Crystal-field effects in magnetic superconducting $Er_{1-x}Tm_xRh_4B_4$ and $Er_{1-x}Ho_xRh_4B_4$

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The magnetic and superconducting transitions have been measured in $Er_{1-x}Tm_xRh_4B_4$ and crystal-field theory has been used to explain these transitions and those in $Er_{1-x}Ho_xRh_4B_4$. The minimum observed in the magnetic transition temperature versus x curve in $Er_{1-x}Ho_xRh_4B_4$ has been identified as the first example of a "decoupled" ferromagnetic tetracritical point. The theoretical phase diagrams are in reasonable agreement with the data and hence lead to further understanding of the details. The absence of the specific-heat shoulders above the superconducting-to-ferromagnetic transitions in these pseudoternaries is discussed.

Much attention has been given to rare-earth (R) rhodium borides RRh_4B_4 because of the interplay between superconductivity and magnetism.[1] For example, the nonmagnetic YRh_4B_4 is superconducting below $T_c = 11.3$ K, while $GdRh_4B_4$ and $HoRh_4B_4$ are ferromagnetic below $T_M = 5.6$ and 6.4 K, respectively. However, $ErRh_4B_4$ becomes superconducting at 8.7 K and returns to the normal state at the ferromagnetic transition at 0.9 K.[1,2] The superconducting and ferromagnetic transition temperatures T_c and T_M have been observed in such systems as $Y_{1-x}Gd_xRh_4B_4$,[3,4] $Er_{1-x}Gd_xRh_4B_4$,[3] $Er_{1-x}Ho_xRh_4B_4$,[5] and $Lu_{1-x}Ho_xRh_4B_4$.[6]

In this paper, we report that $Er_{1-x}Tm_xRh_4B_4$ provides another example in the series of compounds RRh_4B_4. We have observed that the thulium ions act upon the superconducting transition magnetically and upon the magnetic transition of the erbium ions nonmagnetically. Our data are interpreted in terms of the crystalline field acting on non-Kramers Tm^{3+} ions. Our simple crystal-field model also explains the phase diagram for $Er_{1-x}Ho_xRh_4B_4$ obtained by Johnston *et al.*[5] In particular, we have identified the minimum in the T_M vs x curve as the first observation of a "decoupled" ferromagnetic tetracritical point.

The dc susceptibility measurements[7,8] above 25 K indicated that the magnetic moment of a thulium ion in $TmRh_4B_4$ is very close to its free ion value. The lattice parameters[9] of $TmRh_4B_4$ are quite similar to those of RRh_4B_4, with R = Gd, Ho, and Er, and thus, it is believed that the thulium ions are trivalent in $Er_{1-x}Tm_xRh_4B_4$. Figure 1 shows the transition temperatures T_c and T_M in $Er_{1-x}Tm_xRh_4B_4$ observed from ac susceptibility measurements. The $T_c(x)$ is a linear function with $T_c = 8.7$ K at $x = 0$ and $T_c = 9.6$ K at $x = 1$, which is lower than the T_c of nonmagnetic YRh_4B_4. Therefore, the thulium ions, believed to be in the singlet ground state, act on the superconducting transition as pair breakers.[10,11] This is consistent with the dc susceptibility measurements.[7] On the other hand, T_M decreases with increasing x, and for $x = 0.4$, no re-entrance was observed down to 0.075 K. Thus, thulium ions appear to act on the

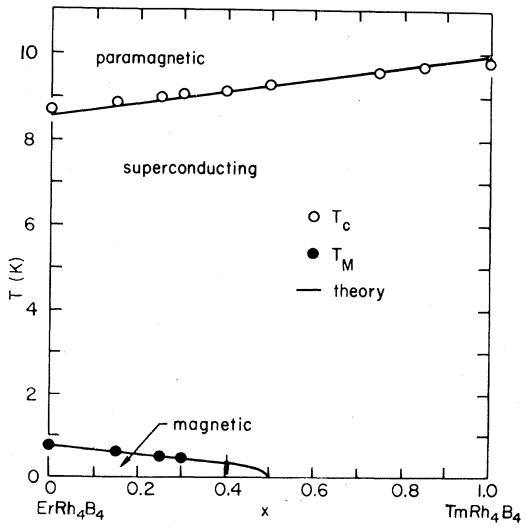

FIG. 1. Phase diagram for $Er_{1-x}Tm_xRh_4B_4$.

magnetic transition as nonmagnetic ions. In order to explain these observations, we propose a simple crystalline-field model for the rare-earth ions in $R\,Rh_4B_4$.

Let us introduce the uniaxial crystal field due to the tetragonal structure of $R\,Rh_4B_4$ as

$$H = DJ_z^2 \ , \tag{1}$$

where the tetragonal axis is taken to be the z axis. Here D is the crystal-field parameter of the rare-earth ion with angular momentum $\vec{J}$. The higher-order terms of the crystal-field energy are neglected. The point-charge model[12] gives the relation $D = \alpha A \langle r^2 \rangle$, where α is the Stevens factor, A is a parameter that depends on the crystal structure, and $\langle r^2 \rangle$ is the averaged value of the $4f$ wave functions of the rare-earth ion. As mentioned above, the lattice parameters are almost independent of R in $R\,Rh_4B_4$ so that A may be taken to be a constant for these ions. Following the Hartree-Fock calculation by Freeman and Watson,[13] the value of $\langle r^2 \rangle$ is almost constant among Er^{3+}, Ho^{3+}, and Tm^{3+} ions, and the values of α are[12] $+2.54\times10^{-3}$, -2.22×10^{-3}, and $+1.01\times10^{-2}$, respectively. Therefore, the sign of D of Er^{3+} ions is positive (the sign of A is positive). This is consistent with the neutron scattering result[2] which revealed that the ferromagnetic moment of $ErRh_4B_4$ is perpendicular to the tetragonal axis.

To determine the value of D for Er^{3+} ions in $R\,Rh_4B_4$, we have employed the magnetic part of the specific heat[14,15] in $Er_{1-x}Gd_xRh_4B_4$ ($x=0$, 0.09, and 0.28) which has a broad peak around 10 K that we identify as the Schottky peak arising from the crystalline-field splitting. By comparing Eq. (1) with the heat-capacity peaks in Refs. 14 and 15 we have found that the value of D of Er^{3+} ions in $R\,Rh_4B_4$ to be ~ 5 K. As discussed above, the sign of the Stevens factor α, and hence D, of Ho^{3+} ions is opposite to that of Er^{3+} ions. Therefore, the direction of the magnetization in ferromagnetic $HoRh_4B_4$ will be in the tetragonal direction[16] and as a result, the direction for $Er_{1-x}Ho_xRh_4B_4$ will depend on x. Thus, it is interesting to examine the magnetic phase diagram of these compounds.

Let us consider the magnetic phase diagrams of a mixture of two rare-earth elements of types 1 and 2. In this case the magnetic Hamiltonian in the virtual-crystal approximation[17] is appropriate; it can be written as

$$H = (1-x)\sum_i D_1 J_{1zi}^2 - (1-x)^2 \sum_i \sum_j J_{11}(ij)\,\vec{J}_{1i}\cdot\vec{J}_{1j} + x\sum_i D_2 J_{2zi}^2 - x^2 \sum_i \sum_j J_{22}(ij)\,\vec{J}_{2i}\cdot\vec{J}_{2j}$$
$$-x(1-x)\sum_i \sum_j 2J_{12}(ij)\,\vec{J}_{1i}\cdot\vec{J}_{2j} \ , \tag{2}$$

where x is the concentration of the element 2, D_l is the crystalline-field parameter of the element l ($l=1,2$), and $J_{ln}(ij)$ is the exchange interaction between the angular momenta $\vec{J}_{li}$ at the ith site and $\vec{J}_{nj}$ at the jth site. We use the molecular-field theory to calculate the magnetic phase diagram. The molecular fields acting on elements 1 and 2 are then

$$\vec{H}_1 = (1-x)\bar{J}_{11}\langle\vec{J}_1\rangle + x\bar{J}_{12}\langle\vec{J}_2\rangle \ ,$$
$$\vec{H}_2 = (1-x)\bar{J}_{12}\langle\vec{J}_1\rangle + x\bar{J}_{22}\langle\vec{J}_2\rangle \ , \tag{3}$$

respectively, with

$$\bar{J}_{ln} = \sum_j 2J_{ln}(ij) \ . \tag{4}$$

The magnetic transition temperature for a second-order phase transition is obtained from the condition that the equations

$$\langle\vec{J}_1\rangle = \vec{H}_1\chi_1^0, \quad \langle\vec{J}_2\rangle = \vec{H}_2\chi_2^0 \ , \tag{5}$$

have nontrivial solutions. Here, χ_l^0 is the paramagnetic susceptibility tensor of element l in the absence of the exchange interaction. We assume the Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism for the exchange interaction between magnetic ions. One exchange constant is determined from T_M in $HoRh_4B_4$; this is the interaction between holmium ions. The remaining exchange constants are obtained by scaling the de Gennes factors as

$$\bar{J}_{11}:\bar{J}_{12}:\bar{J}_{22} = (g_1-1)^2:(g_1-1)(g_2-1):(g_2-1)^2 \ , \tag{6}$$

where g_l is the Landé g factor of element l. The calculated phase diagram for $Er_{1-x}Ho_xRh_4B_4$ is given by the solid lines in the lower part of Fig. 2. In obtaining these, we have used $D(\mathrm{Er}) = 5$ K, $D(\mathrm{Ho}) = -5$ K, and $\bar{J}(\mathrm{Ho\text{-}Ho}) = 0.1$ K. In the figure, the solid boundary lines correspond to ordering of only one spin component and they intersect at an angle at the "decoupled" tetracritical point[18,19]: The ferromagnetic moments in phases A and B are then, respectively, parallel to and perpendicular to the tetragonal axis. Phase C is the oblique ferromagnetic phase. The minimum T_M in the T_M vs x curve is thus the first identification of a "decoupled" tetracritical point at which four ferromagnetic transitions occur. Recent specific-heat data[20] show that in $Er_{0.3}Ho_{0.7}Rh_4B_4$ there appears a peak of the specific heat in the ferromagnetic state, which is consistent with the boundary between A and C phases. Here we have not included

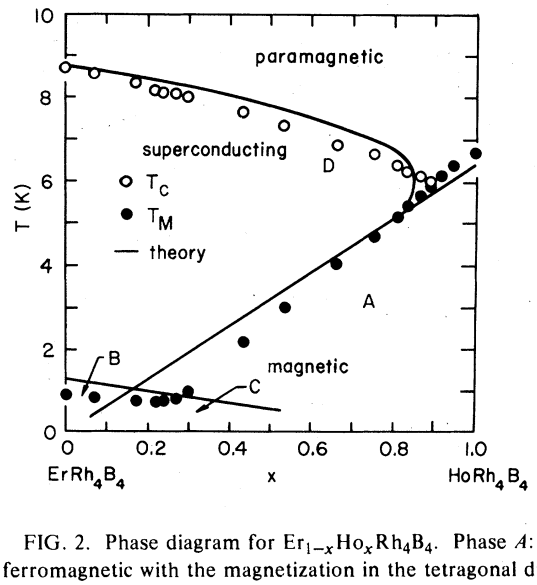

FIG. 2. Phase diagram for $Er_{1-x}Ho_xRh_4B_4$. Phase A: ferromagnetic with the magnetization in the tetragonal direction; phase B: ferromagnetic with the magnetization perpendicular to the tetragonal direction; phase C: oblique ferromagnetic (mixed ferromagnetic); and phase D: paramagnetic or superconducting. The data points are taken from Johnston *et al.* (Ref. 5).

the effects of superconductivity in phase D in the calculation.

Recently, it has been shown[21,20] that the superconducting-to-ferromagnetic transition is slightly first order. However, in view of the fact that the crystalline fields strongly affect the magnetic transition and in spite of the simplicity of the model used in the calculations of the T_M vs x curves in Fig. 2, the agreement between theory and experiment[5] is satisfactory. This calculation also suggests that the exchange interaction is predominantly due to the RKKY mechanism. By employing the above results, we can also conclude that T_M in $Er_{1-x}Gd_xRh_4B_4$ is a linear function of x, as observed experimentally,[3] because the gadolinium ions are S-state ions so that the ferromagnetic moment is perpendicular to the tetragonal axis for all values of x.

We have also calculated $T_c(x)$ of $Er_{1-x}Ho_xRh_4B_4$ in Fig. 2 using Eqs. (3.17) and (3.18) from Ref. 10, the virtual-crystal molecular-field approximation for the spin system, and the following additional parameters using the notations of Ref. 10. The parameters for superconducting electrons are $T_{c0}=11.3$ K, $g_{BCS}N(0)=0.3$, and $I^2N(0)/k_B=0.16$ K. The measure of the range of the exchange interaction is

$$4k_F^2D/k_B=10.0[(1-x)(g_1-1)^2J_1(J_1+1)+x(g_2-1)^2J_2(J_2+1)]$$
$$\times[(1-x)^2(g_1-1)^2/(g_2-1)^2+2x(1-x)(g_1-1)/(g_2-1)+x^2]\ ,$$

where the subscripts 1 and 2 denote the erbium and holmium ions, respectively. Note that the superconducting T_c depends on the crystal field through the susceptibilities of localized spins. As shown, the agreement between theory and experiment is reasonable.

Now, we apply the crystal-field model to the $Er_{1-x}Tm_xRh_4B_4$ case. The parameter values $D=23$ K for thulium ions and $\bar{J}_{11}/k_B=0.045$ K between thulium ions are easily calculated. Contrary to erbium ions, thulium ions are non-Kramers ions ($J=6$) so that the ground state is a singlet state with $J_z=0$. The transverse component of the susceptibility tensor of thulium ions is given as

$$\chi^0_{xx}/(g\mu_B)^2=J(J+1)/2D,\quad T=0\ . \tag{7}$$

Therefore, when $D>\bar{J}_{11}J(J+1)$, $TmRh_4B_4$ has no magnetic transition at finite temperatures. This is consistent with experiment. The exchange constant between erbium and thulium ions is calculated to be $\bar{J}_{12}=0.053$ K, which is also not enough to overcome the crystal field of the thulium ions. Thus, the thulium ions act as nonmagnetic ions as far as their influence on T_M is concerned. On the other hand, when the crystal-field splitting is of the order of or less than k_BT_c, the pair breaking effect on T_c is proportional to the thermal average $\langle\vec{S}^2\rangle=\langle S_x^2+S_y^2+S_z^2\rangle$, with S being the spin angular momentum in the sense of the Abrikosov and Gor'kov theory,[10,22–24] and thus Tm^{3+} ions are pair breakers. The depression of T_c in $Er_{1-x}Tm_xRh_4B_4$ from that in nonmagnetic YRh_4B_4 can be obtained from the following expression:

$$\Delta T_c=-\beta\{(1-x)[(g_1-1)^2J_1(J_1+1)]$$
$$+x[(g_3-1)^2J_3(J_3+1)]\}\ , \tag{8}$$

where $\beta=(\frac{1}{2}\pi^2)I^2N(0)$ with I and $N(0)$ being the s-f exchange constant and the density of state of electrons, respectively. By using $g_1=\frac{6}{5}$ and $J_1=\frac{15}{2}$ for Er^{3+} and $g_3=\frac{7}{6}$ and $J_3=6$ for Tm^{3+}, we derive the upper solid line in Fig. 1, with $\beta=1.06$ K determined by fitting the experimental value of T_c at $x=0.5$. Our theoretical line correctly predicts that T_c increases with increasing x. To obtain T_M vs x, we employ Eqs. (4.2) and (4.5) of Ref. 10. When only nearest-neighbor exchange interactions are considered, the critical concentration x_{cr}, at which $T_M=0$ K is 0.40 for a simple cubic lattice and 0.57 for a bcc lattice. These values are compared with our result $x_{cr}\lesssim 0.4$ in $Er_{1-x}Tm_xRh_4B_4$, which is body-centered tetragonal. By approximating the body-centered

tetragonal lattice by a bcc lattice with nearest-neighbor exchange interactions, the lower theoretical curve in Fig. 1 is found. The parameter values used in calculating T_M gives the value $I^2N(0)/k_B \approx 1.6$ K for the RKKY interaction. On the other hand, the value of β in Eq. (8) for T_c gives the value $I^2N(0)/k_B = 0.21$ K. The large difference between these two values of $I^2N(0)$ suggests that the electrons which contribute to the RKKY interaction are different from those for superconductivity.[10,25] We note that irrespective of the RKKY mechanism, the model of the nearest-neighbor exchange interaction explains the critical concentration x_{cr}. This is because the long-ranged part of the RKKY,[26,27] as well as the dipole interactions,[27,28] are suppressed in the superconducting state.

Finally the broad shoulder of the specific heat above the superconducting-to-ferromagnetic transition in $ErRh_4B_4$ observed by MacKay *et al.*[20] has been attributed to the fluctuations of the spiral spin structure induced by superconductivity.[28] However, the shoulder does not occur in the alloys $Er_{1-x}Ho_xRh_4B_4$ (Ref. 20) and $Er_{1-x}Gd_xRh_4B_4$ (Ref. 15) with $x \neq 0$. In general, the spiral structure is more stable in systems with the easy *plane* crystal field than in those with the easy *axis* crystal field. Therefore, we ascribe the absence of the broad specific-heat shoulder in the pseudoternaries to the fact that the uniaxial crystal field of Ho^{3+} ions depresses the fluctuations of the spiral spin structure.

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[1]B. T. Matthias, E. Corenzwit, J. M. Vandenberg, and H. Barz, Proc. Natl. Acad. Sci. USA 74, 1334 (1977); W. A. Fertig, D. C. Johnston, L. E. DeLong, R. W. McCallum, M. B. Maple, and B. T. Matthias, Phys. Rev. Lett. 38, 987 (1977).

[2]D. E. Moncton, D. B. McWhan, J. Eckert, G. Shirane, and W. Thomlinson, Phys. Rev. Lett. 39, 1164 (1977).

[3]R. H. Wang, R. J. Laskowski, C. Y. Huang, J. L. Smith, and C. W. Chu, J. Appl. Phys. 49, 1392 (1978).

[4]C. Y. Huang, S. E. Kohn, S. Maekawa, and J. L. Smith, Solid State Commun. 32, 929 (1979).

[5]D. C. Johnston, W. A. Fertig, M. B. Maple, and B. T. Matthias, Solid State Commun. 26, 141 (1978).

[6]M. B. Maple, H. C. Hamaker, D. C. Johnston, H. B. Mackay, and L. D. Woolf, J. Less-Common Met. 62, 251 (1978).

[7]J. L. Smith, C. Y. Huang, J. J. Tsou, and J. C. Ho, J. Appl. Phys. 50, 2330 (1979).

[8]Anomalous peaks of the magnetic susceptibility and the specific heat were reported for $TmRh_4B_4$ in Ref. 7. However, it is possible that these anomalous peaks could be due to a ferromagnetic transition in an impurity phase, $TmRh_3B_2$. We thank H. C. Ku for sharing the results prior to publication.

[9]J. M. Vandenberg and B. T. Matthias, Proc. Natl. Acad. Sci. USA 74, 1336 (1977).

[10]S. Maekawa and M. Tachiki, Phys. Rev. B 18, 4688 (1978).

[11]Because T_c is high enough compared with T_M, we may use the Abrikosov and Gor'kov theory [Sov. Phys. JETP 12, 1243 (1961)] to estimate T_c, by neglecting the correlation between magnetic ions (Ref. 10).

[12]See, for example, *Magnetic Properties of Rare-Earth Metals*, edited by R. J. Elliott (Plenum, London, 1972).

[13]A. J. Freeman and R. E. Watson, Phys. Rev. 127, 2058 (1962).

[14]M. B. Maple, Bull. Am. Phys. Soc. 23, 347 (1978); (private communication).

[15]J. C. Ho, C. Y. Huang, and J. L. Smith, J. Phys. (Paris) 39, C6-381 (1978); J. C. Ho (private communication).

[16]G. H. Lander, S. K. Sinha, and F. Y. Fradin, J. Appl. Phys. 50, 1990 (1979).

[17]Per-Anker Lindgard, Phys. Rev. B 14, 4074 (1976).

[18]A. Aharony and S. Fishman, Phys. Rev. Lett. 37, 1587 (1976).

[19]K. Katsumata, M. Kobayashi, and H. Yoshizawa, Phys. Rev. Lett. 43, 960 (1979).

[20]H. B. MacKay, L. D. Woolf, M. B. Maple, and D. C. Johnston, Phys. Rev. Lett. 42, 918 (1979).

[21]S. Maekawa, M. Tachiki, and S. Takahashi, J. Magn. Magn. Mater. 13, 324 (1979).

[22]P. G. de Gennes and S. Sarma, J. Appl. Phys. 34, 1380 (1963).

[23]P. Fulde, L. L. Hirst, and A. Luther, Z. Phys. 230, 155 (1970).

[24]J. Keller and P. Fulde, J. Low Temp. Phys. 4, 289 (1971).

[25]T. Jarlborg, A. J. Freeman, and T. J. Watson-Yang, Phys. Rev. Lett. 39, 1032 (1977).

[26]P. W. Anderson and H. Suhl, Phys. Rev. 116, 898 (1959).

[27]R. A. Ferrell, J. K. Bhattacharjee, and A. Bachi, Phys. Rev. Lett. 43, 154 (1979).

[28]E. I. Blount and C. M. Varma, Phys. Rev. Lett. 42, 1079 (1979).