Neutron Scattering Observations on the Magnetic Phases of Rare-Earth Ternary Superconductors

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ABSTRACT

A number of ternary compounds become superconducting even though they contain a chemically ordered sublattice of magnetic rare-earth ions. Studies of the physical properties of these materials have revealed anomalies below T_c which have been attributed to magnetic ordering transitions. Using neutron spectrometers at the Brookhaven National Laboratory, a group of us has demonstrated that simple magnetic structures with long-range order do occur, and we have solved some of the magnetic structures of these superconductors. Specifically, we have found that in DyMo_6S_8 and TbMo_6S_8 an antiferromagnetic structure coexists with superconductivity. In two other compounds, ErRh_4B_4 and HoMo_6S_8 we have found that the development of ferromagnetism is responsible for the quenching of superconductivity. A study of the critical magnetic neutron scattering near the superconducting $\rightarrow$ ferromagnetic transitions shows the presence of fluctuations into a state with an oscillatory magnetization of wave length $\lambda = 100\text{\AA}$.

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INTRODUCTION

For twenty years, scientists have tried to force magnetism on superconductivity by the introduction of magnetic impurities into superconducting materials [1]. An enormous amount was learned about the superconducting state and the various mechanisms of pair-breaking, and novel approaches were conceived to raise the critical field [2]. Yet one goal - to study the interaction between superconducting order and magnetic order - was not achieved. The magnetic ions which were introduced into the host lattices simply interacted too strongly with the superconducting electrons.

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Superconductivity was destroyed before enough magnetic ions had been added to allow the development of an ordered magnetic structure.

Within the past few years two new classes of superconducting rare-earth ternary compounds have been discovered: the rare-earth molybdenum chalcogenides $REMo_6X_8$ ($X=S, Se$) [3,4] and the rare-earth rhodium borides $RERh_4B_4$ [5,6]. In both cases the crystal structures afford sufficient separation between the moment-bearing rare-earth ions and the conduction electrons that both superconductivity and magnetic order can exist in the same compound—often simultaneously. This work has led to a resurgent interest in the general problem of the competition between superconducting and magnetic cooperative phenomena. In this talk I will review the situation in a number of these materials with particular emphasis on the role of neutron scattering in helping to achieve the level of understanding that we presently have. Let me emphasize at the outset that neutron scattering is a powerful technique for studying magnetism but, with a few important exceptions, it is not a good technique for studying superconductivity. Therefore, it has been crucial to have resistivity, magnetization, and heat capacity data on the materials in question. In fact, in all the cases to date, neutron scattering experiments were performed only after the studies of the thermodynamic and/or electronic properties showed both superconductivity and potentially interesting magnetic effects.

In view of the large number of erroneous claims which have been made over the years for the coexistence of ordered magnetism and superconductivity, the most important initial role for neutron scattering is certainly to study the magnetic structures of the new materials. As a result of such structural studies, we now know that conventional long-range antiferromagnetic order can coexist with superconductivity [7,8] that the development of ferromagnetism leads to the destruction of superconductivity [9, 10].

More recently our studies have focussed on the effects of superconductivity on the magnetic fluctuations which precede entry into ordered antiferromagnetic states, specifically in $ErRh_4B_4$. As pointed out by Blount and Varma [11], the physics of the superconductor/paramagnet → normal/ferromagnet transition is dominated, not

by the pair-breaking effects of individual magnetic ions, but by the coupled fluctuations of magnetization and magnetic field which increases as the Curie temperature is approached. Their theory predicts, and our data show, evidence for a state intermediate between ferromagnetism and superconductivity in which the magnetization oscillates with a short but finite wave vector and the superconductivity persists.

ANTIFERROMAGNETISM AND COEXISTENT SUPER-CONDUCTIVITY

Shortly after the discovery of superconductivity in the rare-earth molybdenum chalcogenides, specific heat studies [12, 13] of GdMo_6Se_8 ($T_C = 5.5\text{K}$) and ErMo_6Se_8 ($T_C = 6\text{K}$) revealed sharp peaks below T_C with an associated entropy close to that expected for a magnetic ordering transition. Following this work Lynn et al. [14] investigated ErMo_6Se_8 by neutron scattering and were able to show that long-range magnetic ordering was indeed responsible for the two specific heat peaks at 1.1 and 0.9K. It proved impossible, however, to index either of the neutron powder patterns on the rhombohedral lattice of the ternary compound. Since the authors were concerned about the possible role of impurity phases, the coexistence of antiferromagnetism and superconductivity is not yet convincingly established in this material.

The situation has been more definitive in the ternary sulphides. Ishikawa and Fischer found interesting features in the upper critical fields of Dy, Tb, and ErMo_6S_8 [15], which they concluded were a result of antiferromagnetic order for Dy. In all three cases the compounds remain superconducting below the ordering temperatures. DyMo_6S_8 was chosen for the first neutron study [7]. This material becomes superconducting at $T_C = 2.05\text{K}$ and the aforementioned anomalies in H_{C2} occur at $T_M = 0.4\text{K}$. Powder neutron diffraction scans taken above and below T_M are shown in Fig. 1. 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. 2 the temperature dependence of the $\{0,0, 1/2\}$ line is compared with the critical field data from Ref. 15. It is clear that the superconducting properties are affected by the antiferromagnetic ordering transition and coexistence of these two cooperative phenomena prevails below 0.4K .

More recently Thomlinson et al. [8] have investigated TbMo_6S_8 by neutron scattering. This compound shows a similar sequence of transitions ($T_C=2.05$, $T_M=1.0\text{K}$) 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 $H_{C2} = 1.2\text{ KOe}$ in DyMo_6S_8 , there is as yet no way to determine if those regions which are ferromagnetic are also superconducting.

FERROMAGNETISM AND REENTRANT SUPERCONDUCTIVITY

In addition to the coexistence behavior described above the development of magnetic order may completely destroy superconductivity. It was first shown by resistivity measurements on ErRh_4B_4 [16] and HoMo_6S_8 [17] that an upper superconducting transition at T_{C1} was followed by another transition at a lower temperature T_{C2} in which the superconductivity disappeared. Neutron scattering studies have been carried out on both of these materials and they confirm that these reentrant transitions are due to the development of long-range magnetic order. In contrast to the antiferromagnets which exhibit coexistence, both of the reentrant superconductors become simple ferromagnets. In Fig. 3, the diffraction profiles [9] for four powder lines

in ErRh_4B_4 are shown above and below $T_{C2} = 0.9\text{K}$. The magnetic intensities have been analyzed and a moment of $5.6\mu_B$ is found parallel to the tetragonal basal plane. This value is not in agreement with a value of $8.3\mu_B$ obtained by Mössbauer measurements reported by Shenoy et al. [18] and the disagreement is not understood at present. However, a second neutron experiment on the sample used in the Mössbauer study also shown a moment of $5.6\mu_B$, thus ruling out the trivial explanations of differences in samples.

The temperature dependence of the magnetic intensity shown in Fig. 4 has two notable features. First, there is considerable rounding near the transition temperature which is considerably greater than that observed in prototypical ferromagnets. Second, the apparent transitions temperature, $T_M = 1.05\text{K}$, is higher than that associated with the lower superconducting transitions $T_{C2} = 0.9\text{K}$ [16]. These features have prompted a new neutron study [19] of the critical magnetic associated with the onset of ferromagnet order. In the following Section preliminary findings from this work will be described.

The case of HoMo_6S_8 is similar to ErRh_4B_4 . Diffraction data [10] for this material show a simple ferromagnetic structure with moments along the rhombohedral [111]-axis as in the other isostructural antiferromagnet. The moment of the Ho^{3+} ion was determined to be $9.06\mu_B$ as compared to $10\mu_B$ for the free-ion. The temperature dependence of the magnetic intensity gives a magnetic transition temperature $T_M = 0.67\text{K}$. As in ErRh_4B_4 this temperature is above that for reentrant superconductivity, $T_{C2} = 0.64\text{K}$ [17], but only marginally so.

FLUCTUATION EFFECTS

Small angle neutron scattering has been used [19] to study the fluctuation effects in the vicinity of the superconducting $\rightarrow$ ferromagnetic transition in ErRh_4B_4 . Fig. 5 shows data taken at temperature between 0.6K and 1.0K over scattering angles $0.6^\circ < 2\theta < 3.0^\circ$ with incident neutron wave vector $K_i = 2.55\text{\AA}^{-1}$. These data show clearly the presence of a peak at $2\theta = 1.4^\circ$ which implies the existence of magnetization fluctuations with a finite wave vector.

It should be noted that the raw data used to produce Fig. 5 has been subtracted from all the lower temperature scans to remove the wings of the main beam. After this subtraction, the data taken at the lowest temperature, less than 0.4K, still exhibit a large component which appears to be centered around $2\theta = 0$. Such scattering was observed previously in similar small angle scattering experiments on both ferromagnets [20] and ferroelectrics [21], and has been attributed to domain walls. Assuming its contribution to the intensity at higher temperatures to be proportional to the square of the spontaneous magnetization, a second correction to the data has been made. However, the peak at $2\theta = 1.4^\circ$ cannot be an artifact of this procedure, since it is apparent in the raw data. Furthermore, theoretical analysis by Blount and Varma [11] based on a Ginzburg-Landau theory of ferromagnetic superconductors predicts the possible existence of a superconducting state coexisting with a long wavelength magnetization. Although ferromagnetism would prevail in this model if superconductivity were not present, its existence leads to a "compromise state" in which the magnetization oscillates on a length shorter than the London penetration length but longer than the magnetic stiffness length. This state of oscillatory magnetization occurs in a second-order phase transition with divergent critical scattering, but a first-order transition to ferromagnetism with concomitant destruction of superconductivity may intervene at any temperature depending on model parameters.

One important unresolved difficulty with this interpretation concerns the presence of the 1.4° peak down to 0.7K. This temperature is nominally below the reentrant transition at $T_{C2} = 0.9K$, where superconductivity is no longer present. One must argue that remnant superconducting domains exist below T_{C2} or that sample differences prohibit such a detailed comparison of results from different laboratories. Whatever the final resolution of these problems, it is clear that the effects of superconductivity on the magnetic ordering of $ErRh_4B_4$ are considerably more interesting and complicated than originally suspected.

CONCLUSIONS

It is now clear that metallic materials occur in nature in which an ordered array of magnetic moments exist whose exchange interaction with conduction electrons is sufficiently small that superconductivity is not destroyed by pair-breaking effects. In such systems magnetic ordering can coexist with superconductivity provided no $\vec{B}$ -field is produced which is uniform on the scale on the penetration depth. Materials such as Dy, Tb and ErMo_6S_8 which order antiferromagnetically, presumably as a result of a positive exchange constant, satisfy this criterion easily. On the other hand, ferromagnets ultimately destroy superconductivity. However, a remarkable effect seems to occur in ErRh_4B_4 in which fluctuations into a state of oscillatory magnetization are forced by the superconductivity in an attempt to prevent $\vec{B}$ -field penetration. We are therefore at the stage in this area of research where it is possible for the first time to study the influence of superconductivity on magnetic ordering.

FIGURE CAPTIONS

- Fig. 1 Powder neutron diffraction data for DyMo_6S_8 above ($T = 0.7\text{K}$) and below ($T = 0.05\text{K}$) the antiferromagnetic ordering transitions at $T_M = 0.4\text{K}$.
- Fig. 2 The temperature dependence of the $(0, 0, 1/2)$ antiferromagnetic peak shown together with the critical field data of Ref. 9.
- Fig. 3 Four powder peaks are shown at temperature above ($T = 1.4\text{K}$, open circles) and below ($T = 0.07\text{K}$, filled circles) the magnetic transition at $T_{C2} = 1.0\text{K}$.
- Fig. 4 The temperatures dependence of the magnetic contribution to the (101) peak intensity.
- Fig. 5 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 $100 \text{ \AA}$.

REFERENCES

- a) Research at Brookhaven supported by the Division of Basic-Energy Sciences, Department of Energy, under Contract No. EY-76-C-02-0016.
1. For a review, see S. Roth, Applied Physics 15, 1 (1978).
2. V. Jaccarino and M. Peter, Phys. Rev. Lett. 9, 290 (1962).
3. Ø. Fischer, A. Treyvaud, R. Chevrel, and M. Sergent, Solid State Commun. 17 (1975) 21.
4. R. N. Shelton, R. W. McCallum, and H. Adrian, Phys. Lett. 56A (1976) 213.
5. B. T. Matthias, E. Corenzwit, J. M. Vandenberg, and H. E. Barz, Proc. Nat. Acad. Sci. USA (1977) 1334.
6. J. M. Vandenberg and B. T. Matthias, Proc. Nat. Acad. Sci. USA 74 (1977) 1336.
7. D. E. Moncton, G. Shirane, W. Thomlinson, M. Ishikawa, Ø. Fischer, Phys. Rev. Lett. 41, 1133 (1977) and Erratum, Phys. Rev. Lett. 41, 1428 (1977).
8. W. Thomlinson, G. Shirane, D. E. Moncton, M. Ishikawa, and Ø. Fischer, Proceedings of this Conference, paper 1C-5.
9. D. E. Moncton, D. B. McWhan, J. Eckert, G. Shirane, and W. Thomlinson, Phys. Rev. Lett. 39 (1977) 1164.
10. J. W. Lynn, D. E. Moncton, W. Thomlinson, G. Shirane, and R. N. Shelton, Solid State Commun. 26 (1978) 493.
11. E. I. Blount and C. M. Varma, to be published.
12. R. W. McCallum, D. C. Johnston, R. N. Shelton, and M. B. Maple, Proc. 2nd Rochester Conf. Superconductivity in d- and f-Band Metals, ed. by D. H. Douglass (Plenum Press, New York) 1976, p. 625.

13. R. W. McCallum, D. C. Johnston, R. N. Shelton, W. A. Fertig, and M. B. Maple, Solid State Commun. 24 (1977) 501.
14. J. W. Lynn, D. E. Moncton, G. Shirane, W. Thomlinson, J. Eckert, and R. N. Shelton, J. Appl. Phys. 49 (1978) 1389.
15. M. Ishikawa and Ø. Fischer, Solid State Commun. 24 (1977) 747.
16. W. A. Fertig, D. C. Johnston, L. E. DeLong, R. W. McCallum, M. B. Maple, and B. T. Matthias, Phys. Rev. Lett. 38 (1977) 987.
17. M. Ishikawa and Ø. Fischer, Solid State Commun. 23 (1977) 37.
18. G. K. Shenoy, B. D. Dunlap, F. Y. Fradin, G. W. Kimbrell, W. Potzel, F. Probst, G. M. Kalvius, Proceedings of this Conference, paper 5A-1.
19. D. E. Moncton, D. B. McWhan, G. Shirane, and W. Thomlinson, to be published.
20. O. W. Dietrich, J. Als-Nielsen, and L. Passell, Phys. Rev. B 14, 4908 (1976).
21. R. A. Cowley, J. D. Axe, and M. Iizumi, Physical Review Letters 36, 806 (1976).

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