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EFFECTS OF MAGNETIC ATOMS ON THE PROPERTIES OF TERNARY SUPERCONDUCTORS

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Until recently it has been commonly accepted that small impurities of magnetic atoms were severely detrimental to superconductivity, and that superconductivity and long-range magnetic ordering could not occur in the same materials. In known binary and pseudo-binary compounds, this is still the case. However, many recent experiments on ternary superconductors have shown that the effects of magnetism are considerably more complex. In some cases, the addition of magnetic atoms has been found to enhance superconducting properties by increasing the superconducting critical field, without significantly lowering the transition temperature. In many cases, compounds will show both superconducting and long range magnetic ordering transitions. The destruction of superconductivity by ferromagnetic ordering and the coexistence of superconductivity with antiferromagnetic ordering is now well established.

Hyperfine interaction measurements have played a significant role in the investigations of these materials, including measurement of the magnitude of the exchange interaction between rare-earth spin and conduction electron spin, elucidation of the mechanism for critical field enhancement, specification of crystalline field ground states, and studies of the nature of magnetic ordering.

INTRODUCTION

The study of the effect of magnetic impurities on the properties of superconducting systems has been of interest for many years (1). Until recently it has been generally assumed that the presence of magnetic ions in a superconducting matrix will have a strong negative effect on superconducting properties, and many experiments have verified this assumption. This is due to the fact that the occurrence of superconductivity depends on there being pairs of electrons in the material which have oppositely directed spin angular momenta and are correlated with one another through the electron-phonon interaction over distances on the order of hundreds of Angstroms (Cooper pairs). Magnetic ions in the material will cause spin-flip scattering through the exchange interaction of the local magnetic moment with the conduction electrons. Since this is a highly localized interaction, it acts on individual spins and so tends to destroy the anti-parallel alignment of the Cooper pairs. Generally the exchange interactions associated with magnetic effects are much stronger than the electron-phonon interactions causing superconductivity. Consequently, small concentrations of magnetic ions will frequently destroy superconductivity entirely. For example, $LaAl_2$ has a superconducting transition temperature T_c = 5.24 K, but substitution of La by Gd to a concentration of 0.59% reduces T_c to zero(2). In other systems the dependence on concentration may not be quite so sharp, but the results are

always rather striking. The above ideas were put on a quantitative basis by Abrikosov and Gorkov (3) who calculated the effective lifetime of the Cooper pairs to the spin-flip scattering within the first Born approximation, and showed that the depression of T_c was given for low concentrations by

$$\Delta T_c = -\frac{\pi^2}{2k} N(E_F) J^2 S(S+1) \Delta x \qquad (1)$$

where $N(E_F)$ is the density of states at the Fermi surface in the vicinity of the magnetic impurity, J is the magnetic exchange interaction between the local moment and the conduction electrons, S is the angular momentum of the magnetic ion and x is the concentration. This theory, with some modifications to include crystal field effects and other scattering mechanisms in some systems, has been very successful in describing observed phenomena in many elemental, binary and pseudo-binary superconductors(1).

As the concentration of magnetic ions increases, the possibility of long range magnetic order also increases. If the depression of T_c is not too rapid, it may then become possible to obtain a situation where superconductivity and long-range magnetic order both coexist in the same material. This possibility has been explored in several systems in the past, all of which were pseudo-binary compounds. For example, $CeRu_2$ is a superconductor and $GdRu_2$ is a ferromagnet. Figure 1 shows the variation of the superconducting transition temperature T_c and of the magnetic transition temperature T_M with concentration(4). Because of the apparent crossover in these two temperatures at concentrations near 13%, it would appear that the materials may exhibit both superconductivity and magnetic order. However, it is difficult to see how long range ferromagnetic order can coexist with superconductivity since ferromagnetism requires all spins to be aligned in one direction, while superconductivity requires them to be paired in opposite directions. Several explanations of this type of behavior have been offered, including the formation of a "crypto-ferromagnetic" state where the magnetism occurs only in small domains throughout the material (5), and the occurrence of superconductivity in the domain walls where the magnetization is changing rapidly(6). The current opinion for most of these types of alloys is that the magnetism is of a spin-glass type behavior(7). In that situation the magnetic order does in fact take place in small clusters throughout the material.

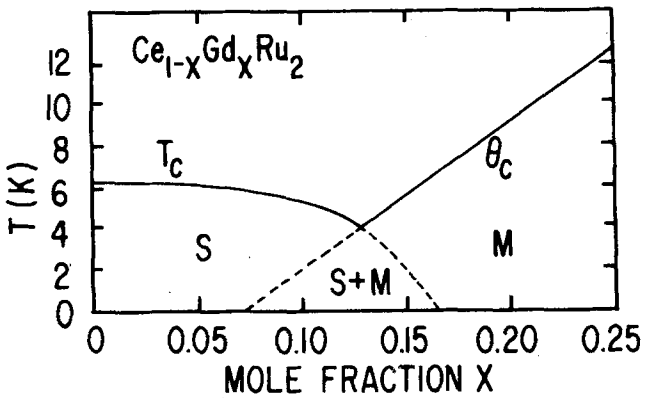

Fig. 1. Superconducting-magnetic phase diagram for $Ce_{1-x}Gd_xRu_2$ (see Ref. 4).

While every magnetic atom in the compound may be ordered, the direction of the magnetic axis for the various clusters is random, so that the net magnetization in zero field is small. If the clusters are smaller than the coherence length over which Cooper pairs are ordered, then they will behave, crudely speaking, like large magnetic impurities and will not totally destroy the superconducting state.

The discovery of superconductivity in ternary alloys has opened up this study of magnetic effects in superconductivity considerably, helping to clarify some of the old results as well as displaying many new phenomena. In contrast to the three component systems discussed above which consist of two binary systems mixed together in random solid solution, these are materials in which the three constituents have simple stoichiometric composition ratios and well defined crystallographic sites. In such cases it sometimes becomes possible to identify spatially the site of the "superconducting electrons" (generally d electrons on transition atoms) and of the "magnetic electrons" (often f electrons on rare-earths). Because of the details of band structure and crystallographic structure, the interaction between the two "bands" may be weaker than in binary systems, exchange interactions may be weaker, and a much wider variety of possible phases may occur. These include magnetic systems, superconductors, and states which can best be characterized as magnetic superconductors.
Hyperfine interaction studies have been very useful in understanding many of the above phenomena. Such measurements have been previously carried out in several binary and pseudo-binary compounds(7). In ternary materials, however, it becomes possible to go to much higher concentrations of magnetic ions and still maintain superconductivity. Because of the weak coupling alluded to above, electron relaxation times are frequently very long, allowing the observation of well-resolved paramagnetic hyperfine spectra in Mössbauer investigations. In addition, the variety of types of phases present offers more possibilities for instructive examinations. In the following we will review a number of recent Mössbauer effect results which have been obtained in the investigation of ternary superconductors.

SUPERCONDUCTING TRANSITION TEMPERATURES AND CRITICAL FIELDS

A group of compounds known generically as Chevrel phases, after the person who first characterized the crystal structure, have been extensively studied by many techniques(8). A typical material in this class is $SnMo_6S_8$, but the Sn may be replaced by a wide variety of transition metal and rare-earth ions, and S may be replaced by Se. Such materials first attracted attention because of their relatively large superconducting transition temperatures and very large values for the magnetic field which can be applied without destroying superconductivity, the upper critical field H_{c2}. For $SnMo_6S_8$, one finds T_c = 10.4 K and H_{c2} = 275 kG. In addition, it was soon realized that the behavior of the materials with the addition of magnetic ions was very unusual. Figure 2 shows(9) the variation with temperature of T_c and H_{c2} in $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$. Mössbauer and magnetization measurements verify that Eu is divalent, and hence has a large magnetic moment of $7\mu_B$. However, one sees that T_c does not change appreciably up to the astonishingly large concentration of x = 0.5. Furthermore, H_{c2} actually increases in this concentration range, to 400 kG for x = 0.5. Thus one has the unusual situation that the addition of magnetic ions to a superconducting material actually improves the superconducting properties. In this section we will discuss both the variation of T_c and H_{c2} with concentration.

Within one's present understanding of magnetic impurities, as expressed by Eq. 1, the suppression of T_c depends on the exchange interaction between magnetic ions and the conduction electrons. The absence of such suppression then implies either a small value of the exchange interaction J, or of the density of states $N(E_F)$, or both. One procedure for measuring these parameters utilizes the fact that

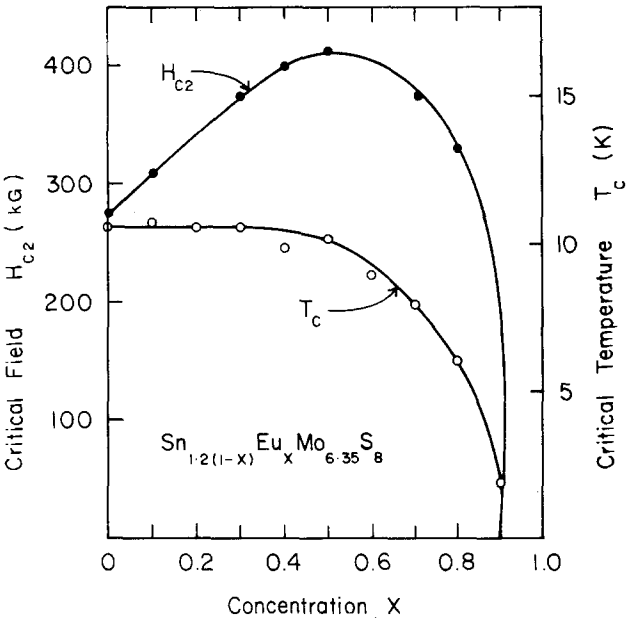

Fig. 2. Dependence of superconducting transition temperature (T_c) and critical field (H_{c2}) on concentration in $Sn_{1.2(1-x)}Eu_xMo_{6.35}S_8$.

the spin-flip scattering of the conduction electrons is necessarily accompanied by electronic relaxation of the paramagnetic ions. This relaxation mechanism, known as the Korringa process, gives rise to a relaxation rate having the temperature dependence

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

and a measurement of this temperature dependence can be used to obtain $|JN(E_F)|$. Mössbauer spectra obtained using the ^{151}Eu resonance in $Sn_{.75}Eu_{.25}Mo_6S_8$ show a strongly temperature dependent line-width which arises from such processes (10). This is very unusual in metallic Eu systems where the combination of high relaxation rates acting on an S-state ion usually leads to linewidths determined only by temperature independent factors. In this case, however, the relaxation rates are such that strong effects are seen. In the limit where the relaxation rates are large compared with Larmor precession frequencies so that only line-broadening is observed, one can use the theoretical developments of Bradford and Marshall (11) to obtain an explicit expression relating the excess linewidth $\Delta\Gamma$ with the relaxation rate:

$$W(sec^{-1}) = 2.75 \times 10^9/\Delta\Gamma(mm/sec) \qquad (3)$$

for the present case. This expression combined with the observed line-widths gives the relaxation rates shown in Figure 3. Here one sees a finite value of 4.7×10^8 sec^{-1} at T = 0 due to spin-spin interactions, and a linear T dependence due to Korringa relaxation. From Eq. 2, one then obtains $|JN(E_F)|=$

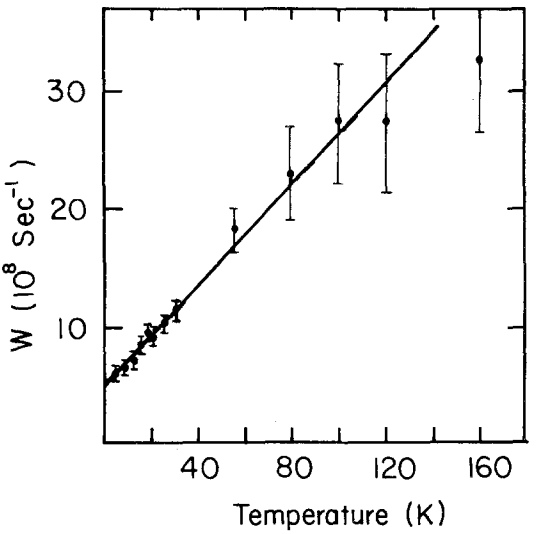

Fig. 3. Temperature dependence of Eu^{2+} electronic relaxation rate in $Sn_{.75}Eu_{.25}Mo_6S_8$.

0.0033/ Eu atom spin. This is approximately an order of magnitude smaller than that found in other superconductors. For example, Eu present as an impurity in $LaAl_2$ gives $|JN(E_F)| = 0.03$ / Eu atom spin (12). This provides at least a partial explanation of the weak suppression of T_c with concentration. Subsequent band-structure calculations for $EuMo_6S_8$ have shown that a very large charge transfer occurs away from the Eu atom, leaving an unusually small $N(E_F)$, in agreement with the above measurement (13). This charge transfer phenomena is also supported by the essentially ionic value of the isomer shift for Eu in these materials.

At lower temperatures, the linewidth in similar materials shows a temperature dependence which is not in agreement with the above results (14). However, in this region (<1 K) the spin-spin effects arising from dipolar interactions are very important, and in fact appear to lead to some type of magnetic order (see discussion below). The results obtained at higher temperatures have been verified by other measurements. EPR results (15) give relaxation rates which provide values of $|JN(E_F)| = 0.006$ for Gd^{3+} in $SnMo_6S_8$ and 0.005 for Gd^{3+} in $PbMo_6S_8$, in general agreement with the Mössbauer conclusions. In principle one also expects a change in the relaxation rate at T_c, due to the fact that an energy gap opens up in the density of states, and so alters $N(E_F)$. This is obscured in the Mössbauer data due to the predominance of spin-spin interactions below T_c. However, the EPR work has been able to use such arguments to obtain a value of the superconducting energy gap of $\Delta \tilde{=} 2.5\ kT_c$.

Although the above arguments all indicate that the coupling between the conduction electrons and the rare-earth moment is weak, nonetheless such a coupling is responsible for the observed increase in H_{c2} when the magnetic ion is present. For $Eu_{0.5}Sn_{0.5}Mo_6S_8$, Mössbauer spectra of ^{151}Eu and NMR Knight shift measurements of ^{95}Mo have been obtained as a function of external field and temperature (16). In both cases, the observed hyperfine fields can be compared with known values of core-polarization fields to obtain estimates of the sign and magnitude of the local conduction electron polarization. In this way one finds

that the polarization of the Eu ion by the external field generates a conduction electron polarization which is positive (i.e., parallel to the external field) at the Eu site, but which shows a spatial dependence such that it is negative at the Mo site. It is generally presumed that the d-electrons originating on the Mo atoms contribute most prominently to the superconducting processes. The effect of the negative conduction electron polarization at the Mo site is to partially shield the external field, so that one can increase this field to a larger value before the net field on the Mo becomes sufficiently high to destroy the superconductivity. Again, these results have been verified by spin-unrestricted band-structure calculations (17).

MAGNETIC ORDERING

Because of the high concentration of magnetic ions present in ternary compounds, magnetic order may be expected. Since these are stoichiometric compounds, the arguments above concerning the formation of a spin-glass state do not apply, and long-range ordering is likely. Therefore these become very interesting systems for the study of the interaction of magnetic ordering with superconductivity. Most of the Chevrel phase compounds show magnetic ordering at sufficiently low temperatures. For example, in the $R_{1.2}Mo_6S_8$ systems, antiferromagnetism occurs for R = Gd, Tb, Dy (18-20) and ferromagnetism for R = Ho(21). The effect of "re-entrant" conductivity is observed in $HoMo_6S_8$ as well as in $ErRh_4B_4$ (22). In the latter material, superconductivity occurs at T_C = 8.7 K. At T_M = 0.96 K, ferromagnetic ordering takes place, coupled with a return to normal conductivity. This is consistent with the above arguments concerning the difficulty of maintaining Cooper pairs in a region of uniform magnetization. On the other hand, in the presence of antiferromagnetism, it is found that superconductivity is retained. This can be understood because the magnetization for an antiferromagnet averaged over the superconducting coherence length will be very small, and the breaking of Cooper pairs is correspondingly inhibited. This

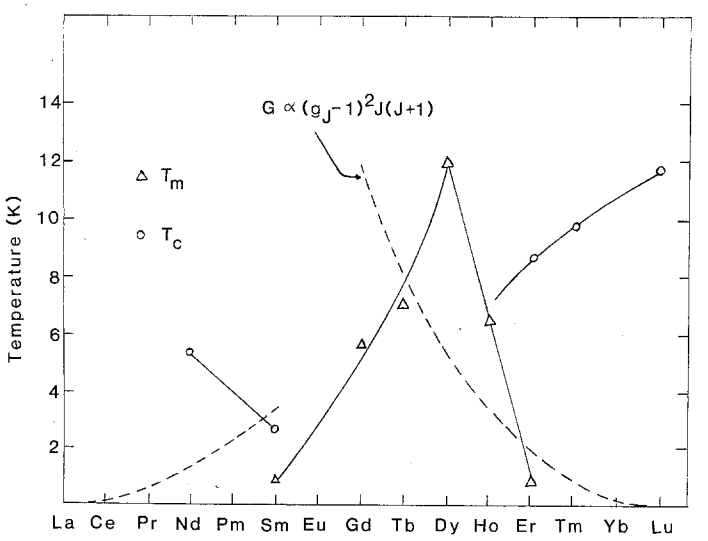

Fig. 4. Dependence of superconducting (T_c) and magnetic (T_m) transition temperatures on rare-earth atom in rare-earth rhodium boride. The dashed line gives the dependence of the de Gennes factor, G.

co-existence has been clearly observed in the $R_{1.2}Mo_6S_8$ compounds mentioned above, as well as in $SmRh_4B_4$ (23).

In rare-earth systems, where the magnetic interactions are generally large compared to crystalline electric field splittings, one expects both the magnetic transition, T_m, and the suppression in the superconducting transition temperature, T_c, to vary with rare-earth ion according to the deGennes factor $G = (g_J-1)^2 J(J+1)$, where g_J is the Lande factor and J is the total angular momentum. In Fig. 4, the observed values of T_M and T_c are compared with G for the RRh_4B_4 compounds. The fact that no correlation is seen suggests that crystal field effects must be included in the discussion of these systematics. Because of changes in the angular momentum character of the rare-earth atom due to crystal field effects, both the value of T_M and T_c will be strongly modified from the above behavior. The effect of such considerations on superconducting systematics has been treated by Fulde and co-workers (24). While other mechanisms may be present, one clearly needs information concerning crystal fields in these materials in order to understand the overall behavior.

Generally, crystal field effects are obtained from Schottky anomalies in specific heat data, bulk magnetization measurements, or inelastic neutron scattering. The Mössbauer effect provides a microscopic probe for these phenomena. In particular, direct information on the crystal field ground state can be obtained from hyperfine spectra which will be observed if the electronic spin relaxation rate is small compared with nuclear Larmor frequencies. Fig. 5 shows spectra taken using the ^{166}Er resonance in $ErRh_4B_4$ at 1.5 and 0.1 K, i.e., above and below the magnetic ordering temperature (25). Above T_M one observes an almost static paramagnetic hyperfine spectrum characteristic of a low lying

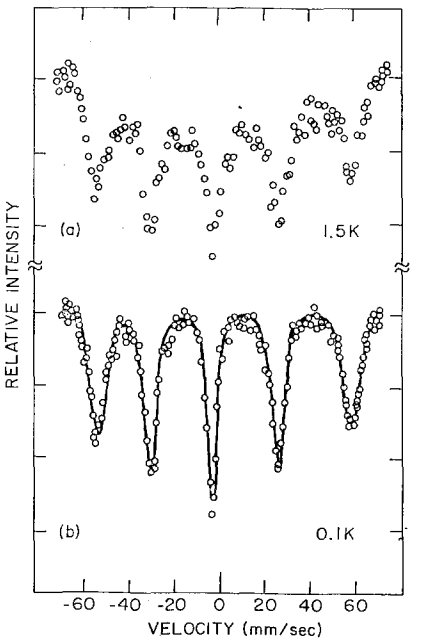

Fig. 5. Mössbauer spectra for ^{166}Er in $ErRh_4B_4$ at 0.1 K and 1.5 K.

Kramer's doublet with a highly anisotropic g tensor (the "effective field" case). Below T_M, this spectrum does not change substantially, showing that the magnetic interactions are small compared with crystal field interactions.

Spectra obtained for ^{169}Tm in $TmRh_4B_4$ and ^{161}Dy in $DyRh_4B_4$ also show slow relaxation. The results can be understood as follows: For Er two doublets predominantly being composed of $J_z = \pm 15/2$ and of $J_z = \pm 13/2$ lie close together, with rapid relaxation occurring between them. As a result, one obtains moments of 8.4 μ_B in $ErRh_4B_4$, in good agreement with experiment. For $TmRh_4B_4$, the ground state is again two close lying doublets primarily composed of $J_z = \pm 6$ and $J_z = \pm 5$ giving a moment of 6.4μ_B. In this case, the temperature dependence of the spectra indicates that the higher excited states lie at 15-20 K. In $DyRh_4B_4$, Dy has a well isolated doublet ground state made up of $J_z \approx \pm 15/2$. In all these cases, it is clear that crystal fields are playing a large role in determining the properties of these materials, and systematic investigations of these phenomena are under way.

Generally, the detailed nature of magnetic order cannot be understood from Mössbauer spectra alone, since such measurements give information only on single-ion properties rather than on coherent phenomena. In the case of S-state ions such as Eu^{2+} or Gd^{3+}, this is even more difficult since the hyperfine field predominantly arises from core polarization and so is not sensitive to environmental effects. Nonetheless, such measurements frequently provide one with the only microscopic information available. Mössbauer studies of the Chevrel phase compounds $Eu_xSn_{1-x}Mo_6S_8$ have been carried out at very low temperatures (26). Magnetic hyperfine splitting is observed below ~0.5 K for $X \geq 0.6$. However, both ordered and disordered regions are seen near T_m, reflecting either crystallographic or magnetic inhomogeniety in the materials. Spectra obtained with ^{119}Sn give no measurable transferred hyperfine field, showing the weak electron overlap between the Eu ions and those on other sites discussed in the previous section. At these temperatures, it is likely that the magnetic ordering originates from dipolar or superexchange coupling, and that the observed phenomena arise from short-range magnetic order or spin-glass type behavior.

In other materials, as mentioned above, long range ordering is clearly present. Neutron diffraction work on $ErRh_4B_4$ has shown that the material is ferromagnetic with $T_C = 0.9$ K (27). However, those experiments provided a value for the ordered state magnetic moment of 5.6 μ_B, in comparison to the value of 8.3 μ_B obtained by Mössbauer spectroscopy. This discrepancy is much too large to be due to the experimental errors of the two experiments, and represents the only instance where neutron diffraction and Mössbauer spectroscopy have not given the same result in a rare-earth system. At present the reason for the difference is not understood, but two possible explanations have been offered (25). Both explanations depend on noting that the two techniques do not in fact measure the same intrinsic quantity. Diffraction methods, by their very definition, obtain only a value for the coherent moment, and will not see any disordered component. The Mössbauer technique measures the total single atom moment. Thus it may be that the ferromagnetic state of $ErRh_4B_4$ has an ordered moment of 5.6 μ_B, whereas the total moment is 8.3 μ_B, with the remaining component presumably being disordered at these temperatures. The other possible explanation is that the material is not magnetically homogeneous, but may consist of domains of ferromagnetism embedded in a non-ordered matrix. In that case, the process of converting neutron diffraction intensities into a magnetic moment would be in error, since that has assumed that all the material is ordered. However, the Mössbauer spectra, measuring a local property not sensitive to the ordering of neighboring spins, will show the same spectrum for both the ordered and disordered regions. Whatever the explanation may be, it is clear that the magnetic state of this material is not the same as in a simple ferromagnet, and it may be expected to yield some interesting physical information when it is understood. It seems likely that contained in that solution

will be new understanding concerning the detailed interaction of the two kinds of ordering.

CONCLUSION

It is noteworthy that while only two classes of systems (the Chevrel phases and the rare-earth rhodium borides) have so far received extensive study, nonetheless a great many new phenomena have been encountered. This, however, should only be considered the beginning of a new and potentially very rich field, especially if one considers the vast number of possibilities of ternary compounds that can be produced. To take only one other example, recent work has shown that the compound $Sc_2Fe_3Si_5$ is superconducting with a superconducting transition of 4.5 K (29). This at first may appear surprising since even in the Chevrel phase materials, the addition of Fe atoms is detrimental to superconductivity. However, recent Mossbauer effect experiments (29) have shown that the Fe in this material is not magnetic, having a magnetic moment of less than 0.03 μ_B. These silicides have also been made with rare-earth ions in place of the Sc (28). The compounds show magnetic transitions and are currently under investigation. Several other interesting systems have been synthesized, and it appears that many more will be coming in the near future. The results reported above have shown the utility of hyperfine data in clarifying many of the new phenomena that occur, and it should be expected that as this new field grows, these kinds of measurements will continue to play an active role (30).

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K. BABERSCHKE: What is the argument for using unmixed eigenstates for Er^{3+} and Dy^{3+} in $R.E.Rh_4B_4$? In non-cubic metals like Se, Y, and Lu, these ions should have strong cubic contributions to the crystal-electric field.

B.D. DUNLAP: In these materials, the point symmetry for the rare-earth ions requires a crystal-field Hamiltonian $\tilde{H} = B_2^0O_4^0 + B_4^0O_4^0 + B_4^0O_4^0 + B_6^0O_6^0 + B_6^4O_6^4$. If the coefficients B_4^4 and B_6^4 are not very large, unmixed eigenstates will be obtained.