perimentally and theoretically, strong prospects for a new technique, photoelectron diffraction, in the determination of surface structures.

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[a]Present address: Science Research Council, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom.

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Coexistence of Antiferromagnetism and Superconductivity: A Neutron Diffraction Study of $DyMo_6S_8$

D. E. Moncton
Bell Laboratories, Murray Hill, New Jersey 07974

and

G. Shirane and W. Thomlinson
Brookhaven National Laboratory, Upton, New York 11973

and

M. Ishikawa and Ø. Fischer
Département de Physique de la Matière Condensée, Université de Genève, 1211 Genève 4, Switzerland

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Although $DyMo_6S_8$ is a superconductor below $T_c = 2.05$ K previous studies of the resistivity, susceptibility, and upper critical field strongly suggest the development of magnetic order at $T_M = 0.4$ K. The present neutron study shows conclusively that this superconducting compound also develops coexistent long-range (greater than 300 Å) antiferromagnetic order at T_M. The Dy atoms form a simple cubic sublattice (with a slight rhombohedral distortion) in which the observed magnetic structure consists of (100) planes with moments of $8.77\mu_B$ alternately parallel and antiparallel to the [111] direction.

Two classes of ternary compounds are known to become superconducting in spite of the fact that the compounds have a rare earth with a large magnetic moment as one of their constituent elements.[1-3] More dramatically two materials,[4,5] $ErRh_4B_4$ and $HoMo_6S_8$, undergo phase transitions below T_c in which they resume normal conductivity and develop magnetic order. Neutron scattering experiments[6,7] have (1) demonstrated that both materials are ferromagnets with long-range order, (2) identified the spin direction, and (3) measured the temperature-dependent spontaneous magnetization. Although these studies showed some evidence of a small temperature interval

where both the superconducting and the magnetic order parameters are finite, conclusive demonstration of coexistence was not shown. Unlike $ErRh_4B_4$ and $HoMo_6S_8$, other members of the Chevrel-phase class MMo_6X_8 (M = rare earth; X = S, Se) are reported to remain superconducting to low temperatures although anomalies in various physical properties suggest that magnetic-ordering transitions occur. Specifically, McCallum *et al.*[8] claimed coexistence of superconductivity and antiferromagnetism in $ErMo_6Se_8$ on the basis of specific heat studies. Furthermore, Ishikawa and Fischer[9] have found unusual behavior in the superconducting upper critical field, the resistivity and the magnetic susceptibility of $TbMo_6S_8$, $DyMo_6S_8$, and $ErMo_6S_8$, which they attribute to magnetic ordering in the superconducting state.

In the case of $ErMo_6S_8$, neutron scattering experiments[10] have been performed. However a complicated diffraction pattern and substantial impurity content not only prevented solution of the magnetic structure but raised the possibility that all the magnetic-ordering effects were occurring in impurity phases. It is, therefore, of considerable importance to examine the other above-mentioned superconductors, e.g., $DyMo_6S_8$, $TbMo_6S_8$, and $ErMo_6S_8$, to asses the possibility of coexistent magnetism. In this Letter we report an initial study of $DyMo_6S_8$ ($T_c = 2.05$ K) which reveals the coexistence of simple long-range (greater than 300 Å) antiferromagnetic order of the Dy^{3+} ions and superconductivity in the Chevrel phase below $T_M = 0.4$ K. We find (100) planes of spins directed alternately parallel and antiparallel to the unique [111] rhombohedral axis. We have measured the temperature dependence of the staggered magnetization and determined the saturation moment to be $\mu_{eff} = (8.77 \pm 0.2)\,\mu_B$.

Our experiments were carried out at the Brookhaven National Laboratory high-flux-beam reactor using a conventional triple-axis spectrometer set for elastic scattering. The incident beam of wavelength 2.462 Å was provided by a pyrolytic graphite (PG) monochromator and higher-order wavelengths were removed with a PG filter. Temperatures down to 50 mK were obtained in a He dilution refrigerator. The sample studied was identical in its superconducting properties to those reported earlier[1,9] except that its T_c was higher. Its preparation is described elsewhere.[11] We note that the nominal composition of the present sample is $Dy_{1.2}Mo_6S_8$ which reflects the proportion of starting materials. However, our diffraction intensities are consistent with the stoichiometric composition. The question of possible Dy interstitial impurities is not yet resolved.

In Fig. 1 we show powder diffraction scans taken above and below the magnetic-ordering transition. Within the range of scattering angles studied, $5° < 2\theta < 65°$, we find six nuclear peaks from the Chevrel structure. With the resolution used to obtain the data in Fig. 1, only the {1, 1, 1} peak shows detectable splitting of the cubic degeneracy caused by the small deviation of the rhombohedral angle (89.4°) from 90°. A few small additional peaks are present in both low-

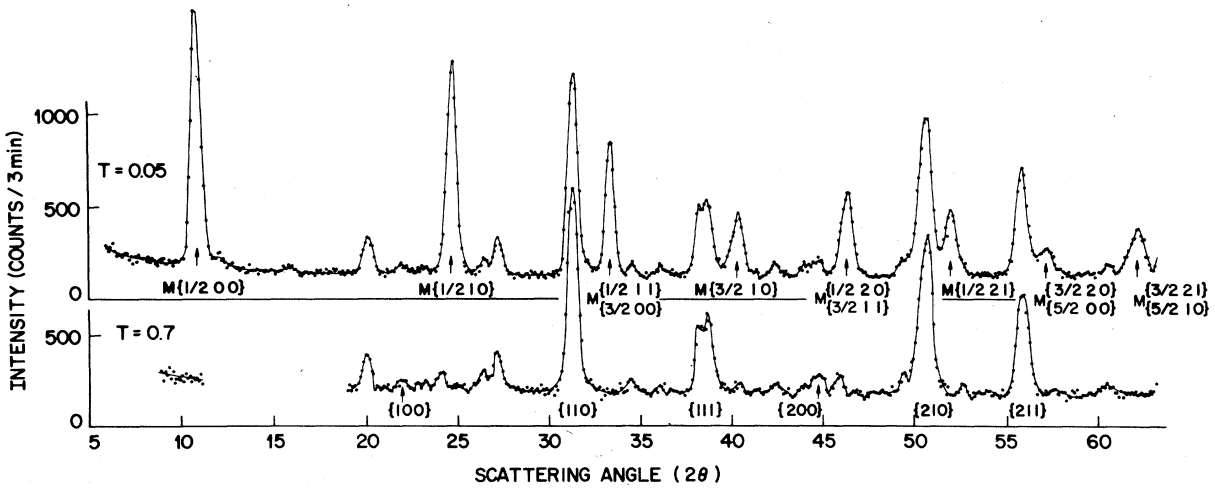

FIG. 1. Powder neutron-diffraction data for $DyMo_6S_8$ above ($T = 0.7$ K) and below ($T = 0.05$ K) the antiferromagnetic-ordering transitions at $T_M = 0.4$ K.

temperature scans shown but are absent at room temperature. Although this scattering must be due to magnetic impurities, we estimate that they constitute less than 5% of the sample.

Using the intensities integrated over all the peaks in each cubic group, we have compared the strong nuclear peaks with calculations based on positional parameters supplied by Yvon[12] and the results appear in Table I (upper portion). This comparison serves as a check on the structure and provides an absolute calibration of intensities necessary for analyzing the magnetic intensities. Below $T_M = 0.4$ K we find eight new magnetic peaks which can be easily indexed with half-integral values as shown in Fig. 1. In order to establish that the magnetic order is of long-range character, we have taken high-resolution scans through the $\{\frac{1}{2}, 0, 0\}$ peak. Since it is a single unsplit peak, its width should result solely from instrumental resolution and finite correlation effects. However, as in the previous neutron studies,[6,7,10] only instrumental width is observed and we can set a lower limit of ~300 Å on the correlation length.

To solve the magnetic structure, we note that the magnetic Bragg peaks are associated with scattering vectors $\vec{Q} = \vec{G} + \vec{q}_m$ where $\vec{G} = (h, k, l)$ are the reciprocal lattice vectors for the Chevrel structure and $\vec{q}_m = (\frac{1}{2}, 0, 0)$ is the wave vector of the magnetization. This simple magnetic structure consists of alternate (100) planes with opposite magnetic moments. The direction and magnitude of the magnetic moment may be obtained from analysis of the peak intensities. We find that the best agreement with our data is obtained when the magnetic moment axis makes about a 55° angle with the wave vector of the magnetization $\vec{q}_m = (\frac{1}{2}, 0, 0)$.

This agreement suggests that the magnetic moment is in the [111] direction since it makes an angle of 54.7° with $\vec{q}_m$. In Table I (lower portion) we compare the measured and calculated intensities for this angle using $\mu_{eff} = 8.77\mu_B$ and the spherical magnetic form factor calculated by Blume, Freeman, and Watson.[13] It is also important to show that the moment does not lie along a $[11\bar{1}]$ direction which makes essentially the same angle with $\vec{q}_m$. This can be done by measuring the relative intensities of the different components of certain peaks groups which are split by the rhombohedral distortion. We chose to study the $\{\frac{3}{2}, 1, 0\}$ peak under high resolution and the data are reported in Fig. 2. The line through the points is the result of a least-squares fit of two Gaussian peaks. This fitting procedure allows us to extract an intensity ratio $I(\frac{3}{2}, 1, 0)/I(\frac{3}{2}, 1, 0) = 2.55 \pm 0.4$. Except for the magnetic interaction vector,[14] all the quantities in the calculation of the magnetic intensities vary slowly with angle and can be ignored for the present purpose.

TABLE I. Comparison of the measured and calculated powder neutron-diffraction intensities ($T = 0.07$ K).

$\{h,k,l\}$	I_{meas}	I_{calc}
Main nuclear reflections[a]		
{1,1,0}	188(3)	187.4
{1,1,1}	96(3)	94.9
{2,1,0}	179(3)	173.2
{2,1,1}	99(3)	107.0
Antiferromagnetic reflections[b]		
{1/2,0,0}	216(6)	203.3
{1/2,1,0}	162(5)	154.1
{1/2,1,1}, {3/2,0,0}	100(4)	101.9
{3/2,1,0}	54(5)	53.8
{1/2,2,0}, {3/2,1,1}	78(4)	79.8
{1/2,2,1}	51(4)	61.5
{3/2,2,0}, {5/2,0,0}	30(4)	30.8
{3/2,1,2}, {5/2,1,0}	57(3)	61.4

[a] Calculations based on positional parameters supplied by Yvon (Ref. 12).

[b] With $\mu_{eff} = 8.77\mu_B$ and the spherical magnetic form factor calculated by Blume, Freeman, and Watson (Ref. 13).

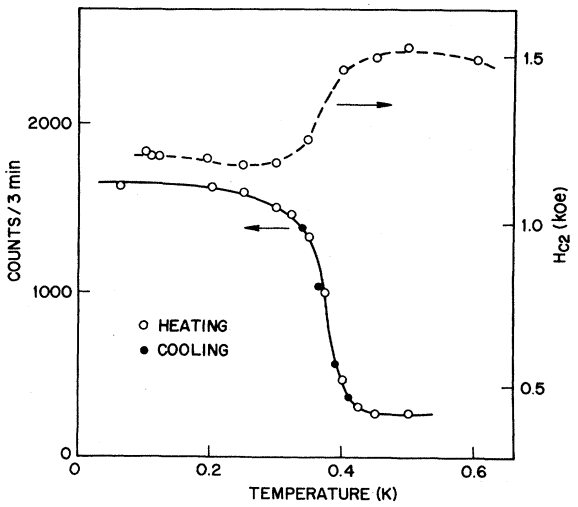

FIG. 2. High-resolution scans through the $\{\frac{3}{2}, 1, 0\}$ peak show the splitting which results from the rhombohedral distortion. The solid line is a least-squares fit of two Gaussian peaks with intensity ratio $I(\frac{3}{2}, 1, 0)/I(\frac{3}{2}, 1, 0) = 2.55$.

Thus we calculate the following intensity ratios:

$$\frac{I(\frac{3}{2}, 1, 0)}{I(\frac{3}{2}, 1, 0)} = \begin{cases} 2.71, & \text{with magnetic moment along } [111] \\ 0.73, & \text{with magnetic moment along } [11\bar{1}]. \end{cases}$$

The comparison with the observed intensity ratio allows us to conclude that the moment must lie along the rhombohedral [111] axis. We note that Lynn *et al.*[7] found the same spin direction in $HoMo_6S_8$ in the ferromagnetic state. The magnetic moment of $8.77\mu_B$ obtained in this analysis is not in agreement with that estimated from low-temperature magnetization data.[11,15] However, both values are considerably smaller than the free-ion value of $10.63\mu_B$ thus demonstrating the importance of crystal-field effects.

We turn now to Fig. 3 which shows the temperature dependence of the $\{\frac{1}{2}, 0, 0\}$ peak intensity. This curve is a measure of the square of the staggered magnetization. The data show no apparent hysteresis which would occur if the transitions were first order, but the rate at which the magnetization rises below 0.4 K is uncharacteristically high for a second-order transition. In order to demonstrate that the anomalies observed in the upper critical field by Ishikawa and Fischer are now clearly associated with magnetic ordering, we have replotted their H_{c2} data in this figure. The anomaly in H_{c2} starts at the onset of magnetic ordering and saturates when the staggered magnetization reaches saturation. Although this correlation clearly shows that the H_{c2} anomaly is due to magnetic ordering, the apparent relation to the order parameter is surprising since the H_{c2} measurements were done in a magnetic field strong enough to nearly completely polarize the magnetic state is produced by an additional, nearly-field-independent, pairbreaking parameter which varies as the magnetic-order parameter.

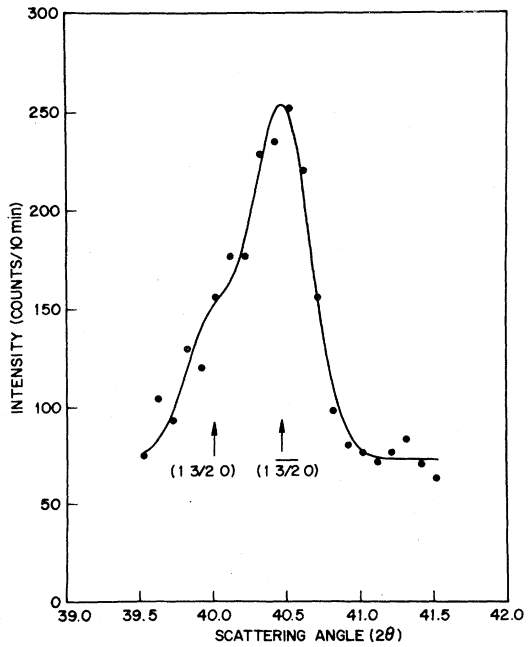

FIG. 3. The temperature dependence of the $\{\frac{1}{2}, 0, 0\}$ antiferromagnetic peak shown together with the critical-field data of Ref. 9.

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