Four Magnetic Structures of Arsenic-Modified Mn_2Sb

W. H. CLOUD

Central Research Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware*

(Received 8 August 1967)

X-ray diffraction and magnetization measurements show the presence of four different ordered magnetic states in $Mn_2Sb_{1-y}As_y$ with $y=0.10$ and 0.15. First-order transitions take place in the ferrimagnetic (F)→intermediate antiferromagnetic (I_{AF})→intermediate ferrimagnetic (I_F)→antiferromagnetic (AF) sequence during cooling. Magnetic structures that correspond to x-ray and magnetization data are collinear layered structures. In terms of c, the tetragonal axis of the x-ray unit cell, the magnetic unit cells of the various structures have tetragonal axes of c (F), $6c$ (I_{AF}), $3c$ (I_F), and $2c$ (AF). The I_{AF} structure is not found in the $Mn_{2-x}Cr_xSb$ system, in which similar magnetic transitions were first observed.

I. INTRODUCTION

STUDIES of chromium-modified Mn_2Sb ($Mn_{2-x}Cr_xSb$) have shown that for $x\leq 0.035$, there are first-order transitions between three distinct magnetic states: ferrimagnetic (F), intermediate ferrimagnetic (I_F), and antiferromagnetic (AF).[1,2] The transitions take place in the sequence F→I_F→A upon cooling. The magnetic structures of the three states can be derived from various alignments of ferrimagnetic layers [see Figs. 1(a), 1(c), and 1(d)]. In the Mn_2Sb structure, space group $P4/nmm$, the atoms are located as follows (with $z\cong u\cong 0.3$): Mn(I) at 0, 0, 0, $\frac{1}{2}$, $\frac{1}{2}$, 0; Mn(II) at 0, $\frac{1}{2}$, z, $\frac{1}{2}$, 0, $\bar{z}$; Sb at $\frac{1}{2}$, 0, u, 0, $\frac{1}{2}$, $\bar{u}$. The ferrimagnetic layer is really a three-plane sandwich with a Mn(I) plane between two planes, each containing Mn(II) and Sb atoms. Each unit cell contributes two Mn(I), two Mn(II), and two Sb atoms to the layer. The magnetic moment of Mn(II) is different from and antiparallel to that of Mn(I) within the layer, so that the layer is ferrimagnetic. The arrows in Fig. 1 represent the net moment per layer. The interlayer distance is c, the tetragonal axis of the x-ray unit cell. The plane of the layers is perpendicular to c. The three structures can be described by propagation vectors k along c. For F, $k=2\pi/c$, and for AF, $k=\pi/c$. The I_F state requires a linear combination of $k_1=2\pi/c$ and $k_2=2\pi/3c$.

II. THEORY

Kittel[3] treated first-order transitions in layered structures, using the molecular-field approach. His results predict all the essential features of the F→AF transitions observed in $Mn_{2-x}Cr_xSb$ for $x>0.035$. His theory does not account for the F→I_F→AF transitions observed for $x\leq 0.035$, because it deals only with the exchange interactions between nearest-neighbor layers. It does, however, have two important results that should apply to structures other than the F and AF structures. The first is that the interlayer distance c is

$$c=c_T+GM^2\cos\Phi, \tag{1}$$

where c_T is the "thermal" value that would obtain if there were no magnetic interactions, M is the net magnetization per layer, Φ is the angle between the magnetic moments of neighboring layers, and G is a constant containing exchange and elastic constants. The second result is that the strain energy is proportional to $-M^4\cos^2\Phi$, which has minima at $\Phi=0$ and $\Phi=\pi$.

Jarrett[4] has shown that the I_F state of Fig. 1(c) can exist if there is a spiral state that has the same energy as the F state. Lyons and Kaplan[5] pointed out that if a degeneracy occurs between two spins states, then a linear combination of the spin eigenfunctions of the two states is a valid spin eigenfunction. Jarrett showed that the spirial $k_2=2\pi/3c$ was the only state that could combine with the F state ($k_1=2\pi/c$) if, as in $Mn_{2-x}Cr_xSb$, with $x\leq 0.035$, a strong negative uniaxial anisotropy confines the moments to the basal plane. This result arises from the normal requirement that the magnitude of the spin at a given site in the unit cell be unchanged from cell to cell. In this case, M^2 must be constant from layer to layer. One can express $\mathbf{M}$ as a linear combination of ferromagnetic and spiral wave functions:

$$\mathbf{M}=\mathbf{F}+\mathbf{u}\cos k_2nc+\mathbf{v}\sin k_2nc, \tag{2}$$

where n numbers the layers, and $\mathbf{u}$ and $\mathbf{v}$ are in the basal plane, with $\mathbf{u}\cdot\mathbf{v}=0$. In order for M^2 to be independent of n, there must be restrictions on values of $\mathbf{F}$, $\mathbf{u}$, $\mathbf{v}$, and k_2. For example, a conical spiral has $\mathbf{F}\cdot\mathbf{u}=\mathbf{F}\cdot\mathbf{v}=0$ and $u^2=v^2$, but k_2 can have any value. If, however, $\mathbf{F}$ is in the basal plane, then $\mathbf{F}\cdot\mathbf{u}$ and $\mathbf{F}\cdot\mathbf{v}$ cannot both be zero. In this case, the only values of k_2 that could make M^2 independent of n are those that

* Contribution No. 1361.

[1] F. J. Darnell, W. H. Cloud, and H. S. Jarrett, Phys. Rev. **130**, 647 (1963).

[2] A. E. Austin, E. Adelson, and W. H. Cloud, Phys. Rev. **131**, 1511 (1963).

[3] C. Kittel, Phys. Rev. **120**, 335 (1960).

[4] H. S. Jarrett, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and the Physical Society, London, 1965), p. 546.

[5] D. H. Lyons and T. A. Kaplan, Phys. Rev. **120**, 1580 (1960).

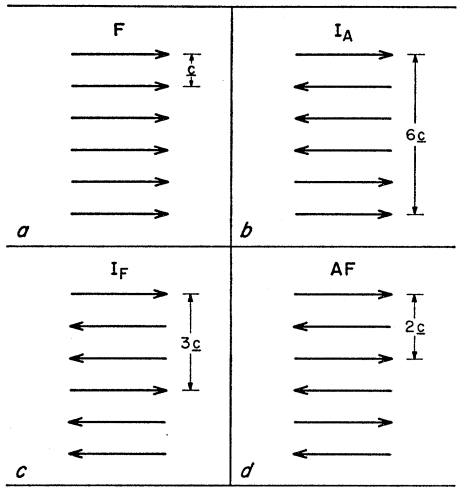

FIG. 1. Four possible magnetic structures of layered structures with negative uniaxial anisotropy. Arrows represent net moments of the layers.

are commensurate with the interlayer distance, i.e., $k_2=2\pi/Nc$, where N is an integer. By simply setting up the equation for M^2 with $n=0$, 1, 2, Jarrett showed that the only possible value for k_2 was $2\pi/3c$. There are many possible combinations of $k_1=2\pi/c$ and $k_2=2\pi/3c$, but the combination giving the I_F state of Fig. 1(c) has the lowest strain energy ($-M^2\cos^2\Phi$).

The problem of explaining the I_F state in $Mn_{2-x}Cr_xSb$ has been reduced to proving that a spiral state has an energy that is equal to or lower than the energy of the F state. A molecular-field treatment will give a spiral state if next-nearest-neighbor layers are coupled by an antiferromagnetic exchange interaction that is at least half as large as the nearest-neighbor exchange. This seems unreasonable, since the distances involved are greater than 10 Å. Jarrett[4] applied the generalized Luttinger-Tisza method of Lyons and Kaplan[5] and found that a spiral state had the same energy as the F or AF states for reasonable values of the exchange integrals between various sites involving much shorter

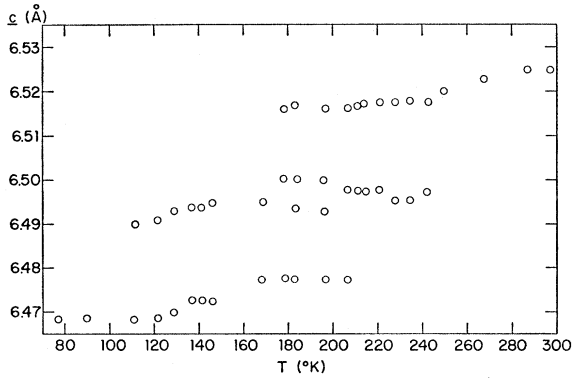

FIG. 2. Tetragonal axis (c) of $Mn_2Sb_{0.85}As_{0.15}$ versus temperature.

TABLE I. Observed and calculated values of tetragonal axis.

	State	c (Å)[a]	c (Å) Calculated from Eq. (5)		
$y=0.10$	A	6.518	F	6.518	
	B	6.502	I_{AF}	6.503	$\Delta c=0.045$
	C	6.489	I_F	6.488	$c_T=6.5955$
	D	6.473	AF	6.473	
$y=0.15$	A	6.516	F	6.516	
	B	6.500	I_{AF}	6.503	$\Delta c=0.038$
	C	6.492	I_F	6.491	$c_T=6.497$
	D	6.478	AF	6.478	

[a] Values taken at midpoint of temperature range at which the four states occur simultaneously, i.e., 160°K for $x=0.10$ and 190°K for $x=0.15$.

distances. As mentioned above, the strain energy favors the combination of spiral and F state over the spiral itself.

Let us assume that there is a threefold degeneracy in which spiral, F, and AF states have the same energy and search for linear combinations that have low strain energy ($\cos^2\Phi=1$). As before, the moments are confined to the basal plane. A combination of F and AF can occur only if the F spin direction is perpendicular to the AF spin direction, making $\cos^2\Phi\neq 1$. The combination F and spiral giving the I_F state has been discussed. The third possibility, namely, the combination of spiral and AF, can be expressed as

$$\mathbf{M}=\mathbf{A}\cos n\pi+\mathbf{u}\cos k_2nc+\mathbf{v}\sin k_2nc, \qquad (3)$$

with $\mathbf{A}$, $\mathbf{u}$, and $\mathbf{v}$ in the basal plane, and $\mathbf{u}\cdot\mathbf{v}=0$. As in the case of Eq. (2), k_2 must be commensurate with c in order to have M^2 independent of n. Solving the three equations for $n=0$, 1, 2 gives $k_2=2\pi/6c$. Substituting this value into equations for $n=3$, 4, 5 gives a value of M^2 that is the same as it is for $n=0$, 1, 2. Thus the combination $k_1=\pi/c$, $k_2\pi/3c$ gives a constant magnitude for $\mathbf{M}$. The particular combination that has lowest strain energy ($\cos^2\Phi=1$) is that of the I_{AF} state of Fig. 1(b). Therefore, if there is degeneracy

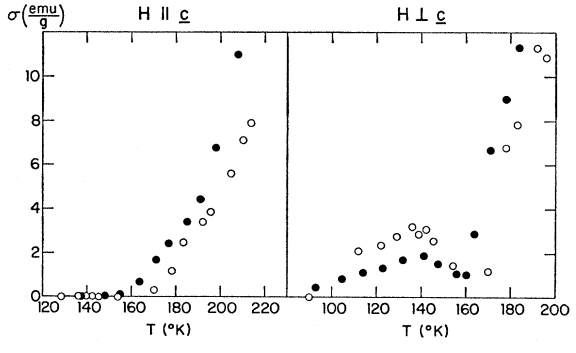

FIG. 3. Magnetization curves for $Mn_2Sb_{0.85}As_{0.15}$ in an applied magnetic field (H) of 1000 Oe. Closed circles are observed points. Open circles are points calculated from x-ray data.

between F, AF, and spiral states, it is possible to have two intermediate states: I_F (intermediate ferrimagnetic) and I_{AF} (intermediate antiferromagnetic).

From Eq. (1), the total change in c between F and AF states is

$$\Delta c = 2GM^2. \tag{4}$$

The c axis for the x-ray unit cell for the various states in Fig. 1 can then be expressed as follows:

$$\begin{aligned} &\text{F} && c = c_T + \tfrac{1}{2}\Delta c, \\ &I_{AF} && c = c_T + \tfrac{1}{6}\Delta c, \\ &I_F && c = c_T - \tfrac{1}{6}\Delta c, \\ &\text{AF} && c = c_T - \tfrac{1}{2}\Delta c. \end{aligned} \tag{5}$$

III. RESULTS AND ANALYSIS

Exchange-inversion transitions in the $Mn_2Sb_{1-y}As_y$ system were first observed by Bither and co-workers.[6] Synthesis of uniform products is difficult because arsenic tends to evaporate and deposit on the coolest portion of the sealed tubes. The values of y for the crystals discussed below represent the fusion charges. Neutron-diffraction studies of the $y=0.3$ compound showed that the high- and low-temperature states have the same magnetic structures as the F and AF states, respectively, of $Mn_{2-x}Cr_xSb$.[7]

X-ray measurement of the c axis of the unit cell shows the presence of four distinct states in $MnSb_{1-y}As_y$ for $y=0.10$ and $y=0.15$. The 0017 reflection was observed by use of a General Electric XRD-5 diffractometer. Data for $y=0.15$ are shown in Fig. 2. Data for $y=0.10$ are similar, except that the intermediate states occur at lower temperatures. The fact that more than one state is present in the 110–240°K range demonstrates the lack of uniform stoichiometry throughout the crystals of approximately 1-mm dimensions. The states are denoted as A, B, C, and D, in order of their appearance during cooling. A crystal with $y=0.20$ showed only the $A \rightarrow D$ transition. A $y=0.05$ crystal showed only the $A \rightarrow B$ transition down to 77°K, the lowest temperature observed.

Values of c for the four states of $y=0.10$ and $y=0.15$ are shown in Table I. Also shown in Table I are values of c calculated from Eqs. (1), (4), and (5). Observed and calculated values agree quite well if the four states A, B, C, and D are assumed to be F, I_{AF}, I_F, and AF, respectively.

Magnetization-temperature curves in an applied field of 10 000 Oe showed only broad transition from high-temperature state with a net moment of approximately 25 emu/g to a low-temperature state of zero net amount. However, the magnetization measured in a field of 1000 Oe perpendicular to c showed the presence of some type of intermediate state. The data for $y=0.15$ are shown in Fig. 3. Similar behavior was observed for $y=0.10$, but not for $y=0.05$ or $y=0.20$. The curve for $H \perp c$ in Fig. 3 shows a minimum at approximately 160°K. No such minimum is observed in the $F \rightarrow I_F \rightarrow AF$ transitions in $Mn_{2-x}Cr_xSb$ ($x \cong 0.03$).[1]

TABLE II. Magnetization of various states at 1000 Oe estimated from studies of $Mn_{1.97}Cr_{0.03}Sb$.

State	$H \parallel c$	$H \perp c$
F	$0.3\sigma_s$	$0.7\sigma_s$
I_{AF}	0	0
I_F	$0.05\sigma_s$	$0.2\sigma_s$
AF	0	0

In addition to giving the c-axis data of Fig. 2, the x-ray-diffraction studies also enable one to estimate the fraction of the crystal in each of the four states from the measured intensities of the $00l$ reflections of each state. Peak intensities rather than integrated intensities were used because the lines from simultaneously occurring states partially overlap. If one assumes that the magnetic structures of the various states are the F, I_{AF}, I_F, and AF states of Fig. 1, a magnetization-versus-temperature curve can be constructed from the x-ray data. The magnetization of the I_{AF} and AF states is zero, and the magnetization of the F and I_F states in a field of 1000 Oe can be estimated from studies of these two states in $Mn_{1.97}Cr_{0.03}Sb$.[1] Estimated values of magnetization at 1000 Oe are shown in Table II. The saturation magnetization of the F state, σ_s, was found to be 25.8 emu/g from high-field measurements. Using the fraction of the crystal in each of the four states obtained from x-ray data and the magnetization data of Table II, curves of magnetization versus temperature were computed and are shown in Fig. 3. The main features of the observed and calculated curves are in agreement, i.e., a magnetization minimum for $H \perp c$, but not for $H \parallel c$. X-ray and magnetization studies were made on the same crystal.

The agreement between the observed and calculated curves of magnetization versus temperature indicates that the four states A, B, C, and D are the F, I_{AF}, I_F, and AF structures of Fig. 1. The c-axis data of Table I also indicate the existence of these four states. It would be desirable to observe the magnetic structures of the various states by neutron diffraction, but crystals of uniform stoichiometry and of sufficient size for neutron-diffraction studies are not available.

IV. CONCLUSION

The magnetization and x-ray data lead to the conclusion that in $Mn_2Sb_{0.90}As_{0.10}$ and $Mn_2Sb_{0.85}As_{0.15}$, first-order transitions take place in the $F \rightarrow I_{AF} \rightarrow I_F \rightarrow AF$

[6] T. A. Bither, P. H. L. Walter, W. H. Cloud, T. J. Swoboda, and P. E. Bierstedt, J. Appl. Phys. **33**, 1346 (1962).

[7] A. E. Austin, E. Adelson, and W. H. Cloud, J. Appl. Phys. **33**, 1356 (1962).

sequence during cooling. The I_{AF} state is not found in the $Mn_{2-x}Cr_xSb$ system. An explanation of why the I_{AF} state is found in one system and not in the other would require a detailed knowledge of how the exchange integrals vary with interatomic distances in the Mn_2Sb structure. It is relevant to note that in the course of the present studies, negative uniaxial anisotropy was found to exist up to 245°K in $Mn_2Sb_{1-y}As_s$, but previous studies[1] have shown that it exists only below 200°K in $Mn_{2-x}Cr_xSb$. Both the I_F and I_{AF} states are energetically favored only if negative unaxial anisotropy confines the moments to the basal plane. The wider range of negative anisotropy in $Mn_2Sb_{1-y}As_y$ is undoubtedly interrelated with the existance of the I_{AF} state.

ACKNOWLEDGMENTS

The crystals used in these experiments were prepared by T. A. Bither and P. H. L. Walter. The x-ray measurements were performed by E. P. Moore.

PHYSICAL REVIEW VOLUME 168, NUMBER 2 10 APRIL 1968

Low-Temperature Behavior of the Anisotropic Heisenberg Antiferromagnet in the Neighborhood of the Magnetic Phase Boundaries

J. FEDER AND E. PYTTE
IBM Zurich Research Laboratory, 8803 Rüschlikon, Switzerland
(Received 16 October 1967)

Using spin-wave theory, including spin-wave interactions to leading order in $1/2S$, the temperature dependence of the critical magnetic field curves between the antiferromagnetic, the flop, and the paramagnetic phases have been calculated for a Heisenberg antiferromagnet with both uniaxial single-ion anisotropy and anisotropic exchange interaction. The free energy has been obtained for all three phases, and the behavior of the specific heat and the susceptibility in the neighborhood of these phase boundaries as a function of magnetic field for a fixed temperature is discussed in detail.

I. INTRODUCTION

IN this paper we discuss the low-temperature properties of a uniaxial Heisenberg antiferromagnet. In particular we determine the temperature dependence of the several phase transition boundaries, and discuss the behavior of thermodynamic properties such as the specific heat, the magnetization, and the susceptibility in the neighborhood of these phase boundaries.

The model we consider consists of a simple cubic array of magnetic ions of spin S, interacting by a negative nearest-neighbor exchange interaction. The exchange interaction is assumed to be anisotropic favoring alignment along the crystalline z axis. In addition we assume the presence of a uniaxial single-ion anisotropy and an external magnetic field, both parallel to the crystalline z axis. In this model calculation we consider only a simple cubic structure but the results are trivially extended to any other crystal structure which can also be resolved into two sublattices such that the nearest neighbors of an ion on one sublattice lie only on the other sublattice.

In the low-temperature region $T \ll T_N$, where T_N is the Néel temperature, the spins will be antiferromagnetically ordered for sufficiently small magnetic fields. As the field is increased, a phase transition occurs to the flop phase with the spins in a generally transverse direction to the field. As the field is increased further, the average direction of the individual spins will eventually become parallel to the external field. The particular value of the field for which this occurs defines a second phase transition to the paramagnetic (ferromagnetic) phase. About these average directions there will be thermal fluctuations in the form of spin waves.

In the transition from the spin-flop to the paramagnetic phase, the two phases are indistinguishable at the transition and it is therefore of the second order. At the antiferromagnetic spin-flop phase boundary, the phases are clearly distinct and the transition is of first order. Near a first-order transition, metastable superheated and supercooled states will usually be possible.

The general properties of the system described by the Hamiltonian [Eq. (1)] are most simply appreciated by performing a simple molecular-field calculation at zero temperature. We assume that all the spins on the same sublattice α point in the same direction. Then if we call the angles that $\mathbf{S}_\alpha$ and $\mathbf{S}_\beta$ make with the z axis, θ_α and θ_β, respectively, and ϕ the angle between the projections of $\mathbf{S}_\alpha$ and $\mathbf{S}_\beta$ onto the xy plane, the energy in molecular-field theory takes the form

$$E(\theta_\alpha, \theta_\beta, \phi) = \tfrac{1}{2}NS^2zJ[\sin\theta_\alpha \sin\theta_\beta \cos\phi + \cos\theta_\alpha \cos\theta_\beta + (K/J)\cos\theta_\alpha \cos\theta_\beta - (L/zJ)(\cos^2\theta_\alpha + \cos^2\theta_\beta) - (\mu H/SzJ)(\cos\theta_\alpha + \cos\theta_\beta)].$$