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by

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# Magnetic Interactions in Ternary Superconductors (Invited)

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## ABSTRACT

Numerous ternary superconductors containing rare-earth atoms have recently been studied in order to investigate the magnetic interactions between the conduction electrons and local magnetic moments. These investigations range from the evaluation of the strength of spin-flip scattering of the conduction electrons off the rare-earth moments to the problem of the coexistence of superconductivity and magnetic order. We present results of our studies on $(Eu,Sn)Mo_6S_8$, $ErRh_4B_4$, $Er_{1-x}Ho_xRh_4B_4$ and $Er_{1-x}Gd_xRh_4B_4$ using primarily the Mössbauer effect in $^{151}Eu$ and $^{166}Er$, and nuclear magnetic resonance of $^{95}Mo$. The paramagnetic hyperfine spectra of the rare-earth ions indicate a weak coupling of the 4f magnetic moment to the conduction electrons. The enhanced $H_{c2}$ value in $(Eu,Sn)Mo_6S_8$ is found to be related to a negative s-band polarization at the Mo site. The magnetic moment on the Er atom in $ErRh_4B_4$ (and in related materials) in the magnetically ordered state is found to be about 8.3 $\mu_B$. This is 30% larger than that measured from neutron diffraction studies, indicating that only a component of the moment shows long-range magnetic order.

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## INTRODUCTION

The discovery of ternary materials which are superconducting while at the same time containing large concentrations of rare-earth (RE) atoms [1,2] (e.g., $REMo_6S_8$, $REMo_6Se_8$ and $RERh_4B_4$) has presented new opportunities for exploring questions related to the interaction between magnetism and superconductivity [3,4]. As a result of various investigations of these materials, a number of important questions have arisen. Some of these are listed below.

(1) In these materials there is a large concentration ($\sim$ 15%) of magnetic atoms. Why is superconductivity not destroyed by the breaking of Cooper pairs (spin depairing) due to the exchange interaction between conduction electron and rare-earth magnetic moments?

(2) The critical field ($H_{c2}$) values of $SnMo_6S_8$ (and related compounds) are quite large ($\sim$ 300 kG). Partially replacing Sn atoms by paramagnetic $Eu^{2+}$ atoms increases $H_{c2}$ without depressing the superconducting transition temperature [1,5]. What is the mechanism by which magnetic impurities enhance superconducting properties?

(3) $ErRh_4B_4$ becomes superconducting at 8.5 K. On lowering the temperature to 0.9 K, the superconductivity is destroyed [6] and long-range magnetic ordering is observed [7]. What is the nature of the magnetically ordered state?

In the following we will review recent work which has addressed these questions. Measurements of magnetic interactions, degree of magnetic order, etc. as obtained from microscopic tools such as the Mossbauer effect, NMR and neutron scattering will be discussed.

## SPIN DEPAIRING INTERACTIONS

It is well known that paramagnetic impurities in superconducting materials will depress the superconducting properties. This arises from an exchange interaction between the magnetic impurity and the conduction electron spin which breaks up the superconducting electron pairs. The theory developed by Abrikosov and Gor'kov [8] shows that the depression in $T_c$ is related to the product of the density of states at the Fermi surface $N(E_F)$ and the exchange coupling constant J. The validity of this theory has been tested in many superconducting materials[4]. However, the suppression of $T_c$ is much less pronounced in the ternary superconductors than in other compounds. As an example, Fig. 1 shows [5] $T_c$ values in the system $Sn_{1.2(1-x)}Eu_xMo_{6.25}S_8$. As x increases

up to about 0.5, $T_c$ is hardly changed, the depression finally occurring only at very high concentrations. It is thus of interest to determine the strength of the depairing interaction in the ternary compounds. In order to measure the exchange coupling between the Eu spin and the conduction electron spins, we have measured $^{151}$Eu Mössbauer effect spectra in $Eu_{0.25}Sn_{0.75}Mo_6S_8$, and several aspects of these measurements will now be discussed.

The value of the Mössbauer isomer shift reflects the total electron density at the nucleus. The measured value of $-14.0 \pm 0.1$ mm/s in this compound (w.r.t. a $^{151}Sm_2O_3$ source) clearly shows that the Eu atom is divalent and hence has a large magnetic moment of 7 $\mu_B$. From the systematics of $^{151}$Eu isomer shifts, this value is found to be typical for $Eu^{2+}$ in an ionic compound. In $Eu^{2+}$ intermetallics, isomer shifts of about half this value are more common [9]. For example, in superconducting $Eu_{1.2}La_{98.8}$ the shift is about -8 mm/s [10]. Thus in an atomic picture, the 6s density at the magnetic Eu site in the Eu-La alloys is considerably higher than in (Eu,Sn) $Mo_6S_8$. One may therefore conclude that the magnetic Eu atoms are fairly isolated from the conduction electrons in $(Eu,Sn)Mo_6S_8$. The direct measure of the depairing interaction is the spin relaxation rate of the Eu spin as a function of temperature. This relaxation rate, if dominated by exchange scattering from the conduction electrons (Korringa process), can be written

$$W = \frac{2\pi}{\hbar} (g_J - 1)^2 [JN(E_F)]^2 kT$$

In the case where the relaxation rate is large compared with nuclear Larmor frequencies, this will produce an excess linewidth $\Delta\Gamma$ proportional to the relaxation time [11]. From Ref. 11, one can show

$$W\ (sec^{-1}) = 2.75 \times 10^9/\Delta\Gamma(mm/sec)$$

for this case. The observed temperature dependence of the relaxation rate is shown in Fig. 2. In the normal state, the Korringa relaxation is obeyed and we obtain $|JN(E_F)| = 0.0077$ states/atom spin. Below the transition temperature of $T_c = 12$ K, the relaxation rate is found to be larger than would be given by an extrapolation of the Korringa law. However, this may simply represent the increasing importance of relaxation due to dipolar interactions among Eu spins at these low temperatures.

The important result is that $JN(E_F)$ is substantially smaller than that for Eu in any other conducting system. For example, in $LaAl_2$:Eu, it is 0.05 states/atom spin [12]. One thus obtains a direct observation of a small density of states at the Eu site and/or a small exchange coupling. This in turn is in agreement with the weak dependence of $T_c$ on Eu concentration for $x \leq 0.5$. In order to obtain a value of J, a calculation of the density of states and its $\ell$-decomposition projected on the magnetic sites (such as was recently obtained for $ErRh_4B_4$ [13]) will be necessary. At higher concentrations, short-range magnetic ordering appears to be present and at very low temperatures ($\sim$ 0.5 K) something comparable to a spin-glass state occurs [14]. This may be related to the eventual decrease in $T_c$, since one knows that $T_c$ can be depressed when the magnetic correlation length becomes comparable with the superconducting coherence length [15].

## ENHANCEMENT OF THE UPPER CRITICAL FIELD

In Fig. 1, we show the variation of the upper critical field with concentration in the system $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$. One sees that the presence of the paramagnetic impurity can actually enhance the superconducting properties. Such an enhancement was suggested by Jaccarino and Peter [16] as a possibility if the paramagnetic ion induced a conduction electron polarization with a sign that would partiically compensate the applied field. The critical field can be described through the following expression [5]

$$H_{c2}(T,x) = H^*_{c2}(T,x) - 0.022 \frac{\alpha}{\lambda_{so} T_c} [H_{c2}(T,x) + H_J(x)]^2 .$$

Here $H^*_{c2}$ is the orbital critical field and the second term describes the reduction in the critical field due to the paramagnetic depairing. $\alpha$ is the Maki parameter and $\lambda_{so}$ is the spin-orbit coupling. The second term also includes the exchange field $H_J$ acting on the conduction electron spins, which is proportional to x. If $H_J > 0$, $H_{c2}$ will decrease with increasing x. However, if $H_J < 0$ and $H^*_{c2}(T,x)$ has a weak (or no) dependence on x compared to $H_J(x)$, then $H_{c2}$ will increase with x. A near independence of $H^*_{c2}$ on x is, in fact, anticipated in this system because of the weak exchange interaction between rare-earth atoms and the conduction electrons, as indicated by the weak depression of $T_c$.

We have investigated this question by looking for conduction electron spin polarization contributions to the hyperfine field in $Sn_{0.5}Eu_{0.5}Mo_6S_8$, using the $^{151}Eu$ Mössbauer resonance and the $^{95}Mo$ Knight shift [17]. The results of this investigation show that the spin-polarization is positive at the Eu site, but has a spatial variation such that it is negative at the Mo site. Since it is presumed that the superconductivity arises from the Mo d-electrons, the negative spin-polarization will provide the compensation discussed above. This, therefore, provides a direct observation of the origin of the critical field enhancement.

The details of these measurements lead to a two band scheme for $Eu_{0.5}Sn_{0.5}Mo_6S_8$. In Fig. 3 we indicate an "s-band" and a "d-band". It is presumed that the superconducting properties are due to the d band, derived largely from the Mo ions. Below $T_c$, it is presumed that a gap opens in the d band, but not in the s band. This is supported by the $^{95}Mo$ measurements. The Knight shift is made up of a s-electron (contact interaction) part, $K_s$, and a d-electron (core polarization) part $K_d$. The second part should show no gross temperature dependence except that it will disappear below $T_c$ due to pairing of the d electrons; this is seen both for $SnMo_6S_8$ and $Sn_{0.5}Eu_{0.5}Mo_6S_8$. In addition, the Eu substituted compound shows a large temperature dependent shift which is not seen in pure $SnMo_6S_8$. This dependence is found to be proportional to the bulk magnetization and so arises from spin polarization due to exchange between the rare-earth and conduction electrons. This shift does not disappear below $T_c$ due to the failure of the s band to participate in the superconductivity. Hence the principal effect of the Eu impurities initially is to polarize the s-band and provide the $H_{c2}$ compensation effect, while the weak s-d coupling prevents a severe attenuation of $T_c$.

## SUPERCONDUCTIVITY AND ORDERED MAGNETISM

There now exist a large number of experiments that deal with the question of co-existence between superconductivity and ordered magnetism. These can be divided into three classes: (1) The bulk of the work has dealt with pseudobinary compounds, largely of C15 cubic Laves phases. It is presently believed that most of these systems do not show long-range magnetic order, but do exhibit either short-range order or something like spin-glass behavior [18]. In many of these cases, there exists regions in the phase diagram where this ordering is co-existent with superconductivity. (2) In some ternary compounds,

(e.g., $Dy_{1.2}Mo_6S_8$), true coexistence has been found between superconductivity and long-range anti-ferromagnetic order [19]. (3) Other ternary compounds exhibit re-entrant behavior where long-range magnetic order develops and, as a result, the superconductivity is destroyed. Examples of this behavior are seen in $Ho_{1.2}Mo_6S_8$ [20] and $ErRh_4B_4$ [1,6]. In both of these cases the ordering is ferromagnetic. In this section we will present results of Mössbauer studies on $ErRh_4B_4$ in the superconducting and magnetic states. These results show that the Er magnetic moment is not fully ordered even in the magnetic state [21].

In Fig. 4 we show the Mössbauer spectra of $ErRh_4B_4$ measured with the 80.6 keV resonance of $^{166}Er$ in $ErRh_4B_4$ at 1.5 K and 0.1 K. The first is below the superconducting transition ($T_c$ = 8.5 K) but above the magnetic transition ($T_M$ = 0.93 K) and the second is below $T_M$. In the superconducting state, a fully split hyperfine pattern is seen due to the fact that the electronic spin relaxation rate of the Er atom is small compared to nuclear Larmor frequencies. In the magnetically ordered state, the spectrum is essentially identical except for some decreases in the linewidths of the different hyperfine components.

From the measured hyperfine field we can obtain a value for the magnetic moment on the $Er^{3+}$ atom. The hyperfine field is given by

$$H_n = 2\mu_B \langle r^{-3} \rangle_{4f} \langle J||N||J \rangle \langle J_z \rangle_T + \frac{8\pi}{3} S_e \delta(r)$$

The second term on the right is the contact interaction, made up of a core polarization contribution [22] and the conduction electron contribution both of which are negligible in this case. The first term represents the orbital hyperfine field. Here, $\langle J||N||J \rangle$ is an appropriate reduced matrix element, $\langle r^{-3} \rangle_{4f}$ is a radial average for 4f electrons, and $\langle J_z \rangle_T$ is the thermal average of the angular momentum over all crystalline elecric field (CEF) levels. One sees that both $H_n$ and the magnetic moment $\mu$ are proportional to $\langle J_z \rangle_T$. The resultant proportionality between $H_n$ and $\mu$ is shown for a large number of $Er^{3+}$ systems in Fig. 5. From the measured hyperfine field at 0.1 K in $ErRh_4B_4$, we obtain a moment of $(8.3 \pm 0.2)\ \mu_B$ on the Er atom. This should be compared with the neutron diffraction result of 5.6 $\mu_B$ in the ordered state [7]. In order to reconcile the Mossbauer and neutron results, it appears that we must have a situation where only a component of the magnetic moment (5.6 $\mu_B$ in magnitude) is ordered, with the other components being disordered in either a static

or dynamic fashion. Since the neutron diffraction technique measures a long-range spin correlation, it will not observe the disordered component. However, the Mössbauer technique measures a single-ion property (auto-correlation) and in the limit of slow electronic spin relaxation will measure the full moment. It will be of considerable interest to find if such a disorder can be reduced by the application of an external field.

Much attention in the past has been paid to the disruptive influence of magnetic spins on the superconducting state. We would like to point out that the role of superconducting interactions in the ordered magnetic state may be equally important. In a system with two coupled order parameters (superconducting and magnetic) which have opposing effects on the conduction electrons, the system may obtain a minimum free-energy by maintaining some disorder in the magnetic moment. Thus, although we expect long-range ordering of the entire moment on the Er atoms at 0.1 K ($\sim T_M/10$), only a portion of the moment is ordered. The suggestion that superconducting correlations are still influential below $T_M$ is supported by the resitivity of $ErRh_4B_4$ in the magnetic state relative to that in the normal state (induced either by external field or temperature) [6].

The Mössbauer measurements on $^{166}Er$ in numerous pseudo-ternary alloys of the type $(Er_{1-x}Gd_x)Rh_4B_4$ and $(Er_{1-x}Ho_x)Rh_4B_4$ in their magnetically ordered, superconducting and normal states yield approximately the same sized magnetic moment on the Er atom [23]. This establishes the generality of some of the results discussed above.

## CONCLUSIONS

We have reviewed here recent Mössbauer effect and NMR work on magnetic interactions in relation to other properties of ternary superconductors. In the Chevrel phase compounds $(Eu,Sn)Mo_6S_8$ we have suggested a two band picture in which Eu spins are only weakly coupled to the "s-band" electron, and does not disturb the "d-band" superconductivity. The "s-band" polarization at the Mo sites, in the presence of Eu atoms, shields the externally applied field, thus enhancing the $H_{c2}$ values.

The re-entrant superconductor $ErRh_4B_4$ has an unusual magnetic order in which only a component of the total Er moment shows long-range ferromagnetic correlation, with the remaining components being disordered down to 0.1 K.

At present, relatively few experiments have been performed utilizing microscopic tools to study magnetic interactions in superconductors. There is

now an established place for work of this nature, and many results may be expected in the near future. Commensurately, there is a need for theoretical studies of the interaction between magnetic and superconducting order parameters, including the possiblity of a combined superconducting-magnetic ground state.

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## Figure Captions

Fig. 1. Concentration dependence of the critical field $H_{c2}$ (solid circles) and transition temperature $T_c$ (open circles) in $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$ (Ref. 5).

Fig. 2. Temperature dependence of the electronic relaxation rate for Eu in $Eu_{0.25}Sn_{0.75}Mo_6S_8$.

Fig. 3. Two band picture for $SnMo_6S_8$ showing (a) conduction bands in the normal state and (b) the energy gap $E_g$ of the "d-band" in the superconducting state. The gap $E_g$ is exaggerated in size. Thermally excited electrons are above the gap in the d-band and above $E_F$ in the s band for $T \leq T_c$.

Fig. 4. Mossbauer spectra for $^{166}Er$ in $ErRh_4B_4$ for (a) the superconducting state and (b) the magnetically ordered state.

Fig. 5. Linear dependence of the Er magnetic hyperfine field on the electronic magnetic moment in various compounds.