Neutron Scattering Study of Magnetic Ordering in the Reentrant Superconductor $ErRh_4B_4$

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Using neutron scattering techniques, we show that the destruction of superconductivity in $ErRh_4B_4$ at $T_{c2} = 1.0$ K is accompanied by the development of long-range ferromagnetic ordering of the Er sublattice. The observed magnetic Bragg intensities indicate that the Er ion has a moment of $5.6\mu_B$ which is oriented in the tetragonal basal plane. The magnetic transiton appears second order, but shows anomalously strong precursor scattering.

Synthesis of new ternary superconductors has recently led to new materials which exhibit a tendency toward both superconductivity and magnetic order when one of the constituent ions is a rare earth with a large magnetic moment.[1-3] Almost two decades have passed since the initial work on the "coexistence" problem began. However, the substantial research effort[4] conducted over this period has revealed no stoichiometric superconducting system which is also an ordered magnet either under the same or different thermodynamic conditions.

All work preceding the study of ternaries has involved systems in which the magnetic ions were introduced randomly in a superconducting host lattice. As a result, these studies of the interaction between magnetism and superconductivity have been studies of the single magnetic ion (Kondo systems[5]) or of ordered magnetic clusters (spin-glass systems[6]) within the superconducting matrix. The recent discoveries that superconductivity in the ternary compounds $ErRh_4B_4$ (Ref. 1) ($T_{c1} = 8.5$ K) and $Ho_{1+x}Mo_6S_8$ (Ref. 2) ($T_{c1} = 1.2$ K) is quenched by a magnetic ordering transition ($T_{c2} = 0.9$ and 0.64 K, respectively) thus provide the first opportunity to examine the superconducting → magnetic transition, and to do so in ordered materials.

In this Letter we present the initial results of neutron scattering experiments on powdered samples of $ErRh_4B_4$ which demonstrate that the destruction of superconductivity occurs during the transition to a *ferromagnetically* ordered state. In addition, the observation of instrumentally narrow Bragg peaks implies that the magnetic order is of long range (greater than 200 Å). Quantitative analysis of the magnetic Bragg intensities gives a saturation moment of $5.6\mu_B$. This value is considerably below the free ion moment of $9.6\mu_B$, indicating the importance of crystal-field effects. Furthermore, we observe anomalously large precursor scattering which may derive either from a distribution of ordering temperatures or from potentially interesting fluctuation effects.

Our experiments were performed on a triple-axis neutron spectrometer at the Brookhaven National Laboratory high-flux–beam reactor. A pyrolytic graphite monochromator, analyzer, and filter were used. All data were obtained with the spectrometer set for elastic scattering with incident wave vector $k_i = 2.5474$. Temperatures were varied between 60 mk and 1.5 K with use of a dilution refrigerator. The sample was prepared by conventional arc-melting techniques and then crushed into a powder. The B^{11} isotope was used to decrease the absorption cross section. X-ray films showed a few weak extra lines which derive from a small amount (less than 10%) of an impurity phase, most likely RhB_{1+x}. All other lines are consistent with the tetragonal structure previously determined by Vandenberg and Matthias,[7] ($a = 5.292$ Å, $c = 7.37$ Å). The superconductivity of the powdered material was examined with ac susceptibility techniques. A single transition was observed with slight broadening over the range 8.5–8.2 K. Some attempts to prepare the sample produced specimens which showed multiple superconducting transitions. This sensitivity to secondary phases increases the confidence gained from neutron and x-ray diffraction data that the sample used in the present experiment was predominantly $ErRh_4B_4$.

In Fig. 1, we show neutron diffraction scans through four Bragg peaks at temperatures above and below the magnetic transition at $T_{c2} = 1.0$ K.[8]

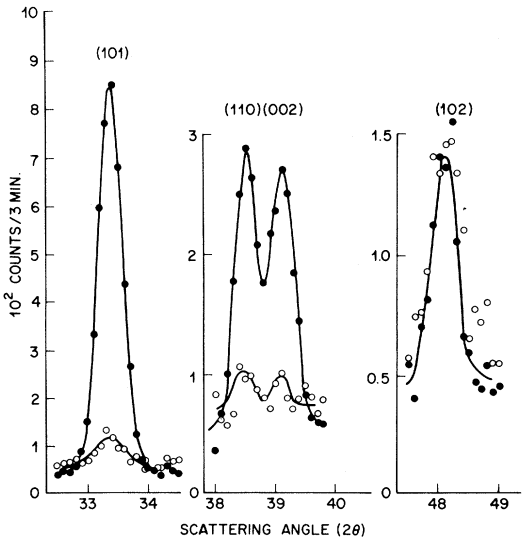

FIG. 1. Four powder peaks are shown at temperature above ($T = 1.4$ K, open circles) and below ($T = 0.07$ K, filled circles) the magnetic transition at $T_{c2} = 1.0$ K.

TABLE I. Calculations of F_{nucl}^2 and F_{mag}^2 are compared with the appropriate measured quantities. F_{nucl}^2 is obtained by using the values $X_{\text{Rh}} = 0.253$, $Z_{\text{Rh}} = 0.148$, $X_{\text{B}} = 0.322$, and $Z_{\text{B}} = 0.856$ which are only marginally different from those given in Ref. 7.

hkl	$F_{1.4\,\text{K}}^2$	F_{nucl}^2	$F_{0.07\,\text{K}}^2 - F_{1.4\,\text{K}}^2$	F_{mag}^2
101	0.42 ± 0.05	0.37	5.57 ± 0.2	6.80
110	0.55 ± 0.13	0.34	3.91 ± 0.41	3.97
002	0.87 ± 0.27	0.73	7.88 ± 0.84	7.90
102	1.35 ± 0.25	1.16	0.20 ± 0.49	0.0
211	19.6 ± 0.6	21.0	3.0 ± 1.4	4.07
103	24.4 ± 1.0	24.8	4.9 ± 2.3	6.14
202	2.26 ± 0.4	1.9	5.2 ± 1.1	5.11
220	41.1 ± 2.3	36.2	3.3 ± 4.9	2.74
004	47.5 ± 3.6	43.5	10.3 ± 8.0	5.42

The intensity for nuclear scattering is weak for the (101), (110), and (002) peaks, thereby revealing a magnetic contribution which clearly dominates at temperatures below T_{c2}. As expected, the (102) peak is unchanged because the Er sublattice does not contribute to (hkl) reflections for which the sum $h + k + l$ is odd. We have scanned a total of nine powder lines above and below T_{c2}. In every case in which the magnetic contribution is important, it has the same angular width as the nuclear contribution. This result implies that the low-temperature phase has essentially long-range ferromagnetic order. More precisely, a lower limit of 200 Å can be set on the correlation length. To obtain this limit we measure the (101) peak half-width $\Delta Q = 2k_i(\cos\theta)\Delta\theta = 0.01$ Å^{-1}. Since this width is essentially the instrumental resolution, we make the conservative estimate that the maximum undetectable width would be $\Delta Q_{\text{res}}/2$. Thus we set the limit on the minimum observable correlation length $\kappa_{\text{min}} = 2/\Delta Q_{\text{res}} \approx 200$ Å.

Our data above T_{c2} agree with the atomic positions established by Vandenberg and Matthias using x-ray diffraction and serve as a calibration for absolute intensity measurements of the magnetic scattering. We note that the neutron measurements, unlike the x-ray results, are sensitive to the positions of the boron atoms, and therefore our data confirm the positions proposed by Vandenberg and Matthias on the basis of crystal-chemical arguments. In Table I we show that the observed structure factors at $T = 1.4$ K compare well with the values calculated for the nuclear structure. A slight refinement of the atomic positions of Vandenberg and Matthias has been made, but the changes are of marginal statistical significance. For the calculation of nuclear intensities we use

$$F_{\text{nucl}}(\vec{Q}) = \sum_i b_i \exp(i\vec{Q}\cdot\vec{r}_i),$$

where b_i is the coherent neutron scattering length of the atom at $\vec{r}_i$. We neglect Debye-Waller corrections at these low temperatures.

In the magnetic state below T_{c2}, the relation

$$F_{\text{tot}}^2 = F_{\text{nucl}}^2 + F_{\text{mag}}^2,$$

for unpolarized neutrons is used to include the contribution from the magnetically ordered Er sublattice. The magnetic structure factor is given by

$$\vec{F}_{\text{mag}}(\vec{Q}) = \sum_i \vec{q}_i p_i \exp(i\vec{Q}\cdot\vec{r}_i),$$

where the magnetic scattering amplitude is

$$p_i = (\gamma e^2/2mc^2)\mu_i f_i,$$

and $\vec{q}_i$ is the magnetic interaction vector.[9] In the above expression, $\vec{\mu}_i$ is the magnetic moment of the ith atom, f_i is its form factor, and $\gamma e^2/2mc^2$ is the neutron-electron coupling constant. Table I shows the magnetic part of the low-temperature intensity, $F^2(0.07\text{ K}) - F^2(1.4\text{ K})$, in comparison with calculations made for F_{mag}^2. In these calculations the best fit is obtained when each Er ion has a moment of $5.6\mu_{\text{B}}$ oriented in the tetragonal basal plane. Although it is not possible to distinguish orientations within the basal plane, the data clearly establish that it must lie in this plane

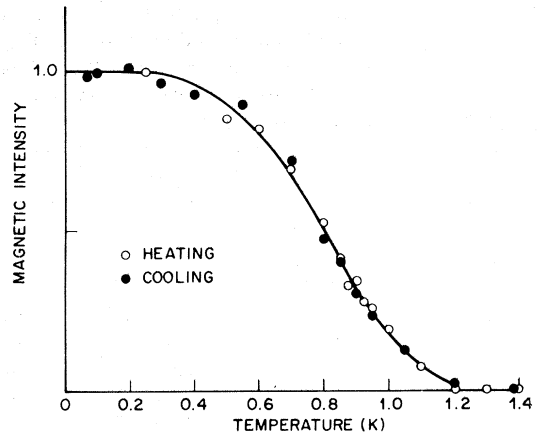

FIG. 2. The temperatures dependence of the magnetic contribution to the (101) peak intensity.

by virtue of the dependence of $\vec{F}_{mag}$ on the interaction vector $\vec{q}_i$.

The temperature dependence of the magnetic intensity of the (101) reflection is shown in Fig. 2. We find smooth, second-order behavior with no apparent hysteresis, in contradiction with the resistive behavior reported by Fertig *et al.*[1] However, the transition is preceded by a large amount of precursor scattering which manifests itself as a rounding of the magnetic intensity above 1.0 K. This behavior masks the expected temperature dependence which would presumably be of the form $I \propto (T_{c2} - T)^{2\beta}$ with $\beta \leq 0.5$, depending on the details of the magnetic system.

Although our experiments establish several important facts about the low-temperature properties of $ErRh_4B_4$, some of the details require further discussion and continued experimental investigation. We have observed an ordered moment of $5.6\mu_B$ which is considerably below the free-ion value of $9.6\mu_B$ that is required by the magnetic susceptibility measured by Fertig *et al.* down to ~ 10 K. However, these workers also find that the entropy associated with the magnetic transition is only about one-half of the value predicted assuming a sixteenfold-degenerate Er^{3+} ground state. We feel that the low moment and the low entropy together provide convincing evidence of the importance of crystal-field effects. However, the fact that the susceptibility measurements show no deviation from Curie-Weiss behavior down to 10 K requires the crystal-field splittings to be unusually small compared to typical effective point-charge calculations.[10] It is not unreasonable to invoke conduction-electron screening effects[11] to explain this situation, but it is premature. Inelastic neutron scattering experiments, should be undertaken to provide more direct experimental information on the crystal-field levels. Another aspect of our research which requires further study is the observation of substantial pretransitional scattering. This intensity may arise simply as a result of a distribution of transition temperatures caused by defects or impurities or as a result of enhanced critical fluctuations, perhaps related to the superconductivity of the system above T_{c2}. Observations of such critical effects in other nonsuperconducting rare-earth compounds[12] are not understood as yet, but they raise the possibility that large critical effects may be unrelated to superconductivity. We hope to explore these precursor effects in more detail using the small-angle neutron scattering technique.

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