taken from Table I) and the RAl$_2$ series (△, taken from Ref. 19).

This would indicate that some very general phenomenon is involved which is not sensitive to the details of the electronic structure of the compounds. It is intriguing to speculate that this is related to the onset of valence instability near the beginning of the series. It would be very interesting to see if this same tendency holds for other RE systems.

Note added in proof. Values for the exchange constant are available for $R\mathrm{Co}_2$ compounds [A. M. Stewart, J. Phys. C **17**, 1557 (1984)] which also show the dependence on rare-earth ion given in Fig. 3.

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