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MAGNETIC ORDERING IN SUPERCONDUCTORS

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ABSTRACT

Several ternary rare-earth compounds display long-range magnetic order in the superconducting state. When this order is antiferromagnetic, coexistence with superconductivity occurs over a wide temperature interval. Although simple ferromagnetic order destroys superconductivity, the competition between the magnetic and superconducting states produces a magnetic modulation of several hundred Ångstroms wavelength which coexists with superconductivity. The modulated state, which has been studied by neutron scattering techniques in $ErRh_4B_4$ and $HoMo_6S_8$, exists over a narrow temperature range and is replaced by a ferromagnetic, normal conducting state at low temperature. Recent small-angle, neutron-scattering experiments with $HoMo_6S_8$ have established that the magnetic order in the modulated state is of long range. Although these experiments have proven that the modulated phase is not a vortex lattice no definitive microscopic description of the phase has yet been confirmed in either $HoMo_6S_8$ or $ErRh_4B_4$. In this review, recent neutron scattering investigations which have attempted to elucidate the nature of the modulated phase will be described.

The first experimental investigations of the interplay of magnetism and superconductivity were performed in the years following the successful formulation of the BCS theory of superconductivity. These experiments showed that the substitution of less than ~ 1 % of magnetic impurities generally destroys superconductivity [1].Exchange coupling between the conduction electron and the unpaired electrons of the magnetic impurities is not invariant under time-reversal and so tends to break Cooper pairs and destroy superconductivity [2]. Evidently the concentration of magnetic impurities which can be tolerated without destroying superconductivity depends upon the strength of this pair-breaking interaction. The first indication that the exchange interaction between conduction electrons and impurity moments could be substantially reduced was the observation that up to 30 % of rare earth atoms could be substituted in $CeRu_2$ before superconductivity disappeared [3]. In this case, neutron scattering experiments [4,5,6] showed that a sufficient concentration of magnetic defects was present for ferromagnetic correlations to develop at low temperatures. Long range magnetic order is not realised however.

All experimental investigations of the coexistence of magnetism and superconductivity have been performed with systems in which the superconducting electrons are contributed by one chemical species (generally a transition metal) while the magnetic moment is contributed by another (generally a rare earth). In $Ce_{1-x}R_xRu_2$ (R = rare earth) the rare earth atoms are structurally isolated from the transition metal atoms and the exchange coupling of the superconducting and magnetic electrons is thereby reduced. This permits large concentrations of magnetic impurities to be added without destroying superconductivity. At low enough temperatures the mutual interaction of the impurities causes magnetic correlations to develop. In the $Ce_{1-x}R_xRu_2$ system the rare earth impurities are randomly distributed so that the competing exchange interactions result in a frozen spin arrangement at low temperatures.

In the limit of very weak exchange interaction between superconducting and magnetic electrons the predominant coupling between superconducting and magnetic order parameters is of electromagnetic origin. The superconducting electrons are influenced by the induction field $\underline{B}$ generated by the spatial distribution of magnetic moments. Just as with the Meissner effect, persistent currents are generated which tend to screen this electromagnetic interaction and suppress a macroscopic induction field. Examples of systems in which this electromagnetic coupling is predominant have recently been found among the Chevrel phase [7], rare-earth molybdenum chalcogenides (RMo_6S_8, RMo_6Se_8) and the rare earth rhodium borides ($R Rh_4B_4$). In contrast to $Ce_{1-x}R_x$,Ru_2 these ternary superconductors are stoichiometric compounds in which the rare earth atoms are arranged on a regular lattice of sites. For this reason magnetic order in these materials tends to be of the canonical antiferromagnetic or ferromagnetic type rather than a frozen spin arrangement.

In this paper we describe the results of a number of neutron scattering experiments which have helped to elucidate the magnetic properties of these ternary materials. Besides the original papers describing this work, several review have already appeared [8,9]. In this paper we attempt to highlight some of the current inadequacies in our understanding of these novel systems.

The majority of the ternary materials of interest here have been found to order in a compensated antiferromagnetic arrangement. This has been confirmed experimentally by neutron powder diffraction measurements such as that performed by Moncton et al. [10] on $DyMo_6S_8$, the first such superconducting antiferromagnet to be identified unambiguously. Since no dipolar field is associated with the development of antiferromagnetic order the latter has very little effect on the superconducting properties. Of greater interest are the cases where the exchange interaction between unpaired electron spins favours ferromagnetic alignment . Parallel spin alignment is, of course, energetically unfavourable for superconductivity because a macroscopic dipolar field is created. Such a field can be tolerated by a superconductor only over distances of the order of the London penetration depth λ. The net result of the competing tendencies of ferromagnetism and superconductivity is that spin fluctuations develop over distances great compared to the magnetic stiffness length γ but short compared to λ. More explicitly, persistent supercurrents are generated which screen the long-wavelength magnetic fluctuations so that the magnetic susceptibility attains a maximum value at a wave-vector q_m which is of order $(\lambda\gamma)^{-1/2}$. Although the various calculations [11, 12 , 13] which have been performed agree on the existence of such a peak in the susceptibility there is disagreement over the microscopic nature of the magnetic modulation and on its expected range. In the early calculations [11,12] fluctuations towards a spiral spin arrangement were predicted. Other authors have suggested linearly polarised modulations [14] and states involving the spontaneous generation of a vortex lattice [15, 16] . A comparison of the free energies of these three possibilities was made by Greenside et al. [14] who found that each state could be stabilized by a suitable choice of parameters. In a series of independent calculations Tachiki [17] and co-workers have analysed a number of microscopic models including those considered in [14]. One of the most promising candidates proposed by Tachiki is the self-induced laminar structure [17] which involves a planar singularity of the phase of the superconducting wavefunction rather than the linear singularities of the vortex lattice. Phases in which magnetic modulations of wavevector q_m coexist with superconductivity have been found in both $ErRh_4B_4$ [18, 19,20,21] and $HoMo_6S_8$ [22,23] . In neither case however, has the microscopic nature of this phase been unambiguously determined. Indeed there is evidence that the state may not be the same in both materials. In this paper we concentrate mainly on results obtained from neutron scattering experiments on $HoMo_6S_8$.

Magnetic susceptibility and conductivity measurements by Ishikawa and Fischer [22] demonstrated that $HoMo_6S_8$ becomes superconducting at a temperature T_{C1} = 1.2K and reenters the normal state at T_{C2} = 0.64K. The latter transition is accompanied by the onset of magnetic order which subsequent neutron diffraction measurements showed to be ferromagnetic [24]. These experiments yielded a value of 9.06 $\pm$ 0.3 μ_B for the saturated magnetic moment at low temperatures and proved that the aligned spins were along the [111] trigonal axis of the rhombohedral, Chevrel-phase structure [7]. More detailed, small-angle neutron scattering experiments [23] subsequently revealed a peak in the magnetic scattering at a wavevector $q \simeq 0.03$ $\mathring{A}^{-1}$. This peak, which is a manifestation of the magnetic modulation described above, occurs in the superconducting phase. Following these early experiments the properties of the modulated phase of $HoMo_6S_8$ have been elucidated by a series of neutron scattering experiments [25, 26] carried out on the small-angle spectrometer D11 at the High Flux Reactor of the Institut Laue-Langevin. The experiments have been performed on a well-characterized powder sample of $HoMo_6S_8$ with an upper superconducting transition of T_{C1} = 1.82K and a (first order) reentrant transition (T_{C2}) at about 0.64K. Spectrometer geometry and the precautions necessary to perform small-angle scattering experiments at low temperatures have been described elsewhere [25].

Above 0.740K the magnetic scattering from $HoMo_6S_8$ tends to peak at zero (or very small) wavevectors and increases in magnitude with decreasing temperature. Such scattering would normally indicate the proximity of a transition to ferromagnetic order. As figure 1 shows, however this transition is preempted by the appearance of a modulated magnetic state at T_M = 0.732K.

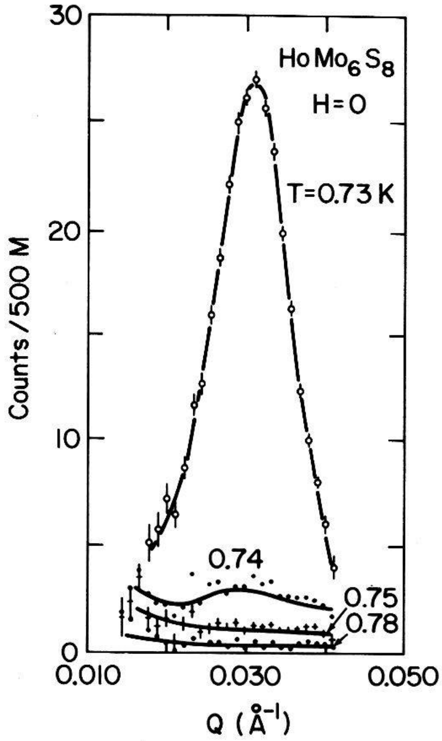

Fig. 1

Temperature (T) and wavevector (Q) dependence of scattering observed on cooling through the transition to the modulated magnetic phase.

There is some evidence for weak critical scattering which peaks at the modulation wavevector q_m = 0.030 $\mathring{A}^{-1}$ in a very small temperature interval ($\lesssim$ 0.01K) above the transition. This scattering has a width which is larger than the instrumental resolution. Below T_M, however, the width of the observed peak is resolution-limited, indicating a coherence length for the magnetic modulation of at least 3100 Å, or about 15 periods. The growth of the (squared) amplitude of the magnetic modulation is shown in figure 2. An important point here is that the modulation appears to reach its maximum amplitude (on cooling) before there is any indication of scattering at small wavevectors associated with ferromagnetic ordering. With the onset of ferromagnetic order at T $\sim$ 0.71K (cf. fig. 2) the amplitude of the $\vec{q}_m$ modulation decreases rapidly and the system eventually reverts to the normal state at $T_{C2}^{(c)}$ = 0.62K. This sequence of events, summarised in figure 2, appears to differ qualitatively from that which pertains in $ErRh_4B_4$ [21]. In this material both ferromagnetic order and magnetic modulation appear at 1.2K (on cooling)and both magnetic order parameters increase until the sudden disappearance of the magnetic modulation at 0.71K. Superconductivity is also destroyed

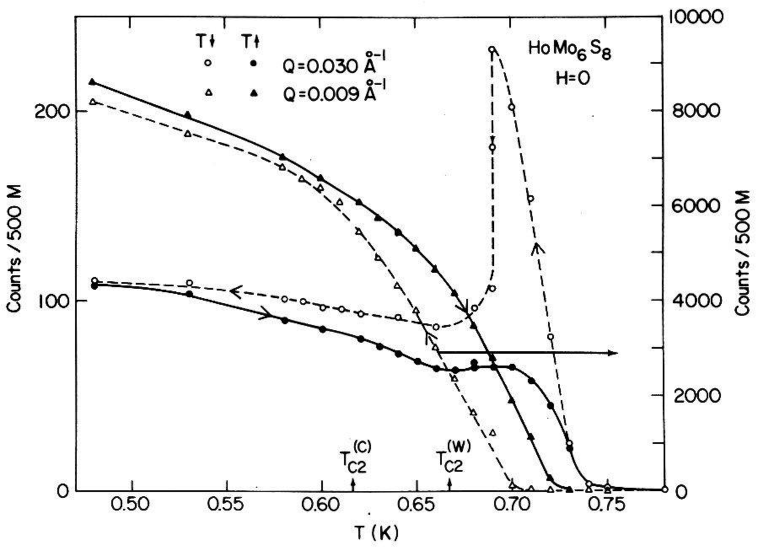

Fig. 2

Temperature dependence of scattering at small wavevector ($Q = 0.009$ Å^{-1}) and at the wavevector of the magnetic modulation ($Q = 0.030$ Å^{-1}).

at the latter transition. Throughout the mixed phase the magnetic response of $ErRh_4B_4$ is dominated by the ferromagnetic component.

In $HoMo_6S_8$ the temperature interval between the first appearance of ferromagnetic order ($\sim$ 0.71K) and the reentrant superconducting transition is characterized by extremely long ($\gtrsim$ 1 hour) equilibration times and by temperature hysteresis of all three order parameters of the system - ferromagnetic, magnetic modulation and superconductivity. The hysteresis is sufficiently marked to suppress almost completely the reappearance of the magnetic modulation on warming (cf. Fig. 2). Since the magnetic modulation occurs in superconducting regions of the sample, the amplitude of the modulation is expected to be smaller on warming than it is on cooling. As figure 2 demonstrates, this behaviour is observed.

The behaviour of the magnetic modulation in $HoMo_6S_8$ in an applied magnetic field is unusual and, as yet, not fully explained. At 0.735K the critical scattering is suppressed by the application of a modest field of $\sim$ 50 Oe. This decrease of intensity is independent of the relative orientation of the scattering vector $\vec{q}$ and the applied magnetic field $\vec{H}$. In contrast, the amplitude of the long-range modulation below T_m is initially *increased* by the application of a magnetic field as shown in figure 3.

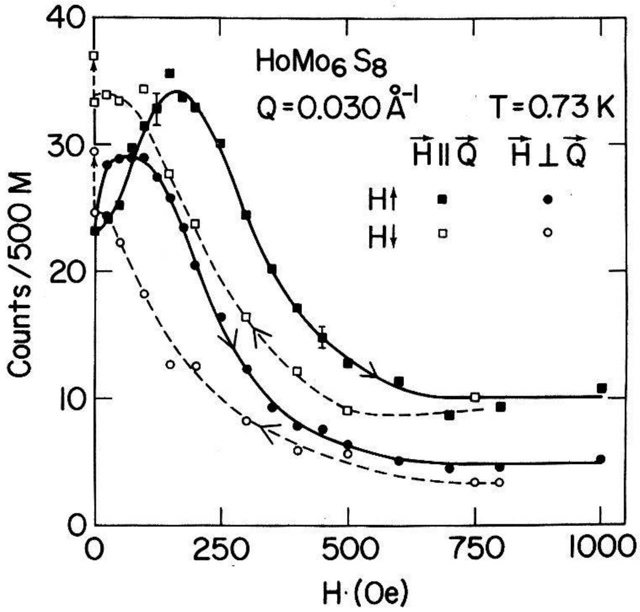

Fig. 3

Magnetic field dependence of the intensity of the peak corresponding to the long-range modulation.

Furthermore the amplitude depends on the relative orientation of $\vec{q}$ and $\vec{H}$. When the applied field is reduced, hysteresis is observed but the modulated phase is reestablished. In fact, after cycling the field, the amplitude of the modulation is *larger* than in the virgin state. This behaviour is consistent with the initial field-increasing data (cf. Fig. 3) and the assumption of a residual field in the system which persists after the removal of the external field. The data displayed in figure 3 were obtained by cooling in zero field and then isothermally increasing H. Cooling in finite field gives qualitatively similar results but does not yield the same intensity distribution at any field and temperature. Isometric plots of intensity measured during field cooling are shown in figure 4. The anisotropy observed is similar to that obtained when the field is applied after cooling in zero field.

In a neutron scattering experiment only those components of magnetization which are perpendicular to the scattering vector $\vec{q}$ are effective in scattering. Thus, provided the magnetic modulation involves a spin component perpendicular to the modulation wavevector $\vec{q}_m$ a neutron spectrometer will observe a peak at this wavevector. With a powder sample and in the absence of an applied magnetic field the azimuthal angle of $\vec{q}_m$ around the incident beam may take any value. The satellite peak corresponding to

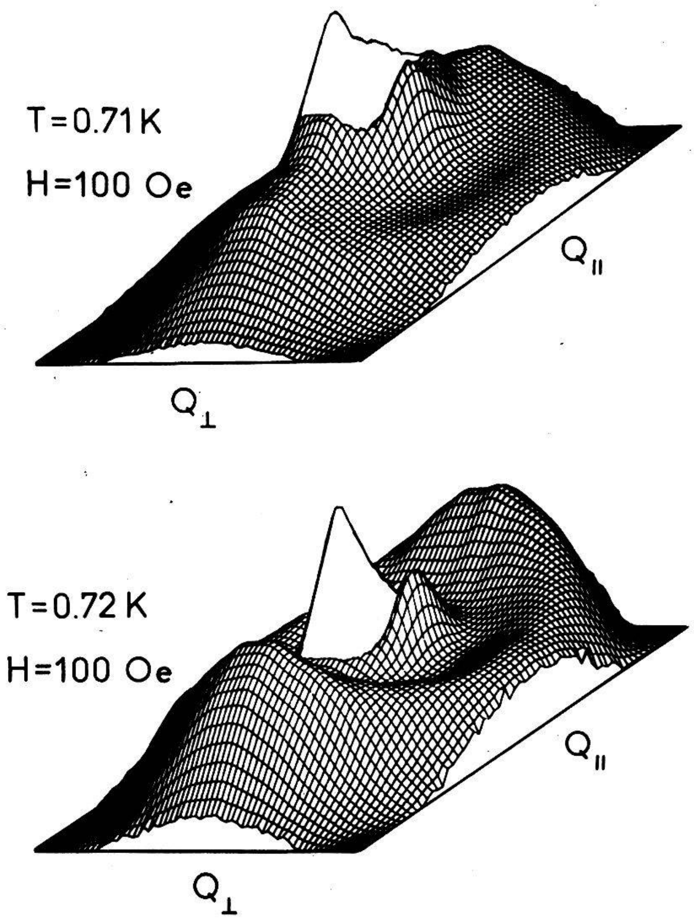

Fig. 4

Isometric plots of scattered neutron intensity in an applied field of H = 100 Oe. $Q_{//}$ is the wavevector component parallel to the applied field. These data were obtained by cooling the sample from 2K in an applied field of 100 Oe. The unshaded region at the centre of each pattern corresponds to the position of the beam stop for the incident neutron beam.

the magnetic modulation then appears as a ring of intensity on a position-sensitive detector placed after the sample. This ring has uniform intensity in zero field but when a magnetic field is applied perpendicular to the incident neutron beam the intensity varies with the angle between $\vec{q}$ and $\vec{H}$ as shown in figure 4. If the applied magnetic field were simply to cause the Holmium moments to align themselves parallel to the field, the selection rule described above for magnetic neutron scattering would imply that the greatest intensity should be observed for $\vec{q}$ perpendicular to $\vec{H}$. The observations do not conform with this description, however. As figure 4 demonstrates, the intensity of the ring corresponding to the magnetic modulation is *minimum* for $\vec{q}$ perpendicular to $\vec{H}$ and maximum for $\vec{q}$ along $\vec{H}$. Similar behaviour is observed at low q for the ferromagnetic component.

We believe that the observed anisotropy of the scattering in a magnetic field, taken together with our failure to observe peaks in the scattering at $2q_m$, effectively mitigate against a modulated phase comprising a vortex lattice. However it is not difficult to imagine that such data could be explained either by the spiral state of Blount and Varma [11] or by the self-induced laminar structure of Tachiki [17]. We tend to prefer the latter model because it can provide a more natural explanation of the long equilibration times and of the hysteresis behaviour. However, none of the models, as currently formulated, seems capable of explaining all aspects of the observed temperature and magnetic field dependence of the neutron scattering. Nor do the marked differences between the properties of $HoMo_6S_8$ and $ErRh_4B_4$ find any natural expression in existing theories.

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