Reentry and Coexistence Behavior of the Magnetic Superconductor $(Th_{1-x}Nd_x)Ru_2$

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The authors have measured, via ac susceptibility $\chi(T, H)$, the superconducting and magnetic phase diagram for the $(Th_{1-x}Nd_x)Ru_2$ system. For $0.3 < x < 0.4$ reentry and coexistence behavior are observed at low temperatures. The field-dependent properties show that a weakened superconducting state can exist in a frozen spin-glass or cluster-glass state. Here a field memory effect can easily destroy the superconductivity. This indicates that the spin-glass phase consists of very large randomly frozen ferromagnetic clusters.

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Coexistence of superconductivity and magnetism remains a topic of considerable interest.[1] During the past 22 years since the Abrikosov-Gor'kov theory,[2] attention has shifted from random binary and pseudobinary alloys to ternary intermetallic compounds, such as RMo_6S_8 and RRh_4B_4 (R denotes a magnetic rare-earth element). For these compounds superconductivity can coexist with various types of antiferromagnetic order, but is destroyed by the onset of long-range ferromagnetism.[3] With the great present day importance of spin-glasses as a uniquely different form of magnetic ordering, it is of consequence to consider the effect of spin-glass or cluster-glass freezing on the superconducting state. A number of experimental[4-6] and theoretical[7-9] works have studied this problem and have come to a favorable conclusion for coexistence. Nevertheless, the experimental evidence for the combined phase is usually implied or extrapolated from the single phases. Recently a series of neutron scattering[10] and Mössbauer effect[11] measurements have indicated a coexistence of a ferromagneticlike spin-glass phase in a superconducting $(Ce_{0.73}Ho_{0.27})Ru_2$ alloy. However, the magnetic ordering temperatures were vastly different as determined by the two experiments. To our knowledge no direct observation has been made of the superconducting state far below the spin-glass freezing temperature T_g and the possibility of reentry behavior has not been established.

In this Letter we present a systematic ac susceptibility $\chi(T, H)$ study of the $(Th_{1-x}Nd_x)Ru_2$ system which shows for the first time *two* normal and *two* superconducting phases as a function of temperature. This system was chosen because of its expected, very small depression of the superconducting transition temperature $T_c \approx -0.02$ K/at.%,[12] which should enable us to go to fairly large x values, and even to reach the percolation limit for long-range ferromagnetism ($x_p = 0.42$). $NdRu_2$ is ferromagnetic at 21.5 K. This then offers the direct opportunity to investigate the superconducting properties over a wide range of ferromagnetic cluster sizes for $x < 0.4$. In this concentration limit the low-temperature magnetic ordering is compsed of a randomly frozen array of large ferromagnetic clusters which we name a cluster glass.[13] Moreover, Nd in $ThRu_2$ is expected from comparison with similar systems[14] to have a large crystalline-field splitting of more than 100 K, which was confirmed by our high-temperature magnetization measurements. At low temperatures Nd can be considered as an effective $S = \frac{1}{2}$ system.

We have determined a most unusual superconducting/magnetic phase diagram, i.e., $T_c(x)$ and $T_g(x)$ (see Fig. 1), for $(Th_{1-x}Nd_x)Ru_2$. On the basis of the various temperature and field dependences we can conclude the following: (i) Spin-glass-like freezing can occur far below T_c without destroying the superconductivity. (ii) If $T_g \lesssim T_c$, a remarkable quenching of the superconductivity occurs at T_g followed by a recovery of superconductivity at very low temperatures where

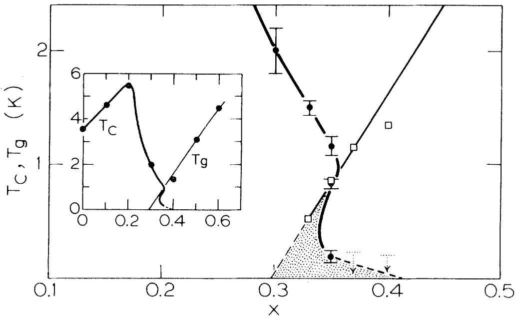

FIG. 1. Superconducting (T_c) and magnetic (T_g) phase diagram for $Th_{1-x}Nd_xRu_2$. The lines are a visual guide.

the larger ferromagnetic clusters are known to become unstable for $x < x_p$.[13] This unique behavior results in one cluster-glass and three superconducting-normal transitions at a single $x = 0.35$ value. (iii) A field memory effect associated with the isothermal remanent magnetization of a cluster glass can be used to suppress the reentry superconductivity at the lowest temperatures (for $T < T_g$). (iv) The coexistence state is that of a weakened superconductor with greatly reduced critical fields. (v) The cluster-glass state is composed of very large, randomly frozen ferromagnetic clusters which can easily be aligned in a small magnetic field.

The samples of $(Th_{1-x}Nd_x)Ru_2$ were prepared by repeated arc melting of the appropriate components which were all at least 99.99% starting purity. Nominal concentrations were deemed reliable based upon the negligible weight losses during melting and the systematic and reproducible behavior of our susceptibility measurements. Each sample had an almost spherical shape and was annealed at 900 °C for three days, followed by quenching into water. The sharpness of the superconducting transitions indicates a well-ordered intermetallic compound and a homogeneous distribution of Th and Nd. The complex, ac susceptibility $\chi = \chi' - i\chi''$ was determined by a standard two-phase mutual inductance technique at 123 Hz and 0.1 G driving field. Temperatures between 20 mK and 4 K were generated by a specially constructed ^{3}He-^{4}He dilution refrigerator[15] with the sample, coil system, and thermometer inside an epoxy mixing chamber to ensure good thermal contact. An external static magnetic field up to 1.25 kG could be applied and swept at any temperature.

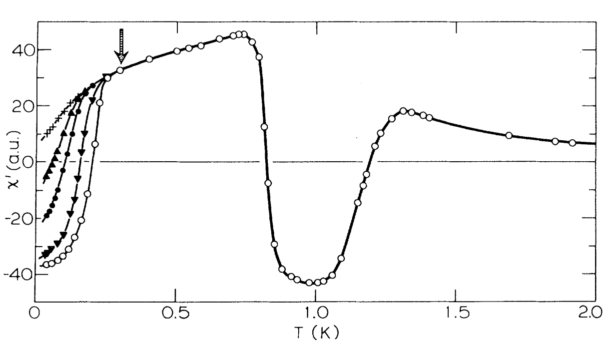

FIG. 2. Reentry and coexistence of superconductivity in $Th_{0.65}Nd_{0.35}Ru_2$ via susceptibility in zero field: open circles. Memory effect (arrow) of applying an H field for two minutes at $T = 300$ mK ($< T_g = 850$ mK) and then zero-field cooling: inverted triangles, $H = 49$ G; circles, $H = 94$ G; triangles, $H = 122$ G; and plusses, $H = 195$ G.

Figure 1 shows the superconducting/magnetic phase diagram for the $(Th_{1-x}Nd_x)Ru_2$ system. The initial rise of T_c with increasing x has previously been observed in other systems[16] and is ascribed to "alloying effects" due to the difference in electronic configurations of Th and Nd. Our main region of interest is between $x = 0.3$ to 0.4. Since the nearest-neighbor site percolation is $x_p = 0.42$ we have denoted the magnetic ordering regime below $x = 0.4$ as a cluster-glass phase where there is certainly no uniform long-range ferromagnetic order.[13] However, the exact nature of this regime is at present unclear, especially for mixed interacting (e.g., Ruderman-Kittel-Kasuya-Yosida) systems. Very recently various descriptions of the magnetism have been proposed with use of the concepts of a frustrated ferromagnet with random fields[17] and a spatially disordered ferromagnet.[18]

In Fig. 2 we exhibit the detailed behavior of the ac susceptibility as a function of temperature for $(Nd_{0.35}Th_{0.65})Ru_2$. Note the reentrance of superconductivity below 200 mK. To illustrate that this low-temperature superconductivity is due to the ferromagnetic clusters we have switched an external field on and off at 300 mK. Then we cool the sample in *zero field* to 20 mK. Before switching on the field to another value, the sample was warmed to ≈1.5 K and then returned to 300 mK to remove any partially frozen in fields. The result of this memory effect is shown in Fig. 2. Notice how the superconductivity is essentially quenched for on-off fields above ≈150 G. Figure 3 presents the ac susceptibility as a function of temperature for $(Nd_{0.33}Th_{0.67})Ru_2$ in various external magnetic fields. In these measurements the field was applied at high temperatures and the sample was

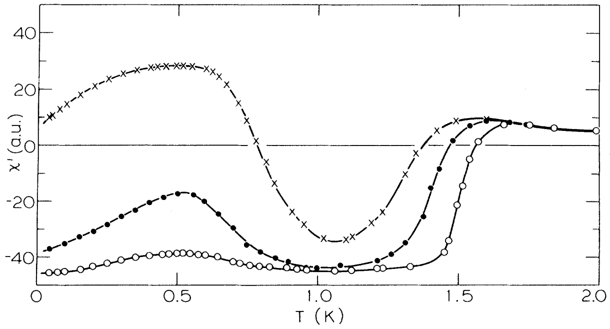

FIG. 3. Temperature dependence of the susceptibility cooled in various fields for $Th_{0.67}Nd_{0.33}Ru_2$. Note the emergence of the cluster-glass maximum as H is increased. Open circles, $H = 0$ G; closed circles, $H = 66$ G; crosses, $H = 170$ G.

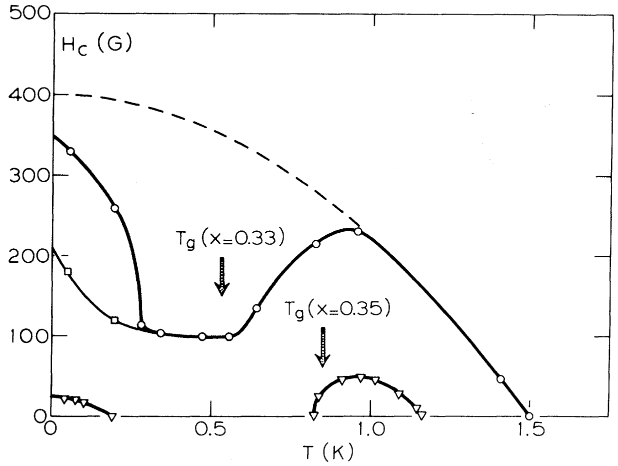

FIG. 4. Critical fields for $Th_{0.67}Nd_{0.33}Ru_2$ and $Th_{0.65}Nd_{0.35}Ru_2$ obtained by field sweeping at constant temperature. T_g represents the freezing temperatures determined by the peak in the susceptibility. The lines are a visual guide and the dashed line represents a $1-(T/T_c)^2$ extrapolation. Circles, increasing field, and squares, decreasing field for $x = 0.33$. Triangles, increasing field for $x = 0.35$; see text.

field cooled. As is clearly seen we were able to drive the system more magnetic with the external field, thereby progressively destroying the superconductivity. Even so a visible $\chi(T)$ maximum remains in the superconducting state denoting the freezing temperature. This means there is a large field penetration into the superconductor probably through these ferromagnetic clusters, i.e., a sort of induced vortex state.

Finally, Fig. 4 gives the critical field for superconductivity as a function of temperature for both samples mentioned above. Here the field was swept at constant temperature to both positive and negative values. The circles were obtained at increasing fields and the squares, at decreasing fields. Note the hysteresis which appears below T_g, characteristic for the strongly ferromagnetic cluster glass. For the $x = 0.35$ sample hysteresis is also present at $T < 200$ mK. Now the isothermal remanent magnetization prevents the superconductivity from reappearing after the field has been reduced to zero. The dashed line represents an extrapolation of $H_c(T)$ according to a $1-(T/T_c)^2$ dependence. Obviously the superconducting state is greatly weakened especially near and below T_g.

By exploiting the small pair-breaking effect of Nd in $ThRu_2$ we were able to track the superconducting transition temperature as the percolation limit for long-range ferromagnetism ($x_p = 0.42$) was approached from below. In doing so, we have proven that superconductivity can coexist with a cluster-glass ordering of ferromagnetic clusters, provided that the mean cluster size is small enough. By taking $x = 0.36$ as the borderline for superconductivity, we can use the expansion of Sykes and Essam[19] to obtain a cluster size of ≈15 atoms or of the order of 20 Å. The inclusion of ferromagnetic clusters in a superconductor has many interesting possibilities not only for memory effects, but also for flux line and pinning behavior.

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[1] M. Ishikawa, Contemp. Phys. 23, 443 (1982).

[2] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. 39, 1781 (1960) [Sov. Phys. JETP 12, 1243 (1961)].

[3] See, for example, M. B. Maple, J. Magn. Magn. Mater. 31–34, 479 (1983).

[4] D. Davidov, K. Baberschke, J. A. Mydosh, and G. J. Nieuwenhuys, J. Phys. F 7, L47 (1977); T. E. Jones, J. F. Kwak, E. P. Chock, and P. M. Chaikin, Solid State Commun. 27, 209 (1978).

[5] S. Roth, Appl. Phys. 15, 1 (1978).

[6] J. B. Boyce and K. Baberschke, Solid State Commun. 39, 781 (1981).

[7] M. V. Sadovskii and Yu. N. Skryabin, Phys. Status Solidi (b) 95, 59 (1979).

[8] C. M. Soukoulis and G. S. Grest, Phys. Rev. B 21, 5119 (1980).

[9] J. Ruvalds and Fu-sui Liu, Solid State Commun. 39, 497 (1981).

[10] J. W. Lynn, D. E. Moncton, L. Passell, and W. Thomkinson, Phys. Rev. B 21, 70 (1980).

[11] J. O. Willis, D. J. Erickson, C. E. Olsen, and R. D. Taylor, Phys. Rev. B 21, 79 (1980).

[12] G. E. Barberis, D. Davidov, J. P. Donoso, F. G. Gandra, C. Rettori, and J. F. Suassuna, Solid State Commun. 28, 427 (1978).

[13] G. J. Nieuwenhuys, B. G. Verbeek, and J. A. Mydosh, J. Appl. Phys. 50, 1685 (1979).

[14] G. E. Barberis, D. Davidov, H. D. Dokter, and F. R. Hoekstra, Solid State Commun. 38, 67 (1981).

[15] G. Frossati, J. Phys. (Paris), Colloq. 39, C6-1578 (1978).

[16] M. Wilhelm and B. Hillenbrand, Z. Naturforsch. 26A, 141 (1971).

[17] H. Maletta, G. Aeppli, and S. M. Shapiro, Phys. Rev. Lett. 48, 1490 (1982), and J. Magn. Magn. Mater. 31–34, 1367 (1983).

[18] W. M. Saslow, Phys. Rev. Lett. 50, 1320 (1983).

[19] M. F. Sykes and J. D. Essam, Phys. Rev. 133, A310 (1964).