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MAGNETIC ORDERING IN RARE-EARTH
TERNARY SUPERCONDUCTORS

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A review is given of current neutron scattering studies of rare-earth(R) ternary superconductors: RMO_6X_2 ($\text{R} = \text{S}$ or Se) and ErRh_4B_4 . Most of these compounds develop antiferromagnetic long-range order with coexists microscopically with superconductivity. Two compounds, HoMo_6S_8 and ErRh_4B_4 , become ferromagnetic causing the destruction of superconductivity. In ErRh_4B_4 , both superconducting and ferromagnetic regions are simultaneously present between 0.9 and 1.2 K but microscopic coexistence is not indicated. However, in this temperature range, magnetic fluctuations occurring in the superconducting regions take the forms of a magnetic spiral with a wavelength of ~ 100 Å in order to accommodate superconductivity. This observation is in good agreement with the theoretical predictions of Blount and Varma.

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Extensive studies have been carried out in recent years on two new classes of rare-earth (R) ternary compounds: RMO_6X_8 ($\text{X} = \text{S}$ or Se) (Fischer et al., 1977). Some of these compounds develop both superconductivity and magnetism and they exhibit fascinating physical properties as a result of the interaction between these two competing order parameters. In two cases, HoMo_6S_8 (Ishikawa and Fischer, 1977a) and ErRh_4B_4 (Fertig et al., 1977), the superconducting state is destroyed at a lower transition temperature T_{C2} . The other compounds remain superconducting (Ishikawa and Fischer, 1977b) below the magnetic transition temperature T_M . In this review, we will discuss recent neutron scattering studies of magnetic ordering in these superconductors.

The results are summarized in Table I together with the appropriate references. This work has been carried out in collaboration with D. B. McWhan and P. H. Schmidt (Bell Laboratories); J. Eckert and C. F. Majkrzak (Brookhaven); M. Ishikawa and Ø. Fischer (Univ. Genève); M. B. Maple, H. B. MacKay, L. D. Woolf, Z. Fisk, D. C. Johnston, and R. N. Shelton (U.C.S.D.); J. W. Lynn (Univ. Maryland). The magnetic transition temperatures T_M in Table I were determined by our neutron scattering measurements and they are in excellent accord with other physical measurements. It was absolutely essential that all of our neutron measurements were done on samples which had been properly characterized by the electrical, magnetic, and thermal measurements. Only by this type of systematic study could we positively identify the correspondence between the magnetic and superconducting characteristics.

As shown in Table I, most of these compounds develop long-range antiferromagnetic (AF) order. Rare-earth ions in these Chevral phase crystals form simple cubic lattices with slight rhombohedral distortion. Except for the complex magnetic structure of ErMo_6Se_8 and the ferromagnetic order in HoMo_6S_8 , all others order in a simple antiferromagnetic scheme of alternating ferromagnetic sheets along the cubic [100] direction. As shown in Fig. 1 for TbMo_6S_8 , some rhombohedral peaks are clearly split. This permits us to determine the spin direction uniquely as the rhombohedral [111] direction.

Experimental details were given in our original publications; we would like to emphasize here only a few specific problems unique to the current studies of ternary superconductors. Large magnetic moments on rare-earth ions permit routine neutron diffraction experiments if one can (1) achieve low temperatures and (2) obtain pure samples. We have utilized two cryogenic systems: a He^3 cryostat (0.3 K) and a dilution refrigerator (0.05 K) with an option of the application of magnetic fields up to 70 kOe. A small amount of

magnetic impurity poses a special problem in these ternary compounds because of a low density of the host magnetic ions. We recall that the magnetic Bragg intensities are proportional to

$$v N_M^2$$

where v is the volume fraction of each component and N_M is the number of magnetic atoms per cubic centimeter. Suppose we have a magnetic impurity such as DyS in which N_M is several times larger than the host DyMo_6S_8 . Then this impurity of a few per cent in volume can give a magnetic peak intensity comparable to those of the host. We have been fortunate, in most cases, to obtain samples with sufficient purity not to cause any difficulty. Moreover, most of the magnetic structures turned out to be very simple as is the case with antiferromagnetic TbMo_6S_8 and ferromagnetic ErRh_4B_4 . Only in one case, ErMo_6Se_8 , did we encounter basic difficulties of resolving the magnetic structure because of impurity phases.

It is now clearly established that antiferromagnetic long-range order can coexist with superconductivity. It was shown by Ishikawa and Fischer (1977b) that antiferromagnetic interactions influence the upper critical field H_{c2} . Fig. 2 depicts the temperature dependence of sublattice magnetization for three sulfides. A sharp rise was noted for the Dy compound compared with the much slower increases observed for Tb and Gd. There is a striking correlation between the magnetic order parameter and H_{c2} , shown in the inset. Further theoretical study is needed along this line.

The most recent neutron scattering activity has been centered around ferromagnetic ErRh_4B_4 . This reentrant superconductor was first reported by Fertig et al. (1977) to undergo a sudden destruction of superconductivity at $T_{c2} = 0.92$ K. Subsequently, Moncton et al. (1977) demonstrated, by neutron scattering, that the compound develops long-range ferromagnetic order below $T_M = 1.0$ K. This point is demonstrated in Fig. 3 by additional magnetic components superimposed on nuclear peaks at low temperatures. Assuming $T_{c2} = 0.92$ K for this sample, we concluded that the temperature region in which the sample had long-range magnetic order and was also superconducting was small if it existed at all. Subsequent measurements of ac susceptibility for this sample (Moncton, 1979) showed that T_{c2} was 0.74 K, and a clear overlap region is indicated. We believe, however, that microscopic coexistence does not obtain; the sample simply contains both ferromagnetic and superconducting domains. Apparently, T_{c2} is quite sensitive to the annealing and other conditions of sample preparation (Rowell et al., 1979). This two-phase behavior is

consistent with the observed smearing of the magnetic intensity versus temperature (Moncton et al., 1977). Furthermore, convincing theoretical arguments by Blount and Varma (1979) preclude the coexistence of ferromagnetism and superconductivity due to electromagnetic interactions.

A new and well-annealed sample of ErRh_4B_4 (with B^{11} isotope) was prepared by M. B. Maple and collaborators; neutron and specific heat measurements were carried out with the results shown in Fig. 4. These data positively establish the relation between the magnetic order and the reentrant temperature T_{C2} . At the temperature $T_{C2} = 0.92$ K, where the superconductivity appears on heating, the magnetization still retains approximately 70% of its saturation value ($I_M \propto M^2$). Observed magnetic peaks remain sharp until their disappearance around 1.2 K, indicating that a long-range magnetic order exists in the domains which are present with superconducting regions above 0.92 K.

One may note a unique hysteresis covering a temperature range of 0.8 - 1.2 K. This hysteresis is not connected with the first order superconducting normal transition at 0.92 K. We actually see no effect on the magnetic intensity connected with the sharp spike in the specific heat at 0.92 K. The hysteresis of neutron intensity indicates some sort of activation process in this temperature range. This probably corresponds to the creation of superconducting "domains" out of uniform magnetization. Similar hysteresis was observed in the temperature dependence of the transverse periodicity of charge density waves (Ellenson et al., 1978).

The most striking feature of the mixed phase region above 0.9 K is the nature of the magnetic fluctuations. In ordinary ferromagnetic phase transitions, the magnetic critical scattering is centered at $q=0$ and peaks at T_C . In ErRh_4B_4 , the magnetic scattering cross section shows a broad maximum around 2° in 2θ for $\lambda = 4$ Å. This scattering indicates spiral magnetization with a wavelength of approximately 100 Å, in agreement with recent theoretical predictions of Blount and Varma. They show that this wavelength results from a minimization of the magnetic free-energy in the presence of superconductivity. It depends upon both a magnetic length and a superconducting penetration depth. We note that this is the first experimental observation of the influence of superconductivity on magnetic fluctuations. The details of this theoretical model will be discussed by the next speaker, Chandra Varma.

We have now reached the stage which requires a single crystal for further study. What is the direction of the propagation vector of spiral fluctuations? What are the spin-wave excitations in this unusual ferromagnet? And, finally, is the mixed phase region above 0.92 K due to sample

inhomogeneity or does it, as we believe, reflect another aspect of the interaction between magnetism and superconductivity?

We are grateful for stimulating discussions with many of our colleagues, in particular Ø. Fischer, M. Ishikawa, J. W. Lynn, C. F. Majkrzak, M. B. Maple, D. B. McWhan, and C. M. Varma.

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TABLE I. *Magnetic Ordering in Superconducting Ternary Compounds*

Compound	T_c (°K)	T_M		Reference	
$GdMo_6S_8$	1.4	0.84	AF	Majkrzak	(1979)
Tb "	2.05	1.05	"	Thomlinson	(1979a)
Dy "	2.05	0.40	"	Moncton	(1977b)
Ho "	1.2	0.67	F	Lynn	(1978b)
Er "	2.2	0.2	AF	Thomlinson	(1979b)
$GdMo_6Se_8$	5.5	0.8	AF	Maple	(1979)
Er "	6.0	1.1	" (complex)	Lynn	(1978a)
$ErRh_4B_4$	8.5	1.2	F	Moncton	(1977a) (1979)

- FIGURE 1. Neutron diffraction data for TbMo_6S_8 above ($T = 4.2 \text{ K}$) and below ($T = 0.07 \text{ K}$) the antiferromagnetic ordering temperature at $T_M = 1.05 \text{ K}$. After Thomlinson et al. (1979a).
- FIGURE 2. Temperature dependence of the magnetization for RMO_6S_8 ($R = \text{Dy}, \text{Gd}, \text{Tb}$) as determined by neutron diffraction, together with the H_{C2} for these compounds. After Majkrzak et al. (1979).
- FIGURE 3. Four powder peaks for ErRh_4B_4 at temperatures above ($T = 1.4 \text{ K}$) and below ($T = 0.07 \text{ K}$). The (102) peak has no magnetic contribution. After Moncton et al. (1977a).
- FIGURE 4. Ferromagnetic Bragg intensities for ErRh_4B_4 , compared with the specific heat data of the identical sample (on heating). After Moncton et al. (1979).

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4