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DIRECT OBSERVATION OF LONG RANGE FERROMAGNETIC ORDER IN THE REENTRANT SUPERCONDUCTOR $HoMo_6S_8$

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The neutron scattering technique has been used to investigate the magnetic properties of the ternary Chevrel-phase superconductor $HoMo_6S_8$. Magnetic critical scattering is observed in the superconducting phase, with the magnetic correlation range increasing with decreasing temperature. At the transition in which the normal state is reentered, the system is found to develop long range ferromagnetic order, with a saturated magnetic moment at low temperatures of 9.06 ± .3 μ_B and the spin direction along the unique [111] trigonal axis.

Since their discovery the ternary Chevrel-phase materials have been found to exhibit a variety of interesting phenomena related to their superconducting and magnetic properties.[1] Although their superconducting transition temperatures are not particularly high, they have high upper critical fields.[2] Moreover, the materials which contain rare-earth elements also display a strong tendency to order magnetically. This latter behavior allows a study of the competitive interplay between these two cooperative phenomena. Neutron scattering is an ideal probe of the magnetic properties of these systems, and the first such study on Chevrel-phase materials was performed on $ErMo_6Se_8$.[3] As anticipated on the basis of specific heat studies,[4] strong magnetic Bragg scattering was found to develop at temperatures near 1 K, well below the superconducting transition at $T_c \sim 5.5$ K. However, the complicated diffraction patterns could not be readily interpreted and the authors were unable to rule out the possibility that only impurity phases were magnetic.

More recently, $HoMo_6S_8$ has been reported[5] to undergo a superconducting transition at 1.2 K and then to reenter the normal state at 0.64 K, with this latter transition being associated with magnetic ordering. This behavior is remarkably similar to that recently reported in the ternary superconductor $ErRh_4B_4$.[6] In this case neutron scattering experiments[7] have clearly demonstrated that the system becomes ferromagnetic as superconductivity is destroyed. It was therefore of considerable importance to undertake a neutron examination of $HoMo_6S_8$ to obtain direct information on possible magnetic ordering. Our neutron scattering results demonstrate that the reentrant transition is accompanied by a transition to long range ferromagnetic order.

Powder neutron diffraction measurements were taken on a triple-axis neutron spectrometer at the Brookhaven High Flux Beam Reactor. The incident wavelength was chosen to be 2.464 Å, with a pyrolytic graphite filter placed in the incident beam to suppress higher-order wavelength contaminations. For the measurements taken at low temperatures the sample was mounted in a helium dilution refrigerator which has a low temperature capability of ∿ 50 mK.

Diffraction measurements above the magnetic transition confirmed that $HoMo_6S_8$ has the rhombohedral (R3) crystal structure with one formula unit per unit cell. The Ho ions occupy a simple primitive lattice which is nearly simple cubic since the rhombohedral angle is close to 90° in these materials. A least-squares refinement of the positions of eight peaks yielded rhombohedral lattice parameters of a = 6.427 ± .003 Å, α = 89.31 ± .04 at 1.0 K.

The positions of the Mo and S in the unit cell have been recently determined[8] at room temperature by X-ray scattering measurements. Our measurements of the intensities at low temperatures agreed relatively well with the intensities calculated assuming the Mo and S positions were identical to those at room temperature, confirming that these positions are not strongly temperature dependent. In particular, the calculated structure factor for the {200} reflection was very small, and no {200} peak was observed in the data. This result provides a sensitive test of the validity of the crystal structure. We note that there was evidence of small amounts of secondary phases in the sample. Because they

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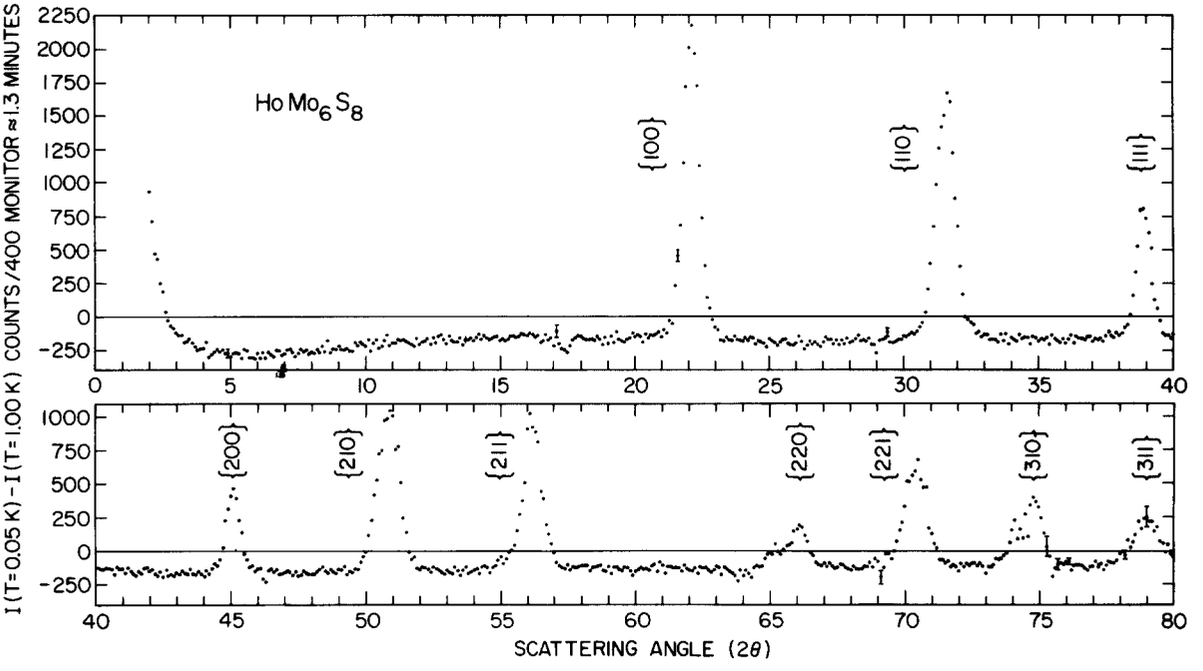

Fig. 1 Magnetic diffraction pattern for $HoMo_6S_8$. Data taken at 1.00 K (Above T_M) have been subtracted from the data taken at 0.05 K. The new Bragg peaks which develop below T_M coincide with the positions of the $HoMo_6S_8$ nuclear peaks, establishing that the transition is to a state of long range ferromagnetic order.

were observed to have no magnetic component, however, their presence is irrelevant as far as our neutron measurements are concerned.

Complete diffraction patterns were taken from scattering angles of 2° to 80° at 1.30 K and 0.05 K. The difference between these two patterns is shown in Fig. 1 and reflects the changes associated with the phase transformation. The data clearly reveal that a new set of Bragg peaks have developed below the phase transition. The positions of these peaks coincide with positions of the $HoMo_6S_8$ nuclear peaks demonstrating conclusively that the material has become ferromagnetic. Further, the observed widths of the peaks in all cases agree with the calculated widths due solely to instrumental resolution, so that the magnetic order is of long range. To be more precise, the limitation on the instrumental resolution places a lower limit on the magnetic correlation range $\xi = \kappa^{-1}$ which we can estimate by the following procedure. We assume that the observed width has contributions both from the instrumental resolution and an intrinsic width. Since the observed width appears to be only instrumental in origin, the intrinsic width κ can certainly be no larger than one-half this value. High resolution measurements place such a limit on κ of 0.003 $Å^{-1}$, which yields a lower limit on the correlation range in real space of $\kappa^{-1} > 300$ Å.

For a simple ferromagnetic structure the neutron cross section for magnetic scattering can be written as[9]

$$\frac{d\sigma}{d\Omega} = \left(\frac{\gamma e^2}{2mc^2}\right)^2 \mu^2 \vec{f}^2(\vec{K}) \left[1-(\hat{K}\cdot\hat{\eta})^2\right] \delta(\vec{K}-\vec{\tau}) \qquad (1)$$

where

$$\left(\frac{\gamma e^2}{2mc^2}\right) = -0.2695 \cdot 10^{-12} \text{ cm} \quad , \qquad (2)$$

μ is the magnetic moment, $\vec{K}$ is the neutron momentum transferred to the crystal, $\hat{\eta}$ is the spin direction, $\vec{\tau}$ is a reciprocal lattice vector and $\vec{f}(\vec{K})$ is the magnetic form factor. For a powder the observed intensity of each peak is a sum of intensities from all reciprocal lattice vectors of the same length. In general information is lost in this powder average, and thus the spin direction $\hat{\eta}$ may not be uniquely determined. However, for a crystal structure in which there is a unique axis, powder data is sufficient to ascertain the angle between the spin direction and this axis, which for $HoMo_6S_8$ is the [111] trigonal axis. Fig. 2 shows a scan of the (111) and ($\bar{1}\bar{1}\bar{1}$) reflections above and below T_M. We see that there is no magnetic contribution to the (111) reflection, and therefore we have from Equ. (1) that $\hat{K} \cdot \hat{\eta} = 1$. Thus the *spin direction is along the trigonal axis.*

The magnetic intensities can be put on an absolute basis by comparison with the nuclear intensities. The ratio of these intensities can be written as

$$\frac{I_{mag}}{I_{nuc}} = \left(\frac{\gamma e^2}{2mc^2}\right)^2 \frac{\mu^2 |f(\vec{\tau})|^2 \langle 1-(\hat{\tau}\cdot\hat{n})^2 \rangle}{|F_N|^2} \qquad (3)$$

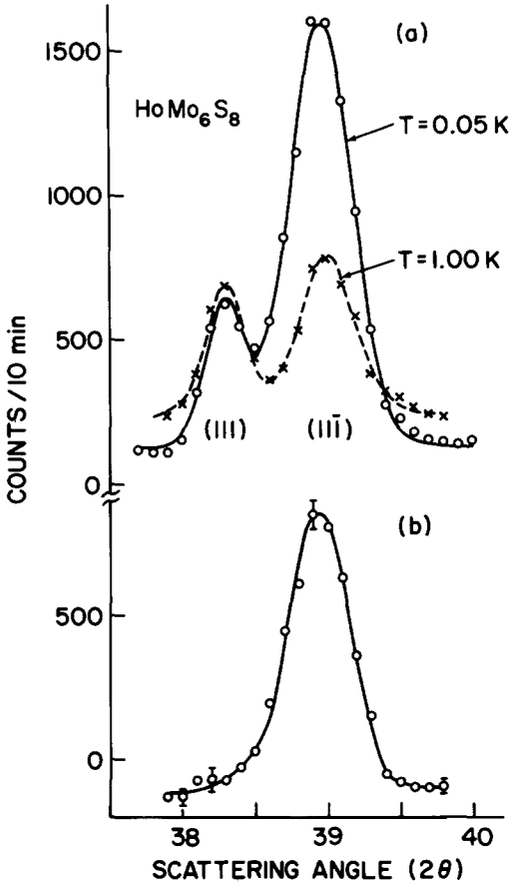

Fig. 2 a) High resolution scans of the (111) and (11$\bar{1}$) reflections above and below the transition. The difference between these two (b) scans shows that the magnetic contribution occurs only for the (11$\bar{1}$) reflection, so that the easy magnetic axis is the trigonal (111) direction.

With the spin direction $\hat{\eta}$ known, the powder average can be calculated for each observed Bragg peak. Having calculated the nuclear structure factors F_N as described above, only the magnetic moment μ and the form factor $f(\tau)$ remain as unknowns. For the {100} reflection we find a value for μf of (8.85 ± .3) μ_B. The quoted error represents one standard deviation due to the statistical error and does not include estimates of possible systematic errors such as might be introduced through uncertainties in the nuclear structure factors F_N. At small momentum transfers the aspherical contributions to the magnetic form factor are very small, so to a good approximation $f\{100\}$ is given by the spherically averaged value[10] of 0.977. The resultant magnetic moment is then μ = 9.06 μ_B. This value is close to the free ion value of 10 μ_B for Ho^{3+}.

The intensity of the {100} Bragg peak is shown in Fig. 3 as a function of temperature. The intensity above T_M is due to nuclear scattering, which is temperature independent, while the additional intensity observed below T_M

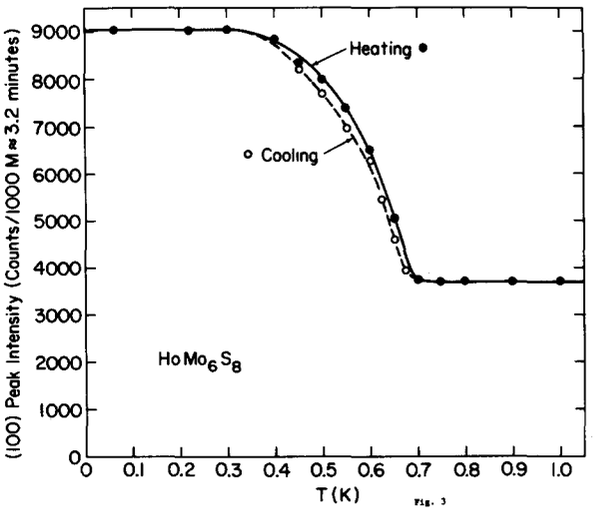

Fig. 3 Peak intensity of the {100} peak as a function of temperature. The intensity above T_M is due to the nuclear scattering, which is temperature independent. The additional intensity below $T_M \sim 0.67$ K is magnetic in origin and is proportional to the square of the order parameter.

is proportional to the square of the order parameter. The ferromagnetic transition temperature is $T_M \sim 0.67$ K, which agrees well with the results of Ishikawa and Fischer[5] for the reentrant transition. Thus the transition to ferromagnetism destroys the superconductivity, which is also the case[6,7] for $ErRh_4B_4$. We note that there is a small but significant hysteresis (∼ 15 mK) ob-

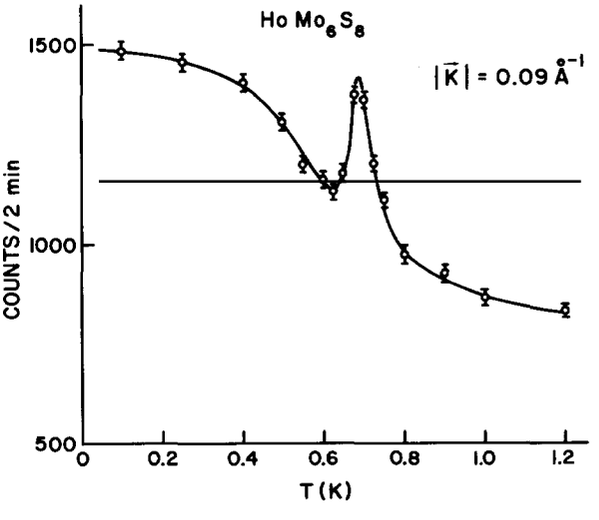

Fig. 4 Temperature dependence of the diffuse scattering at a wavevector of 0.09 Å^{-1}. There is a "critical" component which peaks in intensity near the transition temperature, and additional scattering which builds up at low temperatures.

served, suggesting the magnetic transition is first order.

In addition to the magnetic Bragg peaks, the data in Fig. 1 show that there is a substantial change in the intensity of the "background" scattering. This decrease is due to the absence of paramagnetic scattering in the ordered phase. The temperature dependence of the scattering for a momentum transfer $|\vec{K}|$ of 0.09 Å^{-1} is shown in Fig. 4. We note that there is the usual increase in the intensity of the scattering in the vicinity of the transition temperature as would be expected from critical fluctuations at a weakly first-order transition. We also note a large increase in the scattering at low temperatures, whose origin is clearly not due to critical fluctuations. This scattering is also evident in Fig. 1 at small scattering angles. The origin of this scattering is most likely due to domain wall scattering, which has been seen in ferromagnets such as EuO and EuS,[11] and ferroelectrics such as lead germanate.[12]

Since the magnetic ordering temperature is very low, the energy of the magnetic fluctuations in the system is expected to be small in comparison with our instrumental resolution. Thus at a fixed momentum transfer $|\vec{K}|$ we effectively integrate over all energies of the magnetic excitation spectrum. Above the phase transition we may expect as a first approximation that the wavevector-dependent correlation function will be of the Ornstein-Zernike type:

$$\frac{d\sigma}{d\Omega} \alpha \frac{1}{|\vec{K}|^2 + \kappa^2} \quad . \tag{4}$$

This cross section has been convoluted with the instrumental resolution function and compared with the wavevector dependent intensity data in a least-squares fit, allowing at each temperature the inverse correlation range κ to vary. For $T \geq 0.69$ K a good fit to the data was obtained, with the correlation range κ^{-1} steadily increasing with decreasing temperature. At $T = 0.69$ K we found $\kappa^{-1} = 19$ Å. Thus we may conclude that the magnetic correlations develop while the material is still in the superconducting state. On the other hand, for temperatures closer to the transition Equ. 4 did not give a good fit, with the fit being particularly poor at small wavevectors ($|\vec{K}| < 0.05$ Å^{-1}). This is most likely due to the additional small angle scattering discussed above.

The present results establish unambiguously that $HoMo_6S_8$ becomes ferromagnetic at low temperatures. We note, however, that the observed magnetic transition occurs at a somewhat higher temperature than the reentrant transition temperature found by Ishikawa and Fisher. Although this difference could be ascribed to differences in sample composition or thermometry, a similar disparity was also observed in the case of $ErRh_4B_4$. This suggests the possiblity that there is a temperature region where both ferromagnetism and superconductivity coexist, with the superconducting state being quenched only after the ferromagnetism becomes sufficiently well developed. Additional measurements will be undertaken to ascertain if this is indeed the case.

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