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Magnetic Structure Studies at Brookhaven National Laboratory

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The present communication reports the results of several investigations of magnetic structure and magnetic transitions currently in progress or recently completed at Brookhaven National Laboratory.

Ni₅Er

MASTER

Intermetallic compounds having the Cu₅Ca structure, in which the components are rare earth and transition metals, have been investigated extensively in recent years by Wernick and Geller¹ and by Wallace and coworkers.² These hexagonal compounds, B₅A, in which B is an iron-group element and A a lanthanide, belong to space group P6/mmm (D_{6h}¹) with A in (a): 0,0,0, 2B_I in (c): $\pm (1/3, 2/3, 0)$, and 3B_{II} in (g): 1/2, 0, 1/2; 0, 1/2, 1/2; 1/2, 1/2, 1/2 (Fig. 1). The magnetic measurements of Nesbitt et al.^{3,4} indicate that compounds formed between cobalt and the heavier rare earths are ferrimagnetic, with the cobalt substructure antiparallel to that of the lanthanide. This model has been recently confirmed at Grenoble by the neutron diffraction experiments of James et al.⁵ for the case of Co₅Ho. The Ni₅R compounds, first obtained by Wernick and Geller,¹ appear to exhibit a different magnetic structure. Nesbitt et al.⁶ suggest that in these compounds the nickel behaves as though it possessed zero moment, the three valence electrons of the rare-earth metal filling the holes in the 3d band of the nickel. This hypothesis is based on

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saturation moment data as well as on the absence of compensation points in the ferromagnetic compounds and of antiferromagnetism in Ni_5Y .

Neutron diffraction studies of powdered Ni_5Er lend support to this supposition. The best fit of intensity data taken at 4.2°K was obtained for $\mu_{\text{Ni}} \sim 0$ and $\mu_{\text{Er}} = 7.7$, in agreement with the macroscopic magnetization. The moments are directed along the c axis at helium temperatures. The low value of the saturation moment is thus probably to be associated with a low value for the atomic moment of erbium. The departure of the erbium moment from the theoretical value of $9\mu_{\text{B}}$ is not unusual for the second half of the rare-earth series and may indicate that the exchange interaction and crystal field effects are of comparable magnitude.

MnSn_2

Recent measurements by Kouvel and Hartelius⁷ of the magnetic and electrical properties of the intermetallic compound MnSn_2 , indicate a number of unusual features. The magnetic susceptibility passes through a weak maximum at 325°K , continues to rise on cooling to a pronounced peak at 86°K , and then abruptly decreases at 73°K to a low value which is maintained down to helium temperatures. The salient features of the magnetic behavior are paralleled by anomalies in the electrical conductivity and volume.

MnSn_2 has the body-centered tetragonal C16 structure (Fig. 2), consisting of alternating layers of Mn and Sn perpendicular to the c axis. Each Mn atom is surrounded by eight Sn atoms which connect it to its second and third nearest neighbors through angles of approximately 111° and 146° , respectively. Nearest-neighbor Mn atoms have no intervening Sn atoms and are separated by a distance of $2.72 \text{ \AA}$ in the c direction.

Neutron diffraction studies show that above the abrupt transition at 73°K , MnSn_2 is antiferromagnetic with a Néel temperature in the neighborhood of

325°K, the temperature of the upper susceptibility maximum. The superstructure lines characteristic of the antiferromagnetic state appear, however, to saturate in intensity near nitrogen temperatures and show no anomaly in passing through the region of the large susceptibility maximum at 86°K. The magnetic structure consists of ferromagnetic 110 planes which alternate along the direction perpendicular to the sheets. Individual moments are oriented parallel to the direction of alternation and reach a magnitude of $2.35 \mu_B$ at 77°K. The abrupt transition at 73°K is marked by the disappearance of the high-temperature antiferromagnetic diffraction pattern and the appearance of a new pattern characteristic of a modulated spin structure below this temperature. The low-temperature structure is a simple modification of the spin arrangement above the transition, in which the magnitude of the moments is no longer constant but varies sinusoidally along the direction perpendicular to the ferromagnetically aligned sheets. Thus, the short-range structure and spin direction are essentially the same above and below the transition. The observed modulation has a wavelength of approximately $18.2 \text{ \AA}$; the amplitude of the modulated moment is $3.11 \mu_B$ at 4.2°K.

Partial substitution of indium for tin⁸ lowers the Néel point and raises the temperatures of the lower susceptibility maximum and of the sharp transition, while maintaining the same general shape. The temperature interval between the abrupt transition and χ_{max} increases from about 13° in MnSn_2 to about 30° for 20 percent indium substitution. Neutron measurements for $\text{MnSn}_{1.8}\text{In}_{0.2}$ confirm the lowering of the Néel point and show that the antiferromagnetic structure at intermediate temperatures and the modulated structure at low temperatures remain the same. The temperature range over which the sample transforms from the antiferromagnetic to the modulated structure is broadened and raised, however. Whereas in MnSn_2 the transition appears to start at the

break in susceptibility and end at lower temperatures, in $\text{MnSn}_{1.8}\text{In}_{.2}$ it appears to begin in the neighborhood of χ_{max} and end where the susceptibility drops abruptly. The coexistence of the two magnetic phases of the indium-substituted compound can be seen in Fig. 3, where the proportion of high-temperature antiferromagnetic structure is indicated by the 310 intensity and that of the modulated structure by the 310 satellite. Experiments involving further substitution of indium are currently in progress.

MnSe_2

The low-temperature antiferromagnetic structures of the homologous series, MnS_2 , MnSe_2 , and MnTe_2 , were reported⁹ a number of years ago. These compounds crystallize with the pyrite structure, a NaCl-like arrangement of M and X_2 groups with the axes of the X_2 groups parallel to the various body diagonals. While the location of Mn ions relative to the X_2 groups is the same as in MnO or α -MnS, the presence of nearly tetrahedral Mn-X-Mn linkages suggests that nearest-neighbor interactions might predominate and this, in fact, is what is observed. The disulfide exhibits ordering of the "third" kind, the ditelluride, ordering of the "first" kind, and the diselenide, an arrangement which is intermediate between the two, having the same first neighbor correlations as the other members of the series but differing in the second neighbor environment. The magnetic structures at helium temperatures are shown in Fig. 4.

Recently, Dimmock¹⁰ has pointed out that according to the Landau-Lifshitz theory, the MnSe_2 structure cannot exist in the immediate vicinity of the transition point between the paramagnetic and antiferromagnetic phases, provided there is a single transition and that it is of second order. The reason for this is that the spin distribution does not transform as a basis function for a single irreducible representation of the space group of the

paramagnetic phase, as required for a second order transition. Dimmock proposed a decomposition of the moment density observed at 4.2°K into two parts with different temperature dependences, such that the initial transition would take place to a modulated structure which, as the temperature was lowered, would transform continuously over into the observed low-temperature structure. Experimentally, this results in a division of the antiferromagnetic reflections into two groups (corresponding to the splitting of the moment density into two parts) with different temperature dependences.

Investigation of the behavior of the diffraction pattern with temperature reveals that the transition is in fact very sharp. At 51°K the pattern is well-developed and corresponds to 85 percent of the moment at 4.2°K. Furthermore, the relative intensities of the two classes of reflections are essentially the same as at helium temperatures. However, at 56°K, long-range magnetic order has been replaced by short-range order, whereas the expected Néel temperature, based on a Brillouin extrapolation from the 4.2° and 51°K points, would be 90°K. These results are summarized in Fig. 5. It is difficult, from these observations, to conclude that the transition is actually first order, although this may very well be true. However, the radical departure from Brillouin behavior makes it extremely unlikely that the theory of second order transitions would be applicable to this case. Work is in progress to further characterize the nature of the transition.

The magnetic structure of Cr_2O_3 , shown in Fig. 6, was proposed by Brockhouse¹¹ about ten years ago on the basis of preliminary data which he was not able to extend at the time. The results were sufficiently precise to allow a choice to be made among the three simple structures which did not require

enlargement of the unit cell, but no assignment of the spin direction could be obtained. This information was subsequently supplied by the susceptibility measurements of McGuire and co-workers¹² and more directly by the polarized neutron studies of Nathans et al.¹³ who found the spins to lie along the rhombohedral axis. More recently, Cr_2O_3 has been the subject of detailed experimental and theoretical investigations which include the measurement of the magnetoelectric effect by Astrov¹⁴ and by Rado and Folen,¹⁵ the high-field antiferromagnetic resonance experiments of Foner,¹⁶ and a theoretical study of the magnetic and optical properties by Pratt and Bailey.¹⁷ These investigations have raised a number of questions concerning the precise spin arrangement in Cr_2O_3 . One would like to know the sublattice magnetization at low temperatures as well as its temperature dependence up to the Néel point, whether spiralling or canting of the spins occurs, and whether any unusual features appear in the paramagnetic scattering above the transition point. Investigations currently in progress, in collaboration with R. Nathans and G. Shirane, may provide some of the answers to these questions.

Examination of a very pure powder sample of Cr_2O_3 ¹⁸ reveals that the Cr^{+3} moment is approximately eight percent lower than the spin-only value at helium temperatures. In addition, the sublattice magnetization departs markedly from a Brillouin temperature dependence as shown in Fig. 7. These results were obtained from the temperature variation of the 110 reflection, after subtracting the nuclear contribution remaining above the Néel point (approximately 15 percent of the total at low temperatures). Experiments performed on single crystals indicate the presence of weak diffracted intensity at a number of reciprocal lattice points to which the Cr_2O_3 structure makes no contribution. These results cannot be interpreted until several possible spurious effects

have been eliminated. Polarized neutron studies are capable at present of eliminating canted structures in which the perpendicular component is ordered either in the sequence $+-+-$ (Cr_2O_3) or $++--$ (Fe_2O_3) along the rhombohedral axis.

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Fig. 1. The Cu_5Ca structure.

Fig. 2. The Cl_6 structure.

Fig. 3. Temperature dependence of the 310 antiferromagnetic reflection and the 310(+) satellite.

Fig. 4. Magnetic structures of MnS_2 , MnSe_2 , and MnTe_2 . Positive and negative orientations of the dipoles are shown by black and white spheres. The direction of the magnetic axis is shown by an arrow; in the case of the ditelluride the orientation within the plane is unspecified.

Fig. 5. Sublattice magnetization in MnSe_2 .

Fig. 6. The magnetic structure of Cr_2O_3 .

Fig. 7. Temperature variation of the sublattice magnetization in Cr_2O_3 .

MnSn_2
 C16 Cu Al₂ TYPE, b.c. TETRAGONAL, $M=4$, $I4/mcm$

$a = 6.647$

$c = 5.434$

$x = 0.160$

O-Mn
 O-Sn

O-Mn, $z=0; 1/2$
 ⊗-Sn, $z=1/4$
 ⊙-Sn, $z=3/4$

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FIG. 2

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fig 2

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Fig 3

MnS₂

MnSe₂

MnTe₂

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Fig. 7
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