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POSSIBLE OBSERVATION OF THE COEXISTENCE OF SUPERCONDUCTIVITY AND LONG-RANGE MAGNETIC ORDER IN $NdRh_4B_4$

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The ternary rare earth compound $NdRh_4B_4$ has been studied by means of critical field, low temperature heat capacity, and static magnetic susceptibility measurements. Features in the upper critical field and heat capacity data at 1.31 K and 0.89 K suggest the occurrence of long-range magnetic order in the superconducting state. The temperature dependence of the static magnetic susceptibility follows a Curie-Weiss law with an effective magnetic moment $\mu_{eff} = 3.58 \pm 0.05\ \mu_B$ and a Curie-Weiss temperature $\theta_p = -6.2 \pm 1.0$ K between 20 K and room temperature. However, magnetization vs. applied magnetic field isotherms suggest the development of a ferromagnetic component in the Nd^{3+} magnetization at low temperatures.

During the last two decades, considerable effort has been devoted to the search for the coexistence of superconductivity and magnetism. Recently, two classes of ternary rare earth (RE) compounds have been discovered in which superconductivity and long-range ordering of the RE magnetic moments have been observed, the RE rhodium borides $RERh_4B_4$ and the RE molybdenum chalcogenides $RE_xMo_6X_8$ (x = 1.0 or 1.2 and X = S or Se). In the $RERh_4B_4$ system, compounds with RE = Nd, Sm, Er, Tm and Lu exhibit superconductivity, while compounds with RE = Gd, Tb, Dy and Ho order ferromagnetically.[1] In the $RE_xMo_6X_8$ system, the compounds are superconducting for all RE except Ce and Eu.[2,3] In particular, $ErRh_4B_4$ and $Ho_{1.2}Mo_6S_8$ show re-entrant superconductivity, wherein ferromagnetic order destroys the superconductivity at a temperature T_{c2} below the superconducting transition temperature T_{c1}.[4-7] By means of critical field and magnetic susceptibility measurements, Ishikawa and Fischer[8] deduced the coexistence of superconductivity and antiferromagnetic order in $RE_{1.2}Mo_6S_8$ for RE = Gd, Tb, Dy and Er, the results for $Tb_{1.2}Mo_6S_8$ and $Dy_{1.2}Mo_6S_8$ having recently been confirmed by neutron scattering experiments.[9,10] Coexistence of superconductivity and antiferromagnetic order was inferred in $Gd_xMo_6Se_8$, $Tb_xMo_6Se_8$, and $Er_xMo_6Se_8$ by McCallum et al.[11-14] and Azevedo et al.[15] from the presence of a lambda-type specific heat anomaly at a temperature $T_\lambda < T_c$, where T_c is the superconducting transition temperature, and an accompanying cusp-like feature in the magnetic susceptibility at T_λ. Neutron scattering experiments have confirmed long-range magnetic order below T_λ in $Er_xMo_6Se_8$, but it has not yet been possible to determine the magnetic structure because of complications introduced by impurity phases.[16]

Although such measurements prove that superconductivity and antiferromagnetic order can coexist, no experimental evidence has been found for the coexistence of superconductivity and long-range ferromagnetic order. The presence of both superconductivity and ferromagnetic order in the $RERh_4B_4$ compounds suggests, however, that coexistence of these

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two phenomena might occur in some of the superconducting members of the series. To investigate this possibility, we have measured the upper critical field, heat capacity, and static magnetic susceptibility of $NdRh_4B_4$ which, in zero applied field, becomes superconducting at 5.4 K. The results indicate that long-range ordering of the Nd^{3+} magnetic moments develops in the superconducting state, although we have not been able to establish the nature of the magnetic order.

Two samples of $NdRh_6B_6$ were synthesized by arc-melting the high purity elements under argon. The samples were made off stoichiometry from the $RERh_4B_4$ composition because the additional RhB stabilizes the $NdRh_4B_4$ phase. X-ray spectral analysis revealed the presence of two impurity phases in addition to $NdRh_4B_4$: the compounds RhB and $NdRh_6B_4$. The fraction of Nd^{3+} ions associated with the $NdRh_6B_4$ impurity phase was estimated to be of the order of 0.15. Low frequency ac magnetic susceptibility measurements above 0.06 K reveal no superconducting or magnetic transitions in RhB and a single ferromagnetic transition at 4.9 K in $NdRh_6B_4$. Annealing the samples forms more $NdRh_6B_4$ at the expense of $NdRh_4B_4$ and therefore was not performed.

The first sample was used for both the four-probe electrical resistance and the magnetization measurements. In the former experiment, a long parallelepiped-shaped sample aligned parallel to an applied magnetic field was cooled using a He^3-He^4 dilution refrigerator to achieve temperatures from less than 0.07 to 10 K. Magnetization data were taken using a Faraday magnetometer from 0.80 to 294 K. The heat capacity of the second sample was measured between 0.5 and 36 K in a He^3 semi-adiabatic calorimeter using a standard heat-pulse technique.

Figure 1 shows the sample resistance vs. temperature in various applied magnetic fields. For fields of 2 kOe or less, the sample remains superconducting below the transition temperature T_{c1}. In fields of 3 kOe or more, the initial decrease in resistance is followed at lower temperature by a sharp increase in resistance, and, as the temperature is lowered even more, the resistance again rapidly decreases. These abrupt changes in resistance appear to be associated with two additional superconducting-normal transitions which occur in magnetic fields above 3 kOe. The figure also reveals three characteristic features of the two superconducting-normal transitions below T_{c1}: 1) the pronounced thermal hysteresis associated with the lower temperature transition; 2) the absence of any such hysteresis in the higher temperature transition; and 3) a resistance maximum whose temperature, $T \sim 1.15$ K, is independent of the applied magnetic field. Although the temperature at which the resistance minimum occurs is not constant, its dependence on magnetic field is relatively small.

The insensitivity of these two low tem-

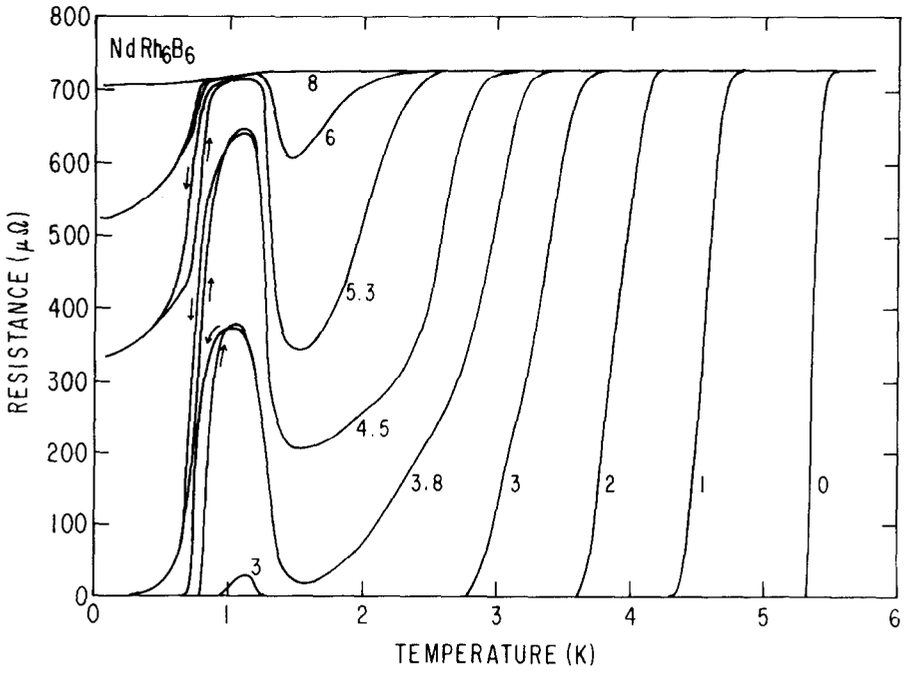

Fig. 1 ac electrical resistance versus temperature for $NdRh_6B_6$ in various applied magnetic fields between 0 and 8 kOe.

perature transitions to magnetic field is evident in the upper critical field H_{c2} vs. temperature data that are displayed in Fig. 2. The transi-

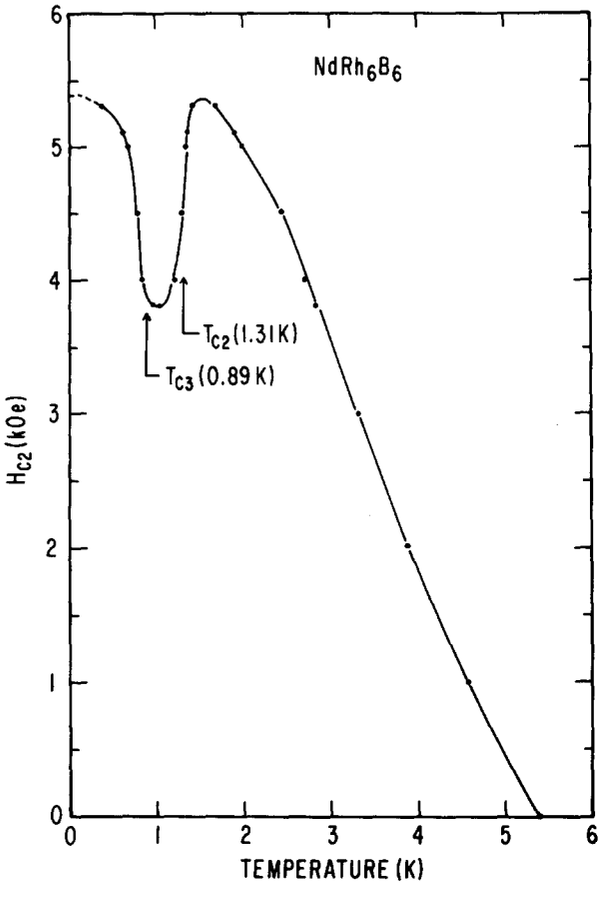

Fig. 2 Upper critical field H_{c2} versus temperature for $NdRh_6B_6$. The arrows represent the transition temperatures defined by the two lambda-type anomalies observed in the heat capacity data.

tion temperatures were defined as the temperatures at which the sample resistance was 50% of the normal state value. The critical field curve shows an abrupt depression below T = 1.6 K, followed by a slightly more gradual increase beginning at T = 1.0 K. However, $H_{c2}(0) \sim 5.4$ kOe remains below the value of ~ 6.5 kOe one would expect from an extrapolation of the data above 1.6 K. Another peculiar feature of the critical field curve is its positive curvature above 3 K.

Magnetization M vs. applied magnetic field H isotherms for $NdRh_6B_6$ in the normal state with $H > H_{c2}$ for five representative temperatures are shown in Fig. 3. As the temperature decreases, the magnetization of the Nd^{3+} ions shows a tendency to saturate with increasing field to a value that is well below that corresponding to the magnetic moment $\mu_s = 3.27\ \mu_B$ predicted for the Hund's rule ground state of Nd^{3+}. Similar behavior was previously observed in the magnetization data of $ErRh_4B_4$.[4] However, the T = 0.80 K magnetization curve differs from the other four curves by showing less of a tendency to saturate. This suggests that the magnetic structure of the sample changes between 0.80 and 1.11 K, consistent with the upper critical field data of Fig. 2.

Figure 4 shows a plot of the inverse magnetic susceptibility χ_M^{-1} of $NdRh_6B_6$ vs. temperature in an applied magnetic field of 8.5 kOe. Above 20 K, the data can be described by a Curie-Weiss law with an effective magnetic moment μ_{eff} of $3.58 \pm 0.05\ \mu_B$ per Nd^{3+} ion, close to the free ion value of $3.62\ \mu_B$, and a Curie-Weiss temperature θ_p of -6.2 K $\pm$ 1.0 K. Below 20 K, however, the susceptibility increases more rapidly than the Curie-Weiss law, until it begins to saturate at temperatures below 5 K. This enhancement of χ_M at low temperatures may, in part, be accounted for by the ferromagnetic ordering of the $NdRh_6B_4$ impurity phase.

The heat capacity C of $NdRh_6B_6$ vs. temperature in zero applied magnetic field is shown in Fig. 5 for the temperature range 0.5 to 7 K. The data reval a relatively broad specific heat anomaly at approximately 5 K, which we attribute to the magnetic ordering of the impurity phase $NdRh_6B_4$, a small specific heat jump at the superconducting transition temperature $T_{c1} = 5.4$ K, and two lambda-type anomalies at $T_{c2} \equiv 1.31$ K and $T_{c3} = 0.89$ K, respectively. Comparison of the heat capacity data with the data of Fig. 2 shows that the peak at T_{c2} occurs at approximately the midpoint of the sharp depression of the H_{c2} vs. temperature curve, while T_{c3} lies slightly below the temperature corresponding to the minimum in the curve. Although critical field curves somewhat similar to that of $NdRh_6B_6$ have been observed in $RE_{1.2}Mo_6S_8$ compounds which display a single antiferromagnetic transition,[8] specific heat measurements for these substances have revealed only one lambda-type anomaly associated with this type of magnetic ordering.[17]

The magnetic susceptibility data suggest that the magnetically ordered states that apparently develop in $NdRh_4B_4$ at T_{c2} and T_{c3} are relatively complex. Whereas the Curie-Weiss temperature dependence of the magnetic susceptibility above 20 K indicates that the Nd^{3+} magnetic moments interact antiferromagnetically, the depression of the critical field at T_{c2} implies the existence of additional pairbreaking in the sample. Furthermore, although the saturation observed in the isothermal magnetiza-

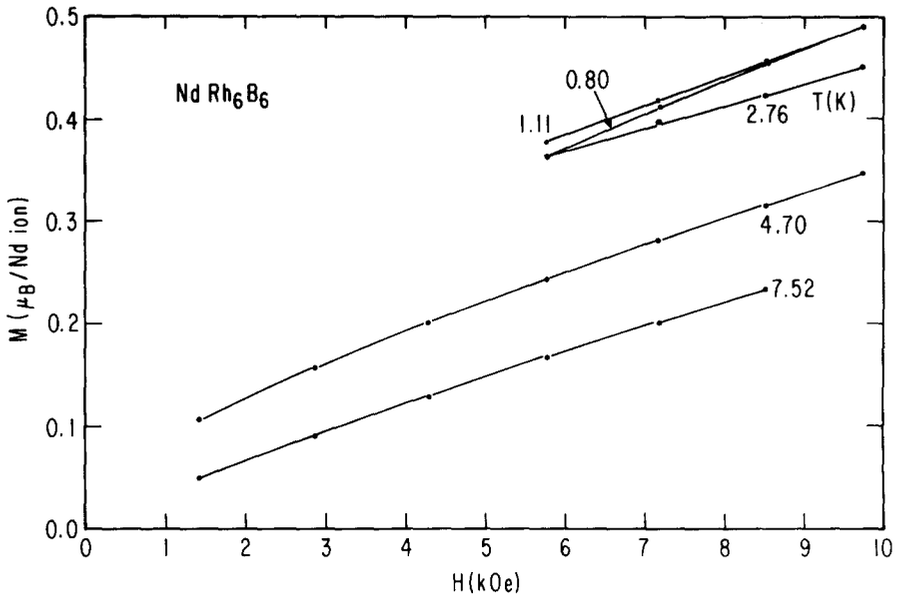

Fig. 3 Magnetization M versus applied magnetic field isotherms for $NdRh_6B_6$ at various temperatures between 0.80 and 7.52 K.

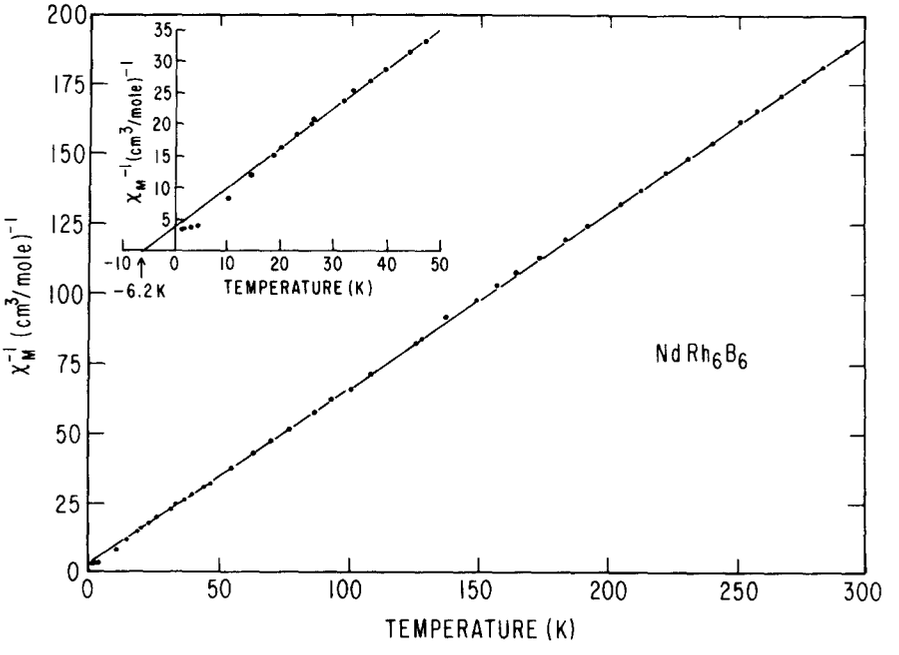

Fig. 4 Inverse magnetic susceptibility versus temperature for $NdRh_6B_6$. The solid line represents a Curie-Weiss law with $\mu_{eff} = 3.58 \pm 0.05\ \mu_B$ and $\theta_p = -6.2 \pm 1.0$ K.

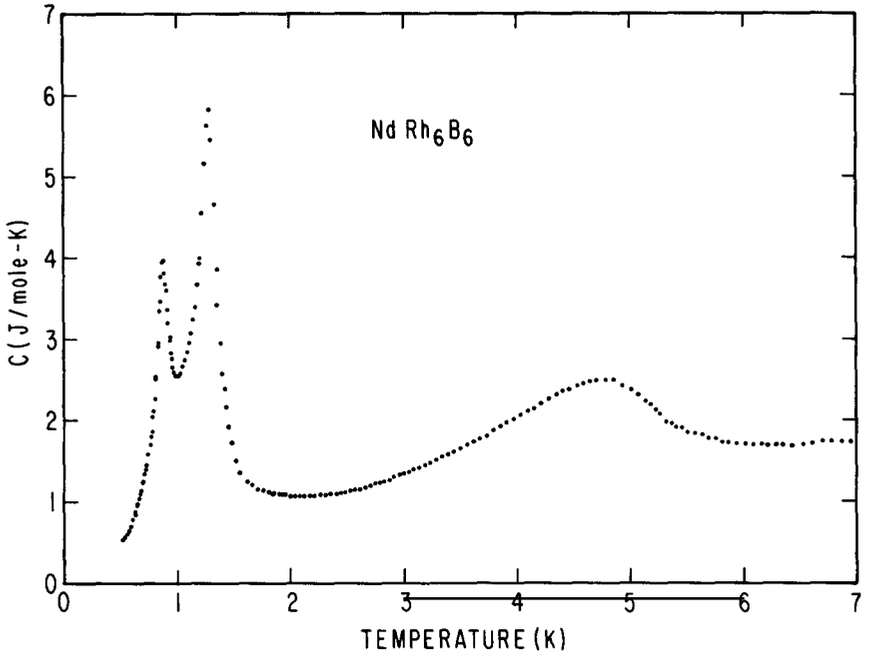

Fig. 5 Specific heat C versus temperature for $NdRh_6B_6$ in zero applied magnetic field.

tion data may partly result from the ferromagnetic behavior of the $NdRh_6B_4$ impurity phase, the greater slope and smaller extrapolated intercept at H = 0 of the M vs. H isotherm at T = 0.80 K suggest a decrease in the ferromagnetic component in $NdRh_4B_4$ below T_{c3}. The data are therefore consistent with the onset of a ferromagnetic component of the Nd^{3+} ions at T_{c2} in the $NdRh_4B_4$ phase followed by a decrease of the ferromagnetic component (possibly to zero) at T_{c3}. The absence of reentrant superconductivity in zero applied field may be due to a combination of the comparatively low magnetization of the Nd^{3+} ions and the large critical field of the $RERh_4B_4$ structure in the absence of magnetic moments, as evidenced by the value of $H_{c2}(0) \sim 65$ kOe for $LuRh_4B_4$.[18]

The exact nature of the transitions at T_{c2} and T_{c3} is difficult to establish because of the presence of the additional impurity phases in the sample. Although it seems improbable that the impurity phases could account for the features observed in the critical field data, such a possibility cannot be dismissed completely. Further experiments are planned which will attempt to determine unambiguously the nature of the magnetic ordering in the $NdRh_4B_4$ phase.

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