Superconductivity, crystal-field effects, and magnetic order in the $(Sm_{1-x}Y_x)Rh_4B_4$ mixed ternary system

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The phase diagram of the superconducting transition temperature T_c and the magnetic ordering temperature T_M versus the composition x has been determined for the mixed ternary system $(Sm_{1-x}Y_x)Rh_4B_4$. The x dependence of T_c is described well by the Abrikosov-Gor'kov theory modified to include the influence of the crystalline electric field on the Sm^{3+} ions. Heat-capacity measurements show that T_M decreases linearly with x at the rate $dT_M/dx = -0.0128$ K/(at. % Y). The influence of this magnetic order on superconductivity suggests that a transition from antiferromagnetism to ferromagnetism takes place for $x \sim 0.4$.

INTRODUCTION

The interaction of superconductivity with long-range magnetic order of rare-earth (R) magnetic moments has been investigated extensively in the RRh_4B_4 compounds.[1] One very useful technique has involved studies of mixed ternary systems formed by alloying two related members in this family of compounds. New phenomena investigated in this way include suppression of ferromagnetic order by superconductivity, compounds which exhibit antiferromagnetic order at a temperature above the superconducting transition, and the influence of competing magnetic anisotropies on superconductivity.[1] Reported herein is the variation of the superconducting transition temperature T_c and magnetic ordering temperature T_M with composition x in the $(Sm_{1-x}Y_x)Rh_4B_4$ mixed ternary system. The compound $SmRh_4B_4$ has a superconducting transition temperature T_c of 2.7 K and exhibits the coexistence of superconductivity and long-range antiferromagnetic order below the Néel temperature of 0.87 K.[2] The compound YRh_4B_4 is nonmagnetic and superconducting with $T_c = 10.7$ K. Making alloys of these two compounds provides a useful reference for comparison with other RRh_4B_4 mixed ternary systems in which another magnetic rare-earth element has been substituted for Sm.[3,4] We calculate the composition dependence of T_c for $(Sm_{1-x}Y_x)Rh_4B_4$ including the influence of the crystalline electric field, and discuss the importance of crystal-field effects for $T_c(x)$ in other mixed ternary systems. Superconductivity is destroyed by magnetic order at low temperatures for $x \sim 0.4$, which may reflect a change from antiferromagnetism for $x = 0$ to ferromagnetism for $x \sim 0.4$. Measurements of the upper critical magnetic field for various compositions in this system have been published previously.[5]

EXPERIMENTAL DETAILS

Master samples of $SmRh_4B_4$ and YRh_4B_4 were prepared by arc-melting together the elemental constituents on a water-cooled copper hearth in a Zr-gettered argon atmosphere. Stoichiometric quantities of the elements were used with the exception of boron where ~4% excess by weight was included to suppress secondary phases.[6] Samples in the $(Sm_{1-x}Y_x)Rh_4B_4$ mixed ternary system were prepared by arc-melting together appropriate quantities of the master samples. After sealing in Ta tubes, the samples were annealed for 3 days at 1200 °C, followed by 10 days at 800 °C. Measurements of the ac magnetic susceptibility χ_{ac} as a function of temperature T were made at 22 Hz in a conventional ^{4}He cryostat. Lower temperature $\chi_{ac}(T)$ data were taken at 16 Hz in a ^{3}He-^{4}He dilution refrigerator. The heat capacity C was measured in a semiadiabatic heat-pulse calorimeter connected to a ^{3}He refrigerator by a mechanical heat switch. The dc magnetic susceptibility χ was determined in an applied magnetic field of 0.5 T in a superconducting quantum interference device (SQUID) magnetometer.

RESULTS

The specific heat C versus T between 0.4 and 2 K of five samples with various compositions in the $(Sm_{1-x}Y_x)Rh_4B_4$ mixed ternary system is shown in Fig. 1. For $x \leq 0.30$, a feature indicative of magnetic ordering of the Sm^{3+} ions is observed in the data. The onset of a similar feature is seen for $x = 0.40$, but the peak was below the low-temperature limit ($T_{min} \approx 0.47$ K) of our calorimeter during that experiment. Long-range magnetic order is certainly indicated for $x = 0$ by the rapid onset and sharp maximum in $C(T)$ for this sample. The situa-

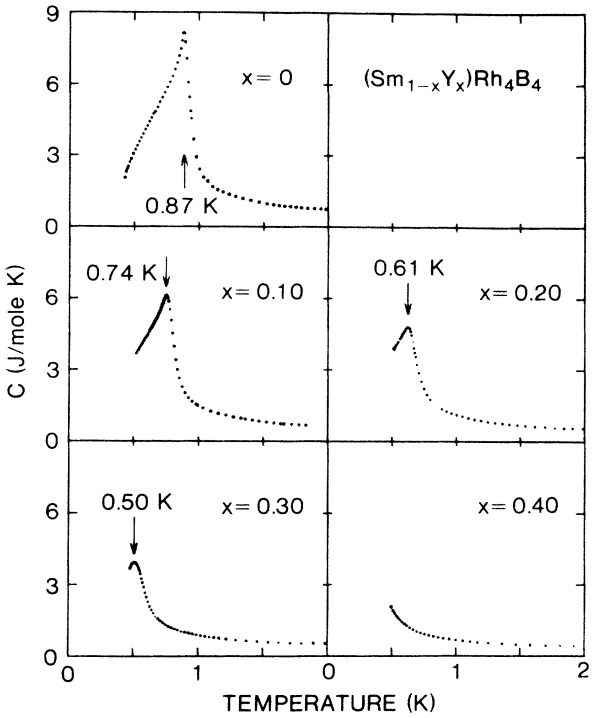

FIG. 1. The specific heat C versus temperature for $(Sm_{1-x}Y_x)Rh_4B_4$ compounds with several compositions. The magnetic ordering temperature defined as the temperature at which C attains a maximum is indicated by the arrow in each case except for $x=0.40$.

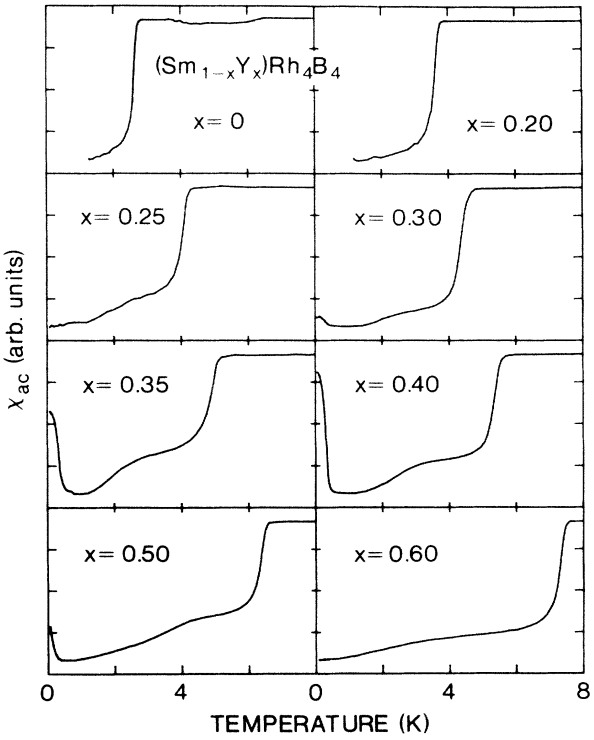

FIG. 2. The ac magnetic susceptibility χ_{ac} vs temperature for $(Sm_{1-x}Y_x)Rh_4B_4$ compounds with various compositions, measured on powdered samples in zero applied magnetic field.

tion is less clear as Y is substituted for Sm since a broader onset and somewhat smeared peak is observed, although the shape of these transitions is very similar over the accessible temperature range. The temperature at which the maximum in $C(T)$ occurs is taken to be the magnetic ordering temperature T_M. A linear decrease of T_M with $dT_M/dx=-0.0128$ K/(at. % Y) is observed as Y is substituted for Sm. An estimate of magnetic contributions to $C(T)$ below $T_{\min}$ is made by a linear extrapolation of $C(T)/T$ to 0 at $T=0$, permitting an estimate of the entropy ΔS associated with the magnetic ordering from

$$\Delta S=\int_0^{T^*}\frac{C}{T}dT\ . \tag{1}$$

With $T^*=1.6$ K, the entropy of magnetic ordering for $x=0$ is 97% of R ln2, the value expected for a doublet ground state where R is the universal gas constant, 8.31 J/mol K. This implies complete magnetic order of all of the Sm^{3+} ions for $x=0$. For $x>0$, ΔS is within 10% of the value expected from scaling the entropy for $x=0$ by $1-x$, indicating complete magnetic order for $x>0$ as well. It should be noted that the $C(T)$ data for $SmRh_4B_4$ ($x=0$) measured for a neutron diffraction sample[7] (sample A) have not been published before. Previously published $C(T)$ data for $SmRh_4B_4$ (Ref. 2) (sample B) showed a similar shape and identical T_M, but the maximum value for $C(T)$ was only 65% of the value observed for sample A. Comparison with the $C(T)$ data for $(Sm_{1-x}Y_x)Rh_4B_4$ measured here for $x>0$ revealed that the data for sample A were consistent with a systematic variation of $C(T)$ as Y was substituted for Sm, while the previously published data for sample B exhibited anomalously low values for $C(T)$. This could arise from larger amounts of impurity phases in sample B, leading to an overestimate of the number of moles of $SmRh_4B_4$

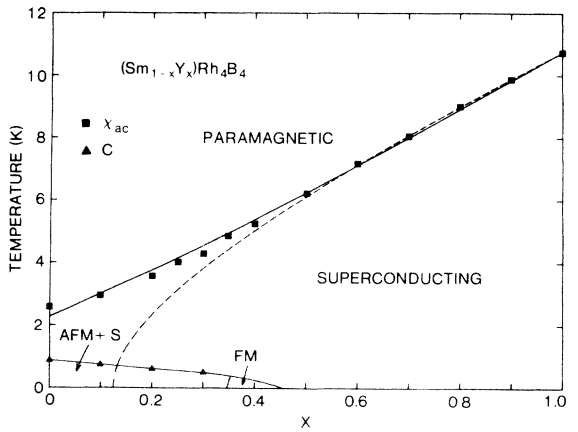

FIG. 3. The phase diagram of transition temperature versus composition x for $(Sm_{1-x}Y_x)Rh_4B_4$. Data points were determined by measurements of the ac magnetic susceptibility χ_{ac} on powdered samples or heat capacity C. The definition of transition temperatures is discussed in the text. Regions labeled include antiferromagnetism coexisting with superconductivity (AFM + S) and a region proposed to be ferromagnetic (FM) where superconductivity is not observed. Calculations described in the text give the paramagnetic-superconducting phase boundary ignoring (dashed line) or including (solid line) the influence of the crystalline electric field.

present in the sample and a consequent underestimate of the molar specific heat. This was confirmed by x-ray diffraction analysis of these two $SmRh_4B_4$ samples which showed considerably larger impurity peaks which appeared to be primarily RhB in sample *B*. This finding does not substantially alter any published conclusions based upon the $C(T)$ data for sample *B*.

Measurements of $\chi_{ac}(T)$ on powdered samples for various compositions of $(Sm_{1-x}Y_x)Rh_4B_4$ are shown in Fig. 2. A rather sharp transition into the superconducting state is indicated by the abrupt decrease of χ_{ac} as the temperature decreases in each case. A second decrease at lower temperature can be seen in the data for many compositions, presumably arising from secondary phases present in the samples. These transitions are broader and exhibit a smaller change in χ_{ac} than the transitions of interest at higher temperature. The superconducting transition temperature T_c is defined from these data as the midpoint of the sharp transition, ignoring any broad transitions at lower temperature. The resulting variation of T_c with composition is shown in Fig. 3. The smooth dependence of T_c on x indicates that any secondary phases present do not substantially alter the composition of the phase of interest. An initially linear depression of T_c is observed as Sm is substituted for Y in YRh_4B_4 with $dT_c/dx = -0.0915$ K/(at. % Sm), in agreement with the value determined for Sm substitutions for Lu in $LuRh_4B_4$.[8] For larger concentrations of Sm, T_c rises above a linear extrapolation of the initial behavior. Also shown in Fig. 3 is the variation with composition of T_M defined from $C(T)$ data as discussed above.

The $\chi_{ac}(T)$ data in Fig. 2 show an unexpected feature. For $0.30 \leq x \leq 0.50$, an increase of χ_{ac} is observed at very low temperature, indicating the destruction of superconductivity in some portions of the sample. The amplitude of this increase grows rapidly as x changes from 0.30 to 0.40, where almost complete destruction of superconductivity is observed. Further substitution of Y for Sm results in a smaller increase, until no feature is observed at low temperature for $x = 0.60$. This destruction of superconductivity is surprising since antiferromagnetic order has been observed to coexist with superconductivity in zero applied magnetic field in almost all cases investigated to date.[1] A possible exception is $Tm_2Fe_3Si_5$, where destruction of superconductivity is observed at the magnetic ordering temperature in samples subjected to pressure, and neutron diffraction experiments at ambient pressure reveal an antiferromagnetic structure for the Tm^{3+} moments.[9] It is possible that antiferromagnetic order also has a destructive effect on superconductivity in the $(Sm_{1-x}Y_x)Rh_4B_4$ mixed ternary system when Y is substituted for Sm. Another explanation for these data is that substitution of Y for Sm changes the antiferromagnetic order observed for $SmRh_4B_4$ into ferromagnetic order. This possibility was investigated further by measuring the dc magnetic susceptibility χ as a function of T for several compositions x. The behavior found for $2\text{ K} < T < 300$ K is similar to that observed previously for $SmRh_4B_4$.[2] We were unable to measure χ in the vicinity of T_M since the low-temperature limit of our SQUID susceptometer is 2 K.

DISCUSSION

A striking feature of the phase diagram shown in Fig. 3 is the curvature of the T_c versus x phase boundary as $x \to 0$. Similar behavior is seen in the $(Sm_{1-x}Er_x)Rh_4B_4$ (Ref. 3) and $(Sm_{1-x}Ho_x)Rh_4B_4$ (Ref. 4) mixed ternary systems. The strong influence of paramagnetic ions on the superconducting transition temperature[10] was explained by Abrikosov and Gor'kov[11] who considered the effect of spin-flip scattering of the conduction electrons due to the exchange interaction between conduction-electron spins and the localized magnetic moments. The variation of the superconducting transition temperature with concentration of paramagnetic ions is given by[11]

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

where ψ is the digamma function, T_{c0} is the transition temperature when $c=0$, c is the concentration of paramagnetic ions with $c=\frac{1}{9}$ for $SmRh_4B_4$, and ρ is the pair-breaking parameter. For R ions, ρ is given by

$$\rho = \frac{cN(0)}{T_{c0}}\mathcal{J}^2(g_J-1)^2J(J+1), \tag{3}$$

where $N(0)$ is the density of states at the Fermi level, g_J is the Landé g factor, and J is the total angular momentum of the R ion. The Hamiltonian for the exchange interaction between the spin **S** of a local magnetic moment and the spin **s** of a conduction electron is given by $H = -2\mathcal{J}\mathbf{S}\cdot\mathbf{s}$. All of the parameters in these expressions are known except $N(0)\mathcal{J}^2$ which can be determined from the linear variation of the transition temperature for small concentrations of paramagnetic ions. The result of such a calculation is shown in Fig. 3 by the dashed line where $J(J+1)=\frac{35}{4}=8.75$ is the free-ion value for Sm^{3+} ions and $N(0)\mathcal{J}^2=3.47$ K was determined from a fit to the data points with $x \geq 0.70$. Large differences are observed between the calculation and the data which exhibit positive curvature as $x \to 0$. Such curvature of $T_c(x)$ has been observed in other superconductors containing R solutes,[12] and Fulde and Peschel have developed a theory which describes this behavior by including the influence of crystalline electric fields.[12] This mechanism was proposed to explain $T_c(x)$ for the $(Sm_{1-x}Er_x)Rh_4B_4$ mixed ternary system, although no calculations were made.[3]

The crystal-field levels for the RRh_4B_4 compounds have been determined recently[13] from an analysis of a variety of experimental data. The result for $SmRh_4B_4$ is that the $J=\frac{5}{2}$ Hund's-rule ground state splits into three nearly pure J_z doublets. The ground state has $J_z=\pm\frac{1}{2}$, the first excited state at 23 K has $J_z \approx \pm\frac{3}{2}$, and the $J_z \approx \pm\frac{5}{2}$ doublet is at 199 K. One effect of this splitting is to reduce the pair-breaking strength of a Sm^{3+} ion at low temperature. Following the analysis of Fulde and Peschel,[12] we can calculate the temperature dependence of the quantity

$$[J(J+1)]_{\text{eff}}=-\sum_{i,j}\frac{n_j}{2}|\langle i|\mathbf{J}|j\rangle|^2\left[1+\frac{\tanh(\delta_{ij}/2T_c)}{\delta_{ij}/2T_c}-\tanh(\delta_{ij}/2T_c)-\frac{A(\delta_{ij}/2T_c)}{\tanh(\delta_{ij}/2T_c)}+\frac{B(\delta_{ij}/2T_c)}{\tanh(\delta_{ij}/2T_c)}\right], \quad (4)$$

where i and j label crystal-field levels, $\delta_{ij}=E_i-E_j$ is the energy difference between crystal-field levels,

$$n_j=e^{-E_j/kT}\Big/\sum_i e^{-E_i/kT},$$

and $A(x)$ and $B(x)$ are expressions given in Ref. 12. At $T_c=10.7$ K, the superconducting transition temperature of YRh_4B_4, $[J(J+1)]_{\text{eff}}$ has the value 8.28, only 5% less than the free-ion value. When the temperature is decreased to $T_c=2.7$ K, the superconducting transition temperature of $SmRh_4B_4$, the influence of the excited state with $J_z\approx\pm\frac{5}{2}$ is sufficiently small that $[J(J+1)]_{\text{eff}}$ has the value 6.41, a reduction of 27% from the free-ion value. A reasonable approximation to the exact calculation[12] of the concentration dependence of T_c is to substitute $[J(J+1)]_{\text{eff}}$ for $J(J+1)$ in the Abrikosov-Gor'kov expression given in Eq. (2). The resulting $T_c(x)$ is shown in Fig. 3 by the solid line where the value for $N(0)\mathscr{J}^2=3.93$ K was determined from a fit to all of the data, and there are no other adjustable parameters. The agreement with the data is excellent, with both the curvature and $T_c(x=0)$ following naturally from the calculation. Another interpretation of these results has been given in which the enhancement of T_c as $x\rightarrow 0$ is caused by antiferromagnetic coupling between Sm^{3+} ions.[14] The agreement between data and theory using two parameters to fit the data is also very good in this case. However, the same theory would predict much stronger suppression of T_c in compounds with ferromagnetic coupling of the R^{3+} ions than is observed in the family of RRh_4B_4 compounds. Inclusion of crystal-field effects in the way presented here shows that correlations between R^{3+} ions are not necessary to explain the data.

The influence of crystal-field effects on $T_c(x)$ for other RRh_4B_4 mixed ternary systems can be determined using the same analysis given above. In all cases except $GdRh_4B_4$, where crystal-field effects are very small, the calculations show that $[J(J+1)]_{\text{eff}}$ can be considerably reduced at low enough temperatures. However, either ferromagnetic order or superconductivity usually occurs at a temperature high enough that no substantial change should be observed in $[J(J+1)]_{\text{eff}}$. A possible exception is $NdRh_4B_4$, where crystal-field effects are expected to be large, and T_c is only 5.3 K.[1] However, direct calculations show that inclusion of crystal-field effects increases T_c by only 10% in this case. Therefore, $SmRh_4B_4$ appears to be the only case in this family of compounds showing pronounced crystal-field enhancement of T_c. These conclusions are supported by an analysis which showed that the conventional Abrikosov-Gor'kov theory provides an excellent description for the concentration dependence of many RRh_4B_4 mixed ternary systems.[6]

Another interesting aspect of the results for the $(Sm_{1-x}Y_x)Rh_4B_4$ mixed ternary system is the destruction of superconductivity observed at low temperature for $x\sim 0.4$. One possibility mentioned earlier is that this signals a transition from antiferromagnetism to ferromagnetism as Y is substituted for Sm. Although we cannot at present measure $\chi(T)$ in the vicinity of T_M, we have analyzed our data for 2 K $<T<$ 300 K using a Curie-Weiss law plus a constant Van Vleck term. Previous work has shown that this provides an excellent description of data for a polycrystalline sample of $SmRh_4B_4$.[2] We anticipated that the Curie-Weiss intercept Θ would change from the value -1.93 K determined previously[2] for $x=0$ to a positive value for $x\sim 0.4$. Unfortunately, deviations from the theoretical behavior for $T<10$ K, as well as uncertainties caused by small amounts of ferromagnetic impurity phases, make it difficult to draw definite conclusions from this analysis. We plan to measure $\chi(T)$ to temperatures lower than T_M so that the question of ferromagnetic order in $(Sm_{1-x}Y_x)Rh_4B_4$ for $x\sim 0.4$ can be resolved. Recent work on thin films of $SmRh_4B_4$ disordered by irradiation was described using a model in which antiferromagnetic nearest-neighbor interactions between Sm^{3+} ions were in competition with next-nearest-neighbor ferromagnetic interactions.[15] This model is consistent with the behavior we observe as Y is substituted for Sm in $(Sm_{1-x}Y_x)Rh_4B_4$.

CONCLUSIONS

We have determined the phase diagram of transition temperature versus concentration in the mixed ternary system $(Sm_{1-x}Y_x)Rh_4B_4$. The behavior of the superconducting transition temperature $T_c(x)$ is very well described by the Abrikosov-Gor'kov theory modified to include the influence of crystalline electric field splitting of the energy levels of the $J=\frac{5}{2}$ Sm^{3+} ions. Substitution of Y for Sm depresses the antiferromagnetic ordering temperature at a rate $dT_M/dx=-0.0128$ K/(at. % Y). The influence of the magnetic ordering on superconductivity for $x\sim 0.4$ indicates a change to ferromagnetic order near this composition, but further work is required to confirm this.

ACKNOWLEDGMENTS

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