Magnetic dilemma in superconducting $ErRh_4B_4$

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The magnetic moment on the Er atom in the reentrant superconductor $ErRh_4B_4$ at 100 mK is found from Mössbauer-effect measurements to be $(8.3 \pm 0.2)\mu_B$. This value is 30% larger than that found by neutron diffraction, indicating that only a fraction of the moment shows long-range magnetic order. The combination of Mössbauer and neutron diffraction results suggest that it is the presence of superconducting fluctuations in the magnetically ordered state which affects the nature of the ordered state.

There has been a great deal of activity in the last two years devoted to investigations of reentrant superconductors. The ternary compound $ErRh_4B_4$ is the prototype for materials showing such a behavior. It is superconducting with a transition temperature $T_c = 8.3$ K. At the temperature $T_M = 0.93$ K, ferromagnetic ordering occurs and the superconductivity is destroyed.[1] Neutron scattering measurements[2] have verified the ferromagnetic state and have shown that the Er moments align in the basal plane of the tetragonal structure with an ordered moment of $5.67\mu_B$. We have carried out Mössbauer-effect measurements on $ErRh_4B_4$ using the 80.6-keV, $0 \rightarrow 2$ nuclear transition in ^{166}Er. The magnetic moment on the Er atom deduced at a temperature of 0.1 K from these measurements is $8.3\mu_B$. This discrepancy of $\sim 30\%$ between the neutron scattering and Mössbauer-effect measurements is well outside the errors of either measurement, and is the first time that such a large discrepancy in the ordered moments of rare-earth compounds obtained by the two techniques has been observed. We have previously presented partial Mössbauer data and its preliminary analysis.[3] In this article we describe the results both of additional data and extended analysis, and suggest that the resulting dilemma in the values of the measured moments may be of fundamental importance in describing the nature of reentrant superconductors.

The ^{166}Er Mössbauer experiments used well-established techniques.[4] Monochromatic γ radiation was obtained from a Y-Ho-H_2 source. Spectra of the $ErRh_4B_4$ absorber were taken at various temperatures between 100 mK and 15 K, with the temperatures below 1.5 K being provided by a ^3He-^4He dilution refrigerator. The samples were prepared with isotopically enriched ^{11}B so that neutron diffraction experiments could be performed on the same material. The crystallographic structure and the superconducting properties were in agreement with earlier work,[1] as were neutron diffraction results.[2,5]

In order to describe the details of hyperfine (hf) structure in this material, we will first discuss the electronic state of the Er atom. In the $\bar{4}2m$ point symmetry of the Er site, the crystalline electric field (CEF) will split the $^4I_{15/2}$ ground-state multiplet into eight Kramers doublets. From specific-heat measurements, the mean CEF splitting is estimated to be 20–30 K.[1,6] For a paramagnetic material, in the limit of slow electronic relaxation (i.e., when the electronic relaxation frequency is small compared with hf frequencies) each of these doublets will result in a ^{166}Er Mössbauer spectrum consisting of five absorption lines having equal intensities.[7] The observed line positions can be analyzed to obtain information on the electronic g values of the Er ion. In the case of a highly anisotropic g tensor ($g_\perp = 0$), the hf splittings are determined primarily by the values of $\langle J_z \rangle$, as is discussed below, and the likelihood of observing slow relaxation spectra is increased.[8]

In Fig. 1 we show Mössbauer spectra measured at 1.5 K and 100 mK. Spectra measured both above (up to 15 K) and below (down to 0.1 K) T_M have line positions which are identical. However, some line shape changes occur which are presumably related to paramagnetic relaxation phenomena. Even at 100 mK, the intensities and widths of the five hf components are not equal, as one would ordinarily expect in a magnetically ordered compound. Such a situation may result either from a dynamic spin disorder, or from a static disorder representing a spread in the values of the magnetic hf field at different Er nuclei. The solid line through the data in Fig. 1 shows

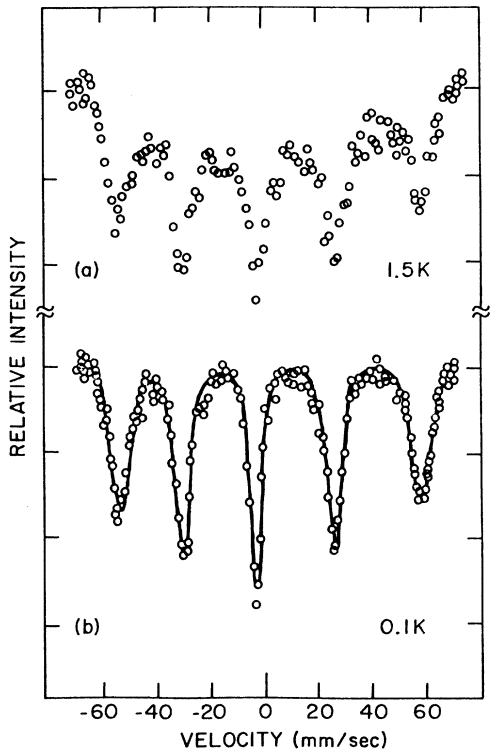

FIG. 1. Mössbauer spectra of $ErRh_4B_4$ measured using the 80.6-keV transition in ^{166}Er for (a) the superconducting state and (b) the magnetically ordered state. The solid line through the data represents a least-squares fit using a static-disorder model discussed in the text.

the results of least-squares fits assuming a static disorder. This fit yields an average magnetic hf field of 7.67 ±0.07 MG and an average electric quadrupole interaction parameter of e^2qQ of 773 ±8 MHz, with a spread in both parameters of about 7% at 100 mK. A fit of equal quality was obtained for dynamic disorder by assuming spin relaxation in an isolated, anisotropic Kramers doublet. That fit yielded hyperfine parameters nearly equal to the mean values given above.

In rare-earth systems, the hf field directly gives the magnetic moment on the rare-earth ion. The magnetic hyperfine field arises[9] from contributions due to the orbital current of electrons in unfilled shells (H_{orb}), a core polarization effect (H_{core}), and a term due to conduction-electron polarization (H_{ce}). For the Er^{3+} ion, H_{core} is less than one percent of H_{orb},[10] and H_{ce} is expected to be equally small. Thus one has

$$H_{hf} \approx H_{orb} = 2\mu_B \langle r^{-3} \rangle \langle |N| \rangle \langle J_z \rangle_T \ , \qquad (1)$$

where $\langle r^{-3} \rangle$ is a radial average for the $4f$ electrons, $\langle |N| \rangle$ is a known reduced matrix element and $\langle J_z \rangle_T$ is the thermal average of J_z taken over all electronic levels. The electric quadrupole interaction arises[8] from one contribution (q_{4f}) due to the local $4f$ charge distribution and another (q_{latt}) due to other electric charge distributions throughout the material. The second term is generally small, and one has

$$e^2qQ \approx e^2q_{4f}Q = -eQ \langle |\alpha| \rangle \langle 3J_z^2 - J(J+1) \rangle_T \langle r^{-3} \rangle \ , \qquad (2)$$

where Q is the nuclear quadrupole moment and $\langle |\alpha| \rangle$ is another reduced matrix element. It should be noted that the values calculated from Eqs. (1) and (2) for a $|\pm\frac{15}{2}\rangle$ doublet (H_{hf} = 8.1 kG and e^2qQ = 930 MHz) are close to those measured. Hence this angular momentum state makes up the principal constituent of the true ground state, which in turn reemphasizes the anisotropic nature of the g value.

From Eq. (1), one sees that H_{hf} is proportional to the Er magnetic moment, $g_J\mu_B\langle J_z \rangle_T$. This has been demonstrated for a large number of conducting and insulating magnetic systems.[3] From this plot, one obtains a value of $(8.3 \pm 0.2)\mu_B$ for the Er magnetic moment in $ErRh_4B_4$, the error primarily being due to empirically establishing the slope of the linear relationship. It should also be pointed out that the present analysis cannot determine the direction of the Er moment. However, for a predominantly $|\pm\frac{15}{2}\rangle$ doublet one would ordinarily expect ordering along the c axis. In view of the neutron scattering result this implies that anisotropy effects other than those due to crystal-field interactions are present.

The previous neutron diffraction measurements established a value of $5.6\mu_B$ for the *ferromagnetic* moment in $ErRh_4B_4$, considerably smaller than the present result obtained from either a dynamic or a static disorder analysis of the Mössbauer data. Attempts to reconcile the discrepancy by considering more complicated types of magnetic structure have not been successful. However, one should note that the two measurements are not identical in that neutron diffraction measures a long-range spin correlation and is insensitive to possible disordered components of the moment, whereas hyperfine techniques measure a single-ion autocorrelation which, in the limit of slow relaxation, yields the value of the *entire* moment. It therefore appears that only a component ($5.6\mu_B$) of the total moment ($8.3\mu_B$) is involved in the ferromagnetism. The other components remain disordered in either a static or dynamic fashion.

A variety of magnetic structures have been observed in which only a fraction of the total localized moment is ordered. This is seen, for example, in the c-axis modulation for the high-temperature ordered phase of Er and Tm metals.[11,12] However, the neutron diffraction data[2] on $ErRh_4B_4$ do not indicate a complex magnetic structure.[13] Furthermore, in the present case the spins remain disordered to an unusually low temperature[2] $\approx (T_M/15)$, which is difficult to recon-

cile with thermodynamic arguments based on currently understood interactions. Comparison of $ErRh_4B_4$ with other magnetic rare-earth systems may be misleading since the present experiments cannot determine whether the disorder is static or dynamic.[14] Nonetheless, our results clearly show that the so-called normal, or ferromagnetically ordered, state of $ErRh_4B_4$ is more complex than hitherto realized.

In Fig. 2 we have compared the neutron diffraction and Mössbauer effect results as a function of temperature, in order to demonstrate the dilemma. In the Mössbauer studies, the same value for the magnetic moment is obtained both above and below the magnetic transition temperature due to a large value of the Er spin-relaxation time in this material. One sees that the average value of $8.3\mu_B$ is an intrinsic property of the electronic state of Er in $ErRh_4B_4$, and is not determined by the presence of magnetic ordering. In the figure we have also shown the temperature dependence of the maximum spread (ΔH_{hf}) in the hyperfine field (normalized to the average value), by a static distribution in its values to explain the intensity and width anomalies as discussed earlier. It should be noted that this value decreases somewhat near T_M. In fact, at 760 mK, the asymmetry in the hyperfine intensities seen in Fig. 1 reduces dramatically. By 1.0 K, the distribution has again returned. This continues to increase at higher temperatures and may reflect the presence of spin-relaxation broadening or the population of higher crystal-field levels.

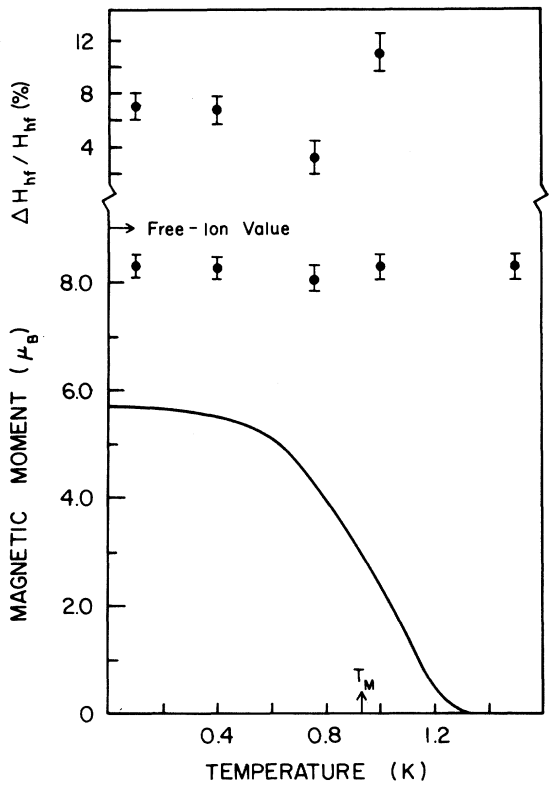

FIG. 2. The temperature dependence of the magnetic moment on Er in $ErRh_4B_4$ from neutron diffraction (solid line) and the Mössbauer effect (average values shown by full circles). The neutron results represent the ordered component of Er moment as discussed in the text. The maximum distribution in the hyperfine field (H_{hf}), assumed to be static as described in the text, is also shown.

We suggest that such disorder can arise if superconducting fluctuations are also present in the magnetically ordered state. The existence of spin-disorder scattering is indicated by the fact that the resistivity of the material does not return to its expected normal value in the magnetic state, but rapidly approaches the normal state on application of a small magnetic field.[15] Whereas some theoretical effort has recently gone into discussing the effect of magnetic fluctuations on ternary superconducting systems,[16–18] the present results indicate the need for a proper microscopic theory of the reverse situation, namely, the effect of superconducting fluctuations on the magnetic state. The microscopic mechanism entering into a proper theory will lie in the modification of the $q=0$ component of the conduction-electron susceptibility by the superconducting interaction. In the superconducting state, this probably results in a severe suppression of the ferromagnetic part of the Ruderman-Kittel-Kasuya-Yosida (RKKY) magnetic interaction between the Er spins. As a result, the magnetic state is initially driven by dipole-dipole interactions. When the magnetic state is formed, the RKKY interaction will reappear; however, this will not be complete due to the remanent superconducting fluctuations. The combined effect then may be a competition between the dipolar interactions, which tend to produce ferromagnetic order, and the RKKY interaction in the presence of superconducting interactions, which will tend to favor a long-wavelength periodicity for the spins.[18] One possibility is that the system will obtain its lowest free energy by forming ferromagnetic domains which are small in comparison with the superconducting coherence length. If this size is $\gtrsim 200$ Å, the neutron diffraction results will indicate long-range order for those spins in the domains, with the "disordered" spins lying in the regions between domains.[19]

The influence of superconducting interactions on the magnetic properties of $ErRh_4B_4$ in the immediate vicinity of T_M has been previously reported by Moncton[20] and described theoretically by Blount and Varma.[21] However, the primary results of the present work is the suggestion that superconducting interactions still play a significant role even at very low temperatures and affect the nature of the magnetic state.[22] Small-angle neutron scattering at temperatures well below T_M, as well as in applied magnetic fields, should be useful to help clarify the nature of the magnetism in $ErRh_4B_4$.

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