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Magnetic ordering of $Gd_xEr_{1-x}Rh_4B_4$ near the superconducting region*

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ABSTRACT

$Gd_xEr_{1-x}Rh_4B_4$ exhibits superconductivity at some critical temperature T_c followed by the onset of long-range ferromagnetic ordering at a lower temperature and a loss of superconductivity for $x < x_c \simeq 0.28$, where x_c is the critical concentration at which superconductivity is suppressed. For x above x_c, the compound is no longer superconducting but is still magnetically ordered. We have made ac resistivity R, ac magnetic susceptibility χ, and dc magnetization measurements on samples with x near x_c. For $x \simeq 0.28$, the salient features for the R and χ measurements are: (1) In zero external field a sharp maximum in the ac $\chi(T)$ and a minimum in R(T) are observed. With a small external dc magnetic field ($\sim 10^2$ Oe), the extrema in $\chi(T)$ and R(T) are depressed and smeared considerably with a corresponding shift in the temperatures at which the extrema occur. (2) The sample is not superconducting down to 0.6 K. (3) In the presence of a dc magnetic field, a second ac χ peak appears at a slightly higher temperature. (4) The field dependence of the ac susceptibility resembles that of a spin glass. Details of the field dependence of these observations and the nature of these phenomena will be presented.

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INTRODUCTION

The study of competing mechanisms between magnetic ordering and superconductivity has been of considerable interest. Using an ac magnetic susceptibility technique, we have investigated the interaction between these two opposing mechanisms for ordering in the re-entrant magnetic superconductor $Gd_xEr_{1-x}Rh_4B_4$. In these compounds, the rare earth (RE) ions account for nearly 11 at.% of the total constituents and occupy regular lattice sites. Measurements of the low-field ac susceptibility on these pseudo-ternary compounds for x between 0 and 1 have revealed three different concentration regimes. For $x \lesssim 0.26$, the samples exhibit a high-temperature superconducting phase followed by a low-temperature ferromagnetic transition and loss of superconductivity. For $x > 0.28$, the samples undergo direct paramagnetic to ferromagnetic transition. A phase similar in certain respects to that observed in spin-glass is seen for $x \approx 0.28$. The temperature-concentration phase diagram was reported elsewhere[1]. A discussion on the nature of the re-entrant magnetic superconductivity in these compounds was recently presented[2]. Here we would like to report our results on ac susceptibility measurements for samples with $x = x_c$ where x_c is the critical concentration at which the superconducting transition temperature T_c and the ferromagnetic ordering temperature T_m coincide. Many observed features are similar to the characteristics of a spin-glass system.

EXPERIMENTAL RESULTS

The samples were prepared following the method employed by Fertig et al.[3]. In order to improve homogeneity, our samples were annealed at 1000°C for 30 days. The samples were cut into rectangular pieces approximately 1 mm x 1 mm x 10 mm. The susceptibility was measured at a frequency of 400 Hz and a driving field of the order of 10^{-2} Oe. Conventional four terminal ac electrical resistance measurements were also made. A superconducting solenoid provided the static magnetic field which was parallel to the ac field and to the long axis of the sample. Due to the geometry and orientation of the sample, the demagnetization factor was negligible and no correction was made for demagnetizing effects on the data presented here.

In Fig. 1 we show the concentration dependence of the superconducting and ferromagnetic transition temperatures, T_c and T_m respectively, in zero external field. For $x > 0.28$ ferromagnetism prevails at temperatures below T_m. Upon decreasing Gd concentrations below $x \approx 0.26$, these compounds become superconducting at T_c followed by a ferromagnetic transition at a lower temperature T_m. The ferromagnetic transitions of $ErRh_4B_4$ have been confirmed by neutron scattering[4] and specific heat measurements [3,5]. Heat capacity data also confirm the ferromagnetic transitions of $Gd_xEr_{1-x}Rh_4B_4$ for x = 0.09, 0.28, and 0.65 [5]. The dashed straight line is the result of the calculated Curie-Weiss temperature θ based on the mean-field theory[2]. Within experimental error (±3%), the θ determined from magnetization measurements agree with the values of the inductively determined T_m. The approximately linear increase of T_m with x suggests the T_m is a measure of the interactions mainly between the Gd ions via the RKKY mechanism. For $x \lesssim 0.1$ the superconducting transition temperature T_c follows the prediction of the Abrikosov and Gorkov (AG) theory [6]. For $x \approx 0.23$ the ferromagnetic exchange interaction competes with superconductivity. An anomalous phase with peculiar ac susceptibility and resistivity behavior occurs near the critical concentration.

In order to better understand these two competing interactions between two given spins, we have measured the field dependence of the ac susceptibility and resistance of $Gd_{0.28}Er_{0.72}Rh_4B_4$ (Fig. 2). The salient features are as follows: (1) In the absence of an externally applied static magnetic field, H, a pronounced maximum in the ac $\chi(T)$ and a minimum in R(T) are observed near 2.4K and 2.6K, respectively.

(2) With a small magnetic field ($H \approx 10^2$ Oe), the extrema in both $\chi(T)$ and $R(T)$ are depressed and rounded with corresponding shifts in the temperatures at which these extrema occur. With increasing fields, there is a displacement of the temperature of the susceptibility peak (T_O) towards lower temperatures, and a second smaller susceptibility bump begins to appear at increasingly higher temperatures. The upward shift in the temperature of the second χ peak manifests itself better at higher fields than the field levels shown. (3) The sample is not superconducting down to 0.6K. (4) The change in the amplitude of the susceptibility $\Delta\chi(T \lesssim T_O, H=0)$ is about an order of magnitude larger than that of a comparable piece of lead at its superconducting transition ($\Delta\chi \approx -(4\pi)^{-1}$). The $\Delta\chi$ for the sample with x=0.28 is only about two thirds of the value in the paramagnetic to ferromagnetic transition of the x=0.65 sample. The relative change in $\chi(T)$ normalized to that of lead increases with increasing Gd concentrations for x near x_c. Finally, (5), the qualitative features of the $\chi(T)$ curve are independent of the direction of temperature changes. However, there is marked hysteresis ($\lesssim 0.1$K) in T_O with a higher T_O when the sample is warmed than during cooling regardless of the field level.

In addition to the susceptibility data, recent calorimetric studies of the heat capacity C(T) showed that the amplitude of the C(T) anomaly near T_O decreases by only about 10% from its field-free value when an external field of 1 kOe was applied [5]. There is neither a noticeable change in the temperature at which the sharp peak in C(T) occurs nor an observable broadening of the peak.

DISCUSSION

The temperature and field dependencies of the magnetic susceptibility in $Gd_{0.28}Er_{0.72}Rh_4B_4$ exhibit striking similarities to that observed in a spin glass. In the absence of an external field

H=0, we have a sharp peak in $\chi(T)$ at T_0. Small external fields (~ 10-10^2 Oe) round the maximum in χ and shift T_0 to lower temperatures. In a spin glass the field hinders the occurrence of the spin glass transition and hence depresses the "freezing temperature," T_f. As shown in Fig. 2, a field of about 200 Oe can depress χ by a factor of about two even though the corresponding magnetic energy, μH, is less than 1% of the characteristic ordering energy $k_B T_m$. A similar phenomenon was observed in La-Gd alloys by Finnemore et al. [8]

Within the experimental error ($\pm 0.3\mu_B$) the effective magnetic moments per RE ion, μ_{eff}, determined from static magnetization measurements agree with the values predicted from Hund's rule by taking the weighted sum of the ground state Gd^{3+} and Er^{3+} ions. With increasing Gd concentrations, both μ_{eff} and the Curie-Weiss temperature increase because of the growing importance of short range magnetic ordering. For values of $x < x_c$, a paramagnetic →superconducting →ferromagnetic transition occurs. For $x > x_c$, these pseudo-ternary compounds change from paramagnetic to ferromagnetic ordering directly without any intervening superconducting or spin glass-like regime. For x near x_c the ordering energies of the two opposing mechanisms present in the system nearly balance each other out. This rather delicate balance results in the mixed regime lying between the two limits. There might be two different transitions very close to each other resulting in a sharp peak of $\chi(T)$ in the absence of field. With finite fields the apperarance of the second susceptibility bump at a temperature higher than T_0 may imply a ferromagnetic transition. According to Verbeck et al. [9], in a system with coexisting ferromagnetism and spin glass behavior, a small applied field can separate the single peak into two overlapping responses for ferromagnetism and spin glass due to their opposite field dependence. An external field is favorable for ferromagnetism and would enhance the ferromagnetic transition temperature, but it depresses the spin glass freezing temperature. Due to the small values of the magnetic fields employed here, superparamagnetism rather than the usual ferromagnetism may be responsible for the second peak in χ. Although the RE ions are located on the regular lattice, the relatively large concentration of Gd ions could form "clusters" which can rotate as a whole in a modest field. These clusters may be ferromagnetically coupled to form superparamagnetic moments [10].

The large drop in ac resistance at a temperature higher than T_o to less than half of its asymptotic values at high or low temperatures suggests that the system attempts to become superconducting but the transition is suppressed by the magnetic ordering. The enhanced conductivity may also be due to paraconductivity and fluctuations may persist for $T< T_o$. The increase in the temperature of the resistive minimum seems to correspond to that of the second susceptibility bump. In contrast to the usual behavior of a ferromagnet, the magnetoresistance of these samples below T_m increases with increasing field for $0 \leq x \leq 0.28$. The ratio of the normal resistance below T_m to that above T_c increases monotonically and approaches unity as x increases from zero toward 0.28. Furthermore, the reduction in heat capacity C(T) with increasing field has also been observed in other spin glass systems where magnetic fields block the formation of spin glass and hence reduce C(T) [11]. The estimated magnetic contribution [5] to the entropy near T_o of about 10 J/mole-K is nearly equal to R ln(2S+1) = R ln 4 = 11.5. This implies that four electronic levels (two doublets) of Er^{3+} lie below ~2K.

In summary, the observed magnetic field and temperature dependencies of the ac susceptibility and the heat capacity for the re-entrant magnetic superconductor $Gd_xEr_{1-x}Rh_4B_4$ near its critical concentration of $x_c \approx 0.28$ resemble many of the characteristics of a spin glass system. However, because of the fact that these anomalous phenomena take place near the critical temperature, these phenomena might result from Cooper pair fluctuations. Undoubtedly more work is needed to further characterize the nature of this intriguing phase.

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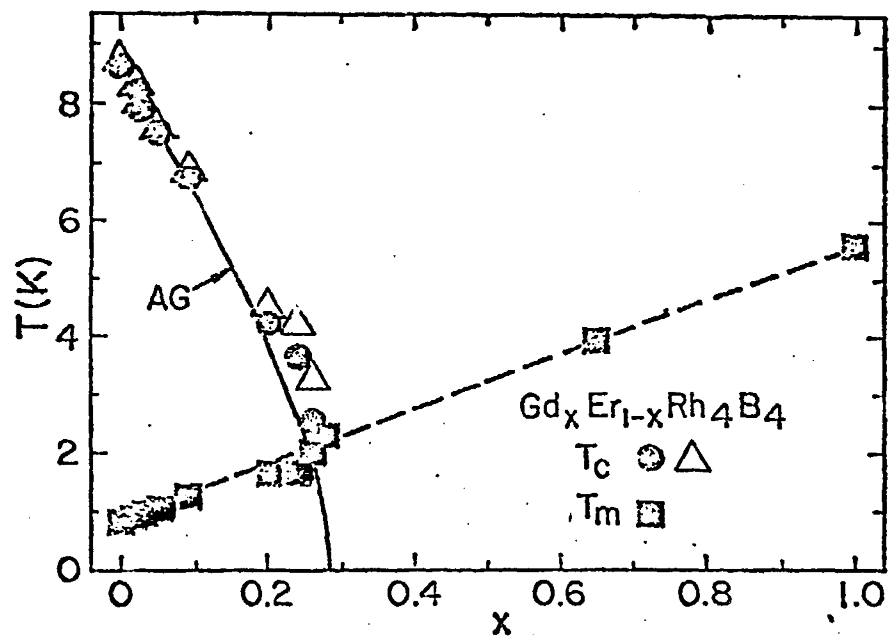

Fig. 1.

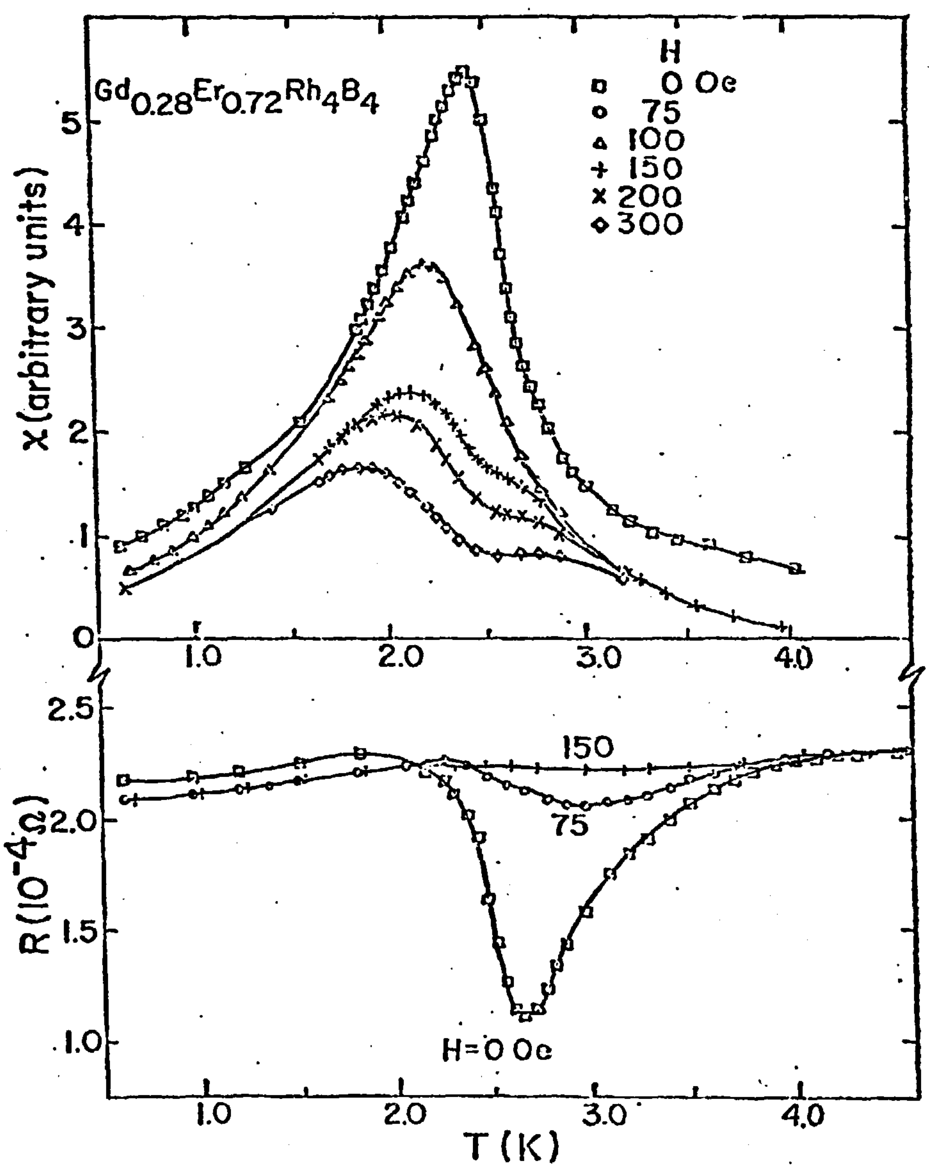
$Gd_{0.28}Er_{0.72}Rh_4B_4$
H
0 Oe
75
100
150
200
300
χ (arbitrary units)
0
1
2
3
4
5
1.0
2.0
3.0
4.0
150
75
H=0 Oe
R(10^{-4}Ω)
2.5
2.0
1.5
1.0
1.0
2.0
3.0
4.0
T (K)

Fig. 2.