Possible observation of the coexistence of superconductivity and long-range magnetic order in NdRh4B4

Permalink
https://escholarship.org/uc/item/5ct9993j

Journal
Solid State Communications, 31(3)

ISSN
0038-1098

Authors
Hamaker, HC
Woolf, LD
MacKay, HB
et al.

Publication Date
1979-07-01

DOI
10.1016/0038-1098(79)90422-8

Copyright Information
This work is made available under the terms of a Creative Commons Attribution License, available at https://creativecommons.org/licenses/by/4.0/

Peer reviewed
POSSIBLE OBSERVATION OF THE COEXISTENCE OF SUPERCONDUCTIVITY
AND LONG-RANGE MAGNETIC ORDER IN NdRh₄B₄

H. C. Hamaker,* L. D. Woolf,* H. B. MacKay,*
Z. Fisk* and M. B. Maple*

Institute for Pure and Applied Physical Sciences
University of California, San Diego, La Jolla, California 92093

The ternary rare earth compound NdRh₄B₄ 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 μₑffective = 3.58 ± 0.05 μₜ and a Curie-Weiss temperature θ = -6.2 ± 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 Nd³⁺ 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 RERh₄B₄ and the RE molybdenum chalcogenides REₓMo₆X₈ (x = 1.0 or 1.2 and X = S or Se) in the RE₄Mo₆B₄ system, compounds with RE = Nd, Sm, Er, Tm and Lu exhibit superconductivity, while compounds with RE = Gd, Tb, Dy and Ho order ferromagnetically. In the REₓMo₆X₈ system, the compounds are superconducting for all RE except Ce and Eu. In particular, ErRh₄B₄ and Ho₁₂Mo₆S₈ show re-entrant superconductivity, wherein ferromagnetic order destroys the superconductivity at a temperature Tₖ below the superconducting transition temperature Tₓ. By means of critical field and magnetic susceptibility measurements, Ishikawa and Fischer deduced the coexistence of superconductivity and antiferromagnetic order in RE₄₂Mo₆S₈ for RE = Gd, Tb, Dy and Er, the results for Tb₁₂Mo₆S₈ and Dy₁₂Mo₆S₈ having recently been confirmed by neutron scattering experiments.

It has been suggested that the coexistence of superconductivity and antiferromagnetic order can exist in the RE₂Mo₆S₈ compounds. However, 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 RERh₄B₄ compounds suggests, however, that coexistence of these
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 NdRh₄B₄, which, in zero applied field, becomes superconducting at 5.4 K. The results indicate that long-range ordering of the Nd³⁺ magnetic moments develops in the superconducting state, although we have not been able to establish the nature of the magnetic order.

Two samples of NdRh₆B₆ were synthesized by arc-melting the high purity elements under argon. The samples were made off stoichiometry from the RERh₄B₄ composition because the additional RhB stabilizes the NdRh₄B₄ phase. X-ray spectral analysis revealed the presence of two impurity phases in addition to NdRh₄B₄: the compounds RhB and NdRh₆B₄. The fraction of Nd³⁺ ions associated with the NdRh₆B₄ 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 NdRh₆B₄. The fraction of Nd³⁺ ions associated with the NdRh₆B₄ 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 NdRh₄B₄. Annealing the samples forms more NdRh₆B₄ at the expense of NdRh₄B₄ 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 He³-He⁴ 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 He³ 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, $T \approx 1.15$ 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 NdRh₆B₆ in various applied magnetic fields between 0 and 8 kOe.](image-url)
temperature transitions to magnetic field is evident in the upper critical field $H_{c2}$ vs. temperature data that are displayed in Fig. 2. The transition 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, $H_{c2}(0) \approx 5.4$ kOe remains below the value of $\approx 6.5$ 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$_6$B$_6$ 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 $\mu_{mag} = 3.27 \mu_B$ predicted for the Hund's rule ground state of Nd$^{3+}$. Similar behavior was previously observed in the magnetization data of ErRh$_4$B$_4$. 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 $\chi_M^{-1}$ of NdRh$_6$B$_6$ 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 $\mu_{eff}$ 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 $\Theta$ 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 $\chi_M$ at low temperatures may, in part, be accounted for by the ferromagnetic ordering of the NdRh$_6$B$_4$ impurity phase.

The heat capacity $C$ of NdRh$_6$B$_6$ vs. temperature in zero applied magnetic field is shown in Fig. 5 for the temperature range 0.5 to 7 K. The data reveal a relatively broad specific heat anomaly at approximately 5 K, which we attribute to the magnetic ordering of the impurity phase NdRh$_6$B$_4$, a small specific heat jump at the superconducting transition temperature $T_{c1} = 5.4$ K, and two lambda-type anomalies at $T_{c2} = 1.31$ 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$_6$B$_6$ have been observed in RE$_1$Mo$_6$S$_8$ compounds which display a single antiferromagnetic transition, specific heat measurements for these substances have revealed only one lambda-type anomaly associated with this type of magnetic ordering.

The magnetic susceptibility data suggest that the magnetically ordered states that apparently develop in NdRh$_6$B$_4$ 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$_6$B$_6$ at various temperatures between 0.80 and 7.52 K.

Fig. 4  Inverse magnetic susceptibility versus temperature for NdRh$_6$B$_6$. The solid line represents a Curie-Weiss law with $\mu_{\text{eff}} = 3.58 \pm 0.05 \mu_B$ and $\theta = -6.2 \pm 1.0$ K.
Fig. 5  Specific heat $C$ versus temperature for NdRh$_6$B$_6$ in zero applied magnetic field.

The specific heat data may partly result from the ferromagnetic behavior of the NdRh$_6$B$_4$ 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$_6$B$_4$ below $T_c$. The data are therefore consistent with the onset of a ferromagnetic component of the Nd$^{3+}$ ions at $T_c^*$ in the NdRh$_6$B$_4$ phase followed by a decrease of the ferromagnetic component (possibly to zero) at $T_c$. The absence of re-entrant 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$_4$B$_4$ structure in the absence of magnetic moments, as evidenced by the value of $H_{c2}(0) \approx 65$ kOe for LuRh$_4$B$_4$.18

The exact nature of the transitions at $T_c^*$ and $T_c$ 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$_6$B$_4$ phase.

REFERENCES

18. HAMAKER, H. C., LAMBERT, S. E., MacKAY, H. B. and MAPLE, M. B., to be published.