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# MICROPROBE FIELD MEASUREMENTS IN $ErRh_4B_4$

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## I. INTRODUCTION

Over two decades ago Matthias, Suhl, and Corenzwit (1958) proposed the coexistence of superconductivity and magnetic order in certain Laves-phase alloys of the system $Ce_{1-x}R_xRu_2$, where R is a rare earth element such as Gd. Verification of coexistence in this and other similar systems was hampered because the usual techniques for characterizing magnetic order, such as bulk magnetic susceptibility, failed because of the superconductor's diamagnetic shielding. Techniques which require external magnetic fields are also suspect because of the possible influence of the field on the superconductivity.

One of the earliest attempts to overcome the difficulties encountered in the conventional measurements of the bulk properties was to use the Mossbauer Effect (ME) to measure local internal magnetic fields (Erickson *et al.*, 1973; Taylor *et al.*, 1974; Steiner *et al.*, 1973). The ME is unaffected by the superconductivity and does not require an applied field to obtain hyperfine spectra signaling the possible presence of magnetic order. Only a limited number of useful ME nuclides exist, but the number includes several rare earth elements common to many of the suggested coexistence systems. Magnetic studies have been reported on $La_{1-x}Eu_x$ (Steiner *et al.*, 1973; 1977), $Ce_{1-x}\,Gd_x\,Ru_2$ (Ruebenbauer *et al.*, 1977), $Eu_xSn_{1-x}Mo_6S_y$ (Bolz *et al.*, 1977; Fradin *et al.*, 1977) and $ErRh_4B_4$ (Shenoy *et al.*, 1979) using the ME of the magnetic rare earth component. Alternatively, Erickson *et al.* (1973) used the well-known ME in $^{57}Fe$ as a

very dilute impurity probe to detect the presence of hyperfine magnetic order transferred to the $^{57}Fe$ in samples of $Ce_{1-x}Gd_xRu_2$. Samples dilute in Gd ($0.08 < x < 0.13$) become superconducting at $T_c$; ME probe measurements (Erickson *et al.*, 1973) show magnetic ordering occurs below $T_c$. Samples more concentrated in Gd ($0.13 < x$) are magnetically ordered at $T_m$. In a narrow composition range just above $x = 0.13$ these samples become superconductors at a $T_c$ below $T_m$; ME probe measurements show the magnetic ordering persists in the superconducting regime. Magnetic Fe sites gave a saturation field of 7.6 T; this large internal field enhanced the capability of the ME impurity method. The concentration of the $^{57}Co$ parent was too low to produce significant impurity-impurity interactions and too low to affect any of the measured bulk properties of the host.

Although the ME is useful to detect magnetic ordering on a microscopic scale, it is generally not possible to determine whether the interaction is ferromagnetic or antiferromagnetic. However, from a concentration-dependence study of the ME hyperfine spectra of $La_{1-x}Eu_x$ Steiner and Gumprecht (1977) concluded that the ordering was of a spin-glass type in the coexistence region. A further complication in the ME technique sometimes arises from relaxation-time effects, which tend to mask any magnetic hyperfine effects due to ordering. Nevertheless the ME technique provides a tool simple in concept and application which provides unique complementary information on magnetic ordering in magnetic superconductors.

The recent neutron scattering experiments (Moncton, 1979) have been extremely valuable in developing a better picture of the nature of the magnetic interaction in superconductors. However, this powerful technique cannot be used with metallurgical systems which have nuclei with a high neutron absorption cross-section.

In this introduction we have emphasized techniques which sense microscopic spin order in the absence of an applied field. Recent more general reviews of the subject of coexistence include Roth (1978) and Fischer (1978).

## II. $ErRh_4B_4$

The discovery of the superconducting and magnetic properties of the ternary compounds $RRh_4B_4$ (Matthias *et al.*, 1977) and more particularly the reentrant behavior of $ErRh_4B_4$

(Fertig *et al.*, 1977) provide the experimentalist an excellent metallurgical system to study the coexistence of superconductivity and magnetism. These ternary compounds have a well-defined crystal structure and can be prepared relatively free of voids and second phases. Pseudoternary compounds obtained by systematic substitution of one or more rare earth elements for Er provide an added dimension for establishing trends in an effort to develop an understanding of the competition of magnetism and superconductivity in this system.

Shenoy *et al.* (1979) measured the ME of $^{166}Er$ in $ErRh_4B_4$ at temperatures from 4.2 to 0.1 K. Resolved hyperfine spectra, mostly attributed to crystal-field and electronic spin relaxation-time effects, were obtained at all temperatures. The differences in the ME spectra between 0.1 K and 1.5 K were subtle but were surely a result of the presence of magnetic order below $T_{c2}$, the temperature at which superconductivity disappears and below which ferromagnetism is present.

Our motivation in using a microscopic magnetic ME probe in $ErRh_4B_4$ was to try to determine whether the ferromagnetic order established below $T_{c2}$ persists above $T_{c2}$, into the superconducting region. We chose the ME of $^{57}Fe$ impurities because the applicability of the technique was already established and because relaxation time effects were not likely to interfere. In $ErRh_4B_4$ one expects the $^{57}Co$ to subsitute for Rh. The sensitivity of the method depends on the electronic configuration of Fe in $ErRh_4B_4$.

## III. EXPERIMENTAL

Two different $ErRh_4B_4$ samples were used in this study. Sample A was made by D. C. Johnson (Fertig *et al.*, 1977) and Sample B was made by F. E. Wang. Sections about 1 mm thick of the annealed samples were doped with $^{57}Co$, the parent of $^{57}Fe$, for the ME studies. About 0.5 mCi of carrier-free $^{57}Co$ was electroplated onto one side of Sample A giving a source whose active area was about 0.1 $cm^2$; the cobalt was diffused into the host by heating at 900°C first in a $H_2$-Ar atmosphere and then in a high vacuum for a total time of 1.3 hours. Source B was similarly prepared except the heat treatment was entirely in a vacuum of $10^{-6}$-$10^{-8}$ torr. A deeper diffusion was achieved by treating for 26 hours at 960°C followed by 17 hours at 1080°C. By observing the relative intensities of the 122- and 14.4-keV γrays of the $^{57}Fe$ as a function of the heat treatment we could determine the average depth of diffusion and the average impurity composition. For Source B we found

that the average concentration of the doped region was roughly 100 ppm $^{57}$Co. For Source A we only know that the average $^{57}$Co concentration was much higher. $T_{c1}$ (superconducting onset), determined from ac magnetic susceptibility measurements for both samples before and after doping agreed with Fertig *et al.*, (1977). $T_{c2}$, determined for the undoped samples, also agreed; $T_{c2}$ was not measured for the doped samples.

The source was cooled in a $^{3}$He cryostat and analyzed by an external room-temperature single-line absorber in conjunction with a conventional constant-acceleration mode ME spectrometer. A superconducting solenoid provided fields up to 6 T on the source.

## IV. DATA DISCUSSION

The ME spectra of $^{57}$Fe impurities in Sample B at 0.38 and 1.1 K are shown in Fig. 1. The splitting of the quadrupole doublet was essentially independent of temperature from 0.38 to 300 K and the same for both samples. Equal intensities suggest that the $^{57}$Fe impurities were in equivalent sites. We have analyzed the low-temperature data assuming a symmetrical Lorentzian doublet. We have summarized the low temperature data for both sources in Table I. Much of the excessive line width quoted is attributable to the rather thick potassium ferrocyanide absorber used. (A thin absorber gave component line widths of 0.33 $mms^{-1}$).

*TABLE I. Measured Field at the Impurity Site*

| *Source* | *Temperature* *K* | *Quadrupole Splitting* *$mms^{-1}$* | *Line width* *$mms^{-1}$* | *Effective field*[a] *T* |
|---|---|---|---|---|
| *A* | *4.0* | *0.523 (15)* | *0.589 (26)* | - |
| | *1.2* | *0.510 (8)* | *0.616 (7)* | *Ref. A* |
| | *0.54* | *0.499 (15)* | *0.627 (13)* | *0.06 (4)* |
| *B* | *4.0* | *0.491 (5)* | *0.591 (7)* | - |
| | *1.1* | *0.488 (4)* | *0.584 (6)* | *Ref. B* |
| | *0.38* | *0.489 (4)* | *0.659 (6)* | *0.49 (6)* |

[a]*Entries calculated with respect to Ref. A or B data.*

In Sample A the spectra at 1.2 and 0.54 K were virtually indistinguishable. For $T/T_{c2} \simeq 0.6$ we assumed nearly complete ferromagnetic ordering of the sample. The absence of any broadening at 0.54 K implied the absence (to within 0.1 T) of any internal field at the Fe sites. To obtain this upper limit to the field we assumed that the electronic state of the Fe was nonmagnetic. Such a nonmagnetic state has been observed for Fe in the superconductors V, Nb, and Ta (Kitchens *et al.*, 1965). In $ErRh_4B_4$ Shenoy *et al.*, (1979) measured the field at the Er nucleus to be 770 T at 0.1 K. Although an internal field at the Er sites does not necessitate a field at the Rh and B neighbors, it does offer the *possibility* of a hyperfine field at the Fe.

The general features of the ME spectra of Source B confirm those of Source A except statistically significant broadening was found at 0.38 K. We presume this broadening is associated with the lower measuring temperature rather than differences in the sample-source preparation, but this point could not be fully checked because the source was ruined in a subsequent heat treatment. The field at 0.38 K at the Fe site, calculated from the fitted ME spectra shown in Fig. 1, was 0.49 T. To obtain this value we assumed that the principal quadrupole and magnetic axes were co-linear, but the value was rather insensitive to this particular choice.

We measured the response of the $^{57}Fe$ ME impurity to an applied magnetic field in order to confirm the supposition that Fe in $ErRh_4B_4$ was in a nonmagnetic electronic state. The measurements showed that the hyperfine field at the Fe site in Sample A at 1.3 and 0.53 K was 5.98 $\pm$0.11 and 6.01 $\pm$0.09 T, respectively, in an applied field of 6.00 T. Measurements at a lower field also indicated that the field at the $^{57}Fe$ nucleus was within a few percent of the value of the applied field. We have taken this as direct evidence that the Fe impurity in $ErRh_4B_4$ is indeed nonmagnetic. The absence of a moment on Fe precludes relaxation effects as the source of broadening at 0.38 K. It seems safe to speculate that the field observed (Table I) arises from the ordered Er moments.

## V. CONCLUSIONS

We have observed a small hyperfine field at Fe impurity sites in $ErRh_4B_4$ at 0.38 K. The magnitude of the field at the nonmagnetic impurity sites was 0.5 T. We presume this hyperfine field reflects spin order at the Er sites but the

sensitivity of the probe technique employed turned out to be marginal for investigating quantitatively the shape of the ordering curve with temperature near and below $T_{c2}$.

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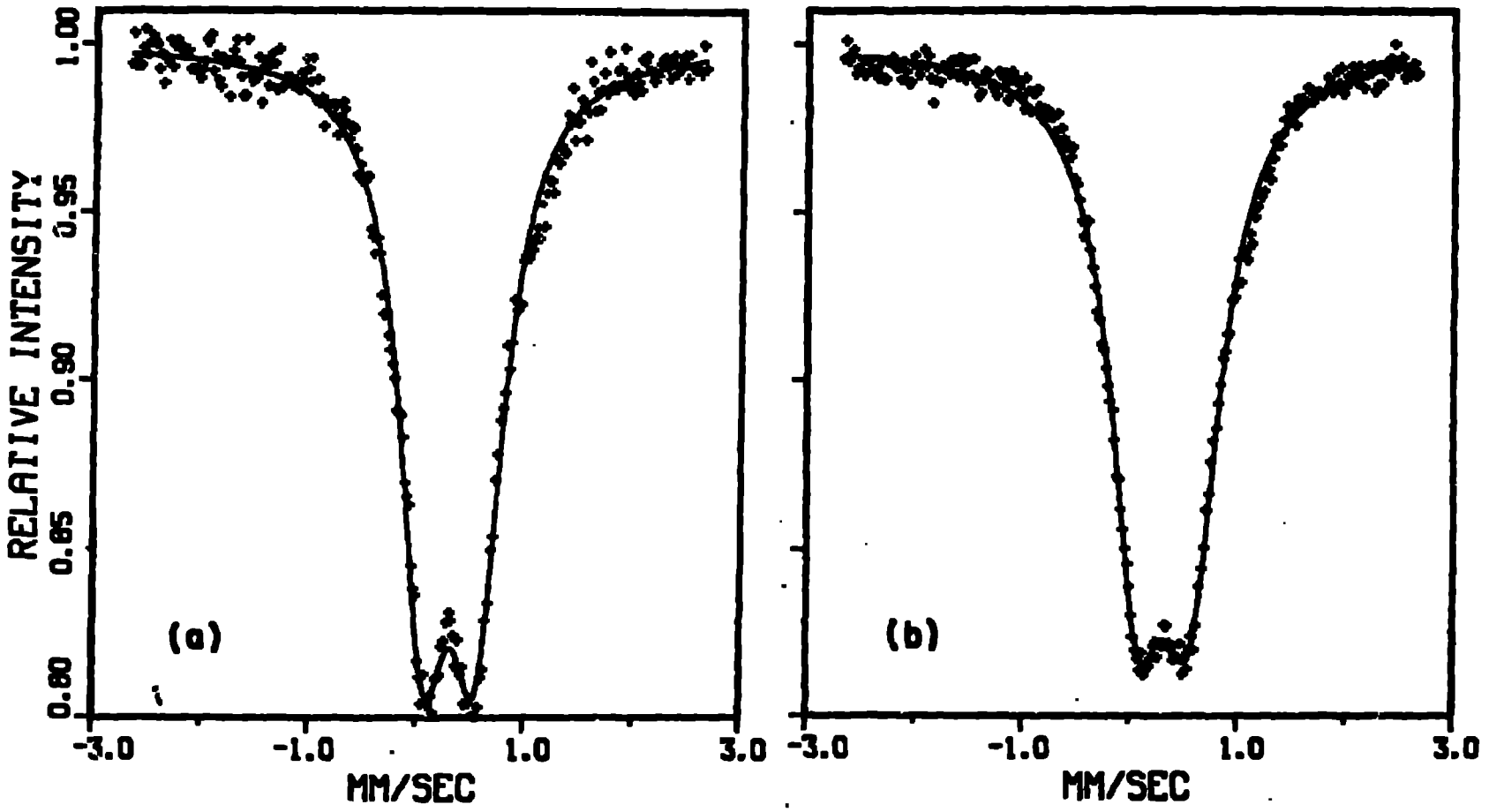
RELATIVE INTENSITY
1.00
0.95
0.90
0.85
0.80
(a)
(b)
-3.0
-1.0
1.0
3.0
MM/SEC
-3.0
-1.0
1.0
3.0
MM/SEC

*FIGURE 1. Mossbauer Effect spectra of $^{57}Fe$ in $ErRh_4B_4$ at 1.1 (a) and 0.38 K (b).*