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The Development of Magnetic Order in Superconducting
Systems

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ABSTRACT

Two different classes of rare-earth (RE) ternary superconductors (RERh_4B_4 and REMo_6S_8 , $\text{X}=\text{S}, \text{Se}$) have provided the first instances in which chemically ordered sublattices of magnetic ions exist in superconductors. Neutron scattering studies show that simple, conventional antiferromagnetism coexists with superconductivity in a number of systems, while destruction of superconductivity occurs with the onset of ferromagnetism. We summarize the magnetic structural details for the coexistent antiferromagnets, and review measurements on the superconducting $\rightarrow$ ferromagnetic transition in ErRh_4B_4 .

I. INTRODUCTION

Exploring the properties of superconductors by introducing magnetic impurities began immediately following the development of the BCS theory. The drastic reduction of the superconducting transition temperature by magnetic impurities first observed by Matthias et al.¹ in $\text{La}_{1-x}\text{Gd}_x$ was even more dramatic when one considered the extraordinary tolerance of superconductivity for nonmagnetic disorder. Shortly after these results were obtained, Anderson² provided a theoretical framework for understanding the disparate behavior of magnetic and nonmagnetic impurities. Whereas the choice of pair wave functions related by time-reversal symmetry preserved superconductivity in the presence of chemical disorder, spin-flip scattering by magnetic impurities destroyed it. The strength of this exchange interaction between impurity spins and the conduction electrons is so large in most systems that, until very recently, few materials existed which could be doped with more than one per cent magnetic impurity. It is obvious from the low concentrations of impurities involved that correlation of magnetic spins is not the most important aspect of these systems. In fact, the pioneering work of Abrikosov and Gor'kov³ on the effects of spin-flip scattering assumed random, uncorrelated spins. Although a great deal of new physics emerged from these studies,⁴ there was an intense effort to find and study systems in which the exchange interaction was small. If large impurity concentrations could be obtained, cooperative magnetic effects would be important, perhaps dominant. Ideally, however, one would like to go beyond impurity systems to find materials in which

the magnetic ions formed a regular periodic sublattice. It is, therefore, no surprise that the relatively recent discovery of two new classes of chemically ordered rare-earth (RE) ternary superconducting compounds has had a tremendous impact in this area of research.

In this talk we will review the role of neutron scattering in studying the development of magnetic order in superconductors. First we will briefly discuss impurity systems with cooperative magnetic effects such as $\text{RE}_x\text{Ce}_{1-x}\text{Ru}_2$ ⁵⁻⁸ and then we will turn to the newest results on superconducting rare-earth ternary systems: REMo_6S_8 , $\text{X}=\text{S}, \text{Se}$;^{9,10} RERh_4B_4 .^{11,12} Neutron experiments together with measurements of the thermodynamic and electronic properties, have conclusively shown that long-range antiferromagnetic order coexists with superconductivity and that the development of ferromagnetic order destroys superconductivity. This superconducting $\rightarrow$ ferromagnetic transition found in ErRh_4B_4 has been studied in some detail and it is now clear that the physics of these materials is dominated not by pair-breaking effects due to exchange scattering and conduction-electron polarization but by the macroscopic electromagnetic interactions between the superconducting system and the magnetic system.

II. IMPURITY SYSTEMS: $\text{RE}_x\text{Ce}_{1-x}\text{Ru}_2$

Although the fruitful study of cooperative magnetism in superconductors had to wait for the rare-earth ternary compounds which we will discuss shortly, a class of materials first studied twenty years ago by Matthias et al.⁵ had some of the essential ingredients. These materials were based on the nonmagnetic binary compound CeRu_2 ($T_c = 5 \text{ K}$) into which various concentrations of magnetic rare-earth ions were substituted to form $\text{RE}_x\text{Ce}_{1-x}\text{Ru}_2$ alloys. Remarkably, 35% of the Ce^{4+} ions can be replaced by magnetic Ho^{3+} ions⁶ before superconductivity is suppressed. The extremely small exchange interaction that must exist in this material is a result of two features of the system. First, the rare-earth ions are not on the lattice sites occupied by the superconducting electrons and, second, the Ru d-electron orbitals are directed toward only neighboring Ru atoms. These facts combine to produce the low exchange interaction necessary to tolerate large magnetic concentrations. Under these conditions one expects substantial correlation of magnetic spins to develop and these have been observed in neutron scattering measurements by Roth et al.⁷ in $\text{Tb}_{0.2}\text{Ce}_{0.8}\text{Ru}_2$ and by Lynn et al.⁸ in $\text{Ho}_{0.27}\text{Ce}_{0.73}\text{Ru}_2$. Fig. 1 shows data obtained by the latter workers on the temperature dependent magnetic correlation length, $\xi = \kappa^{-1}$, which is derived from fits of the Ornstein-Zernike cross section $S(\vec{q}) \sim (\vec{q}^2 + \kappa^2)^{-1}$ to small angle scattering data. This system is quite impressive since correlations grow to $80 \text{ \AA}$ before saturating, a factor of five greater in a linear dimension than the correlations observed in $\text{Tb}_{0.2}\text{Ce}_{0.8}\text{Ru}_2$ in the previous studies by Roth et al. Since a volume of $(80 \text{ \AA})^3$

contains approximately 600 Ho^{3+} ions, one might expect full long-range order to develop. It is not yet understood exactly why the correlation length saturates but there are a number of possibilities pointed out by Lynn et al. which invoke suppressing effects due to either superconductivity or spin disorder. This question is an interesting one to address in future work, particularly if superconductivity plays an important role.

III. COEXISTENT ANTIFERROMAGNETS

The development of the new chemically ordered RE ternary compounds gives rise to the possibility of eliminating the complications of spin disorder. Following the discovery of superconductivity in the rare-earth molybdenum chalcogenides,^{9,10} it was clear that a low exchange interaction existed. Systematic studies¹³ of transition temperatures indicate that it is about 0.01 eV. Specific heat studies by McCallum et al.^{14,15} on GdMo_6Se_8 and

ErMo_6Se_8 (superconducting transitions at $T_c = 5.5$ K and 6 K respectively) showed well-defined peaks below T_c with an associated entropy close to that expected for magnetic ordering. Neutron measurements were made subsequently by Lynn et al.¹⁶ on ErMo_6Se_8 and long-range magnetic ordering was found to be responsible for specific heat peaks at 1.1 and 0.9 K. It proved impossible to rule out impurity phases because indexing the magnetic Bragg peaks on the ternary rhombohedral lattice could not be done successfully. Thus, the microscopic coexistence of superconductivity and antiferromagnetism is not yet convincingly established in this material.

The situation has been more definitive in the ternary sulphides. Ishikawa and Fischer¹⁷ found interesting features in the upper critical fields of Dy, Tb, and ErMo_6S_8 , which they concluded were a result of magnetic order for the RE ions. In all three cases, the compounds remain superconducting below the ordering temperatures. DyMo_6S_8 was chosen for the first neutron study.¹⁸ This material becomes superconducting at $T_c = 2.05$ K and the aforementioned anomalies in H_{c2} occur at $T_M = 0.4$ K. Powder neutron diffraction scans taken above and below T_M are shown in Fig. 2. A new series of lines appears below T_M which is characteristic of a simple antiferromagnetic ordering with magnetization wave vector $\vec{q}_M = (0,0,1/2)$. This structure has (100) planes of moments in the nearly cubic (rhombohedral angle $\alpha = 89.4^\circ$) Dy sublattice which are alternately parallel and antiparallel to a unique direction. Intensity analysis reveals this direction of easy magnetization to be the rhombohedral [111]-axis. A moment of $8.77 \mu_B$ is obtained which is somewhat below the free-ion value of $10.6 \mu_B$ probably due to crystal-field splitting. It is also important to note the powder line shape is instrumentally narrow implying that the magnetic correlations extend beyond $300 \text{ \AA}$. In Fig. 3 the temperature dependence of the magnetic moment derived from the $\{0,0,1/2\}$ line is compared with the critical field data from Ref. 17. It is clear that the superconducting properties are affected by the antiferromagnetic ordering transition and coexistence of these two cooperative phenomena prevails below 0.4 K.

Subsequently, Thomlinson et al.¹⁹ investigated TbMo_6S_8 by neutron scattering. This compound shows a similar transition (see Fig. 3) and the low temperature antiferromagnetic structure is identical to DyMo_6S_8 . Initial data have been

obtained under magnetic field on both DyMo_6S_8 and TbMo_6S_8 . Although it is possible to induce some ferromagnetic Bragg scattering below $H_{c2} = 1.2$ kOe in DyMo_6S_8 , there is as yet no way to determine if those regions which are ferromagnetic are also superconducting.

More recently, Majkrzak et al.²⁰ have seen the same antiferromagnetic structure develop in GdMo_6S_8 (See Fig. 3) also in the presence of superconductivity. Now that it has been possible to study this Gd material with its extremely large absorption cross section, we hope to study the selenium analog in order to resolve some of the ambiguities raised by the earlier work on ErMo_6Se_8 .

Although the majority of the work in the RERh_4B_4 materials has concerned the reentrant ferromagnetic superconductor ErRh_4B_4 , to be discussed shortly, Hamaker et al.²¹ recently reported evidence in critical-field measurements for magnetic ordering in both NdRh_4B_4 and SmRh_4B_4 . These studies are being followed up by neutron scattering measurements by Majkrzak et al.²² which have so far confirmed two different antiferromagnetic transitions below T_c in NdRh_4B_4 .

IV. FERROMAGNETIC SUPERCONDUCTORS

We will now discuss the behavior associated with the development of ferromagnetism in superconductors. So far two materials are known (HoMo_6S_8 and ErRh_4B_4) in which superconductivity is destroyed by long-range ferromagnetic ordering at some lower temperature. Since the more detailed neutron scattering has been done on ErRh_4B_4 , we will begin with a review of these results. Following the discovery of superconductivity^{11,12} at $T_{c1} = 8.5$ K, Fertig et al.²³ showed that another transition of apparently magnetic origin occurred at $T_{c2} = 0.9$ K destroying superconductivity. Neutron diffraction by Moncton et al.²⁴ determined conclusively that the structure was ferromagnetic. In Fig. 4, diffraction profiles for four powder lines are displayed above and below T_{c2} . Analysis of the magnetic intensities gives a moment of $5.6 \mu_B$ oriented in the tetragonal basal plane. This value is well below the free-ion value suggesting crystal-field effects but Shenoy et al.²⁵ claim an ordered moment of $8.3 \mu_B$ from Mössbauer measurements. Although the discrepancy is not understood at present it is not a trivial sample difference since neutron measurements were made on the sample used in Ref. 25. Furthermore, the neutron data are in agreement with bulk magnetization data.^{23,26}

Certainly the most interesting aspect of this system is the reentrant phase transition and the question of the interaction between magnetism and superconductivity. Fig. 5 shows the temperature dependence of the magnetic Bragg intensity, together with specific heat data.²⁷ There are a number of important features. First, the electrical resistance becomes normal at the temperature associated with the specific heat spike, $T_{c2} = 0.93$ K. At this temperature, the magnetization is about 70% of

its saturation value (magnetic intensity is about 50%). Clearly, percolation effects are important for the resistive transition.

A second prominent feature of the intensity curve is that some magnetic scattering is visible up to about 1.4 K. Furthermore, this scattering remains sharp, reflecting long-range order. Therefore, we conclude that there is a distribution of effective magnetic transition temperatures. Of course, one could always ascribe this effect to impurities, but it is our belief that it is a result of the presence of superconductivity. It is very difficult to cause a 40% smearing of a magnetic transition by introducing low level impurities. High impurity concentrations are ruled out by the fact that the nuclear Bragg peaks are fit to within experimental error by the stoichiometric structure factor.²⁴

A third aspect of this transition is its unique hysteretic behavior. We believe this hysteresis denotes the temperature region over which the system contains both superconducting and magnetic regions. Although the details of the interaction between these regions is not clear, it is the process of creating magnetic domains out of the superconducting matrix which is hysteretic.

We have already seen a number of unusual features of the development of magnetism in ErRh_4B_4 which are due to superconductivity. However, the most dramatic illustration of the effects of superconductivity occurs in the magnetic fluctuation spectrum. Although the reentrant transition is first order both experimentally and theoretically, Blount and Varma²⁸ have predicted that above the magnetic ordering temperature, the superconducting system suppresses magnetic fluctuations at $\vec{q}=0$. The response is strongest at $\vec{q} = (\gamma\lambda_L)^{1/2}$ where λ_L is the London penetration depth and

γ is the magnetic stiffness. We have observed these fluctuations²⁷

in ErRh_4B_4 as shown in Fig. 6. Small angle neutron scattering reveals a peak at finite wave vector $\vec{Q} \sim 0.06 \text{ \AA}^{-1}$ which grows in intensity to 0.80 K and then decreases abruptly below 0.7 K. Since this particular sample has $T_{c2} \approx 0.7 \text{ K}$ the data should not be compared directly to Fig. 5 for which $T_{c2} = 0.93$.

In ordinary ferromagnetic phase transitions, the magnetic critical scattering is centered around $\vec{q}=0$ and peaks at T_c . The data of Fig. 6 indicate spiral magnetization fluctuations with a wavelength of about $100 \text{ \AA}$, in agreement with the theoretical prediction. We emphasize that this scattering is due to the fluctuations occurring within the superconducting matrix. The wavelength of the fluctuations is determined by both the superconducting and magnetic properties of the system. They exist down to temperatures slightly below T_{c2} because isolated regions of the sample maintain their superconductivity. But when the hysteresis loop closes and superconductivity has vanished, this scattering has also disappeared. One interesting new result concerns the hysteresis in this small angle scattering signal. Since it comes from the region of the sample which is superconducting, it should be stronger on cooling than on heating. This behavior, opposite to that observed for the ferromagnetic ($\vec{q}=0$) part of the scattering in Fig. 5, has just recently been seen²⁷ and provides further evidence for the interpretation that it is due to the coupling between the superconducting and magnetic systems.

Before closing this section, we should mention that a similar reentrant transition occurs in HoMo_6S_8 ($T_c = 1.2 \text{ K}$). Resistivity measurements by

Ishikawa and Fischer²⁹ showed a reentrant transition at 0.64 K associated with magnetic ordering. Lynn et al.³⁰ carried out neutron studies which showed that the system became ferromagnetic at $T_M = 0.67$ K. Small angle scattering experiments have just begun on this material³¹ and preliminary results show hysteresis effects similar to those described above for ErRh_4B_4 .

V. CONCLUSIONS

There is no doubt that the discovery of ternary superconductors has created a resurgence of interest in the interplay between magnetism and superconductivity. Neutron scattering experiments have played an important role by directly observing the antiferromagnetism which exists in many of these new superconductors and studying the effects of superconductivity on ferromagnetic fluctuations in others. It is now clear that no fundamental physical principle prevents a superconductor from being an ordered magnet. If (1) the exchange interaction is small enough, and (2) the magnetic ions exist in sufficient concentration on an ordered sublattice and (3) there is no B-field produced by the magnetic order on a scale of the penetration depth (i.e. antiferromagnets) then coexistence can occur.

Conversely, if condition (3) above is violated, interesting cooperative interaction effects occur. The long-wavelength magnetic fluctuations are suppressed, and the magnetic system is forced into a state of spiral magnetization. Perhaps the single most important obstacle to future understanding of these interactions is the lack of suitable single crystals. The discovery of a new system with the potential for single-crystal growth would be of immense value.

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FIGURE CAPTIONS

FIG. 1. Temperature dependence of the correlation range ξ (and inverse correlation range $\kappa = 1/\xi$). The range of the correlations increases with decreasing temperature, but does not diverge to produce a state with long-range ferromagnetic order. The limiting value of the correlation range is $\sim 80 \text{ \AA}$. After Lynn et al., Ref.8.

FIG. 2. Powder neutron diffraction data for DyMo_6S_8 above ($T = 0.7 \text{ K}$) and below ($T = 0.05 \text{ K}$) the antiferromagnetic ordering transition at $T_M = 0.4 \text{ K}$. After Moncton et al., Ref.18.

FIG. 3. The temperature dependence of the magnetic moment in Dy, Tb, and GdMo_6S_8 , shown together with the critical-field data of Ref.17. After Majkrzak et al., Ref. 20.

FIG. 4. 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., Ref. 24.

FIG. 5. Ferromagnetic Bragg intensities for ErRh_4B_4 , compared with the specific heat data of the identical sample (on heating). After Moncton et al., Ref. 27.

FIG. 6. Small angle neutron scattering results on ErRh_4B_4 obtained at various temperatures. The peak at $2\theta = 1.4^\circ$ indicates an oscillatory magnetization with a wavelength of $100 \text{ \AA}$. After Moncton et al., Ref. 27.

FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

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