Magnetic Structures of Mn2As and Mn2Sb0.7As0.3

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with the same number of electrons per atom. At lower Cu concentrations the Curie temperature becomes too high to be measured without causing decomposition.

From the difference in color of the two surfaces of films, which were annealed for one hour at 700°C, it appears that the equilibrium phases are not finely dispersed, but rather form a Cu layer and a 90-Co 10-Cu layer, i.e., a sandwich film with the Cu-colored surface always being on the air side. An explanation for this situation can be seen in a preferred nucleation of the Co-rich phase on the quartz side, which may occur when (for technical reasons or because of different sticking coefficients for Co and Cu) a thin Co-richer layer is formed initially. When, namely, a 20- to 30-Å Cu layer is deposited on the quartz before evaporating the alloy, then the Cu color appears on the quartz side.

A more detailed analysis of the structure of the annealed films is possible by an analysis of the perpendicular anisotropy constant $K_\perp$ as determined from Eq. (1). This, together with a study of the kinetics of the decomposition process, will be subject of a later paper.

Concluding, it may be said that the above results seem to encourage a simple way for the study of alloys in metastable states, which cannot be realized by classical methods.

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Magnetic Structures of Mn_2As and $Mn_2Sb_{0.7}As_{0.3}$

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Neutron diffraction has been performed on powder specimens of Mn_2As and $Mn_2Sb_{0.7}As_{0.3}$. Mn_2As has the antiferromagnetic structure found in $Mn_{1.9}Cr_{0.1}Sb$ below the exchange inversion temperature. The atomic moments are 3.7 and 3.5 Bohr magnetons for Mn(I) and Mn(II), respectively. The moments lie perpendicular to the tetragonal axis. The magnetic structure of $Mn_2Sb_{0.7}As_{0.3}$, which undergoes exchange inversion over the 35° to 115°C temperature range, is the same as that of Mn_2As at room temperature and is the same as that of ferrimagnetic Mn_2Sb at 150°C. The atomic moments at room temperature (antiferromagnetic) are 2.3 and 2.8 Bohr magnetons, respectively, for Mn(I) and Mn(II). The moments are perpendicular to the tetragonal axis at room temperature and parallel to it at 150°C.

THE work reported in the paper by Bither *et al.*[1] has shown that exchange inversion in substituted Mn_2Sb compounds can be produced by a variety of substituents, both for Mn and Sb. The compounds for which As has been substituted for Sb are of particular interest because Mn_2As and Mn_2Sb have the same crystal structure but are antiferromagnetic and ferrimagnetic, respectively. Neutron diffraction studies of Mn_2Sb have been made by Wilkinson *et al.*[2] The ferrimagnetic to antiferromagnetic transition in $Mn_{1.9}Cr_{0.1}Sb$ has been studied by neutron diffraction.[3,4] Magnetic susceptibility and specific heat measurements of Yuzuri and Yamada[5] indicate that Mn_2As had a Néel temperature of 573°K, but its magnetic structure has not been determined. We have therefore undertaken neutron diffraction studies of Mn_2As and also $Mn_2Sb_{0.7}As_{0.3}$ which undergoes exchange inversion over the 35–115°C range in order to determine if the antiferromagnetic and ferrimagnetic structures of $Mn_2Sb_{0.7}As_{0.3}$ are the same as those of Mn_2As and Mn_2Sb, respectively.

Since suitable single crystals of both Mn_2As and $Mn_2Sb_{0.7}As_{0.3}$ have proved very difficult to prepare, the neutron diffraction studies were made on powder specimens. Quantitative determinations of scattering amplitudes were made by comparing integrated intensities with those observed from a powdered specimen of $Mn_{1.9}Cr_{0.1}Sb$ for which the scattering amplitudes were known from single crystal studies.[3,4] The absorption and temperature factors were assumed to be the same for the three powders. The experimental constant[6] was determined from the diffraction data of a measured amount of $Mn_{1.9}Cr_{0.1}Sb$.

[1] T. A. Bither, P. H. L. Walter, W. H. Cloud, T. J. Swoboda, and P. E. Bierstedt, J. Appl. Phys. **33**, 1346 (1962).
[2] M. K. Wilkinson, N. S. Gingrich, and C. G. Shull, J. Phys. Chem. Solids **2**, 289 (1957).
[3] W. H. Cloud, H. S. Jarrett, A. E. Austin, and E. Adelson, Phys. Rev. **120**, 1969 (1960).
[4] W. H. Cloud, T. A. Bither, and T. J. Swoboda, J. Appl. Phys. **32**, 55S (1961).
[5] M. Yuzuri and M. Yamada, J. Phys. Soc. Japan **15**, 1845 (1960).
[6] G. E. Bacon, *Neutron Diffraction* (Clarendon Press, Oxford, England, 1955), p. 93.

TABLE I. Neutron diffraction intensities at room temperature.

Compound	Amount of powder	Integrated intensities (arbitrary scale)		Structure factor $\|F\|^2$ (barns)	
		$00\frac{3}{2}$	$10\frac{1}{2}$	$00\frac{3}{2}$	$10\frac{1}{2}$
$Mn_{1.9}Cr_{0.1}Sb$	19.00 g	3.16	1.96	13.22	3.16
Mn_2As	14.66 g	7.57	3.02	40.89	6.73
$Mn_2Sb_{0.7}As_{0.3}$	15.09 g	4.00	1.95	20.09	3.90

Mn_2As

Neutron diffraction studies at room temperature show that the antiferromagnetic structure of Mn_2As is the same as that of $Mn_{1.9}Cr_{0.1}Sb$ below the exchange inversion temperature [Fig. 1(B)]. The magnetic c axis is twice that of the x-ray cell, which has the dimensions: $a=3.78$ A, $c=6.28$ A. The magnetic $00\frac{3}{2}$ and $10\frac{1}{2}$ reflections (index based on the x-ray cell) are clearly resolved. Their integrated intensities are shown in Table I. The $00\frac{3}{2}$ intensity, which is roughly proportional to the sum of the Mn(I) and Mn(II) moments, is clearly larger than that of $Mn_{1.9}Cr_{0.1}Sb$.

In the Mn_2As structure, the Mn(I) atoms are at positions 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, 0. The Mn(II) and As atoms are at positions 0, $\frac{1}{2}$, z and $\frac{1}{2}$, 0, $\bar{z}$. Nowotny and Halla[7] have shown that the positions of the Mn(II) and As atoms in Mn_2As should be very close to those in Fe_2As which had been found to be $z=0.330$ and $z=-0.265$ for Fe(II) and As, respectively. Using x-ray powder intensities measured on a diffractometer we find that these values of the z parameters in Mn_2As give a discrepancy of less than 20% between observed and calculated structure factors of ten reflections for which $l\neq 0$.

Using $z=0.33$ for Mn(II), the moments were determined to be 3.7 and 3.5 Bohr magnetons for Mn(I) and Mn(II), respectively (see Table II). The values of magnetic form factors used in Table II were the same as those used by Wilkinson *et al.* for Mn_2Sb.[2] The moments in Mn_2As are perpendicular to the tetragonal axis.

TABLE II. Atomic moments at room temperature.

Compound	$\|F_0\|^{2a}=\|F\|^2/f^2$ (barns) $00\frac{3}{2}$	$10\frac{1}{2}$	Mn(I)	Mn(II)
$Mn_{1.9}Cr_{0.1}Sb$[b]	18.72	4.58	1.7	2.5
$Mn_2Sb_{0.7}As_{0.3}$	27.81	5.88	2.3	2.8
Mn_2As	57.95	10.65	3.7	3.5
Mn_2Sb (reference 2)			1.8	2.9

[a] f=magnetic form factor.
[b] Recent neutron diffraction studies have shown that the atomic moments given in reference 4 are slightly in error due to extinction effects. The values given here were obtained from neutron diffraction of a thin crystal for which extinction was negligible.

[7] H. Nowotny and F. Halla, Z. physik. Chem. **36B**, 322 (1937).

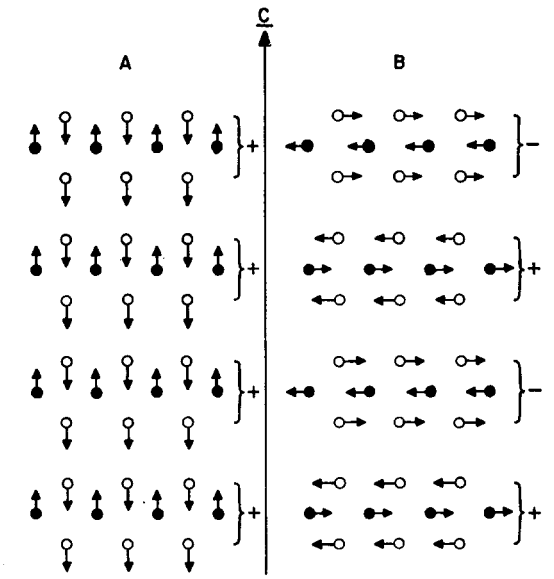

FIG. 1. Magnetic structures: (A), ferrimagnetic state of Mn_2Sb, $Mn_{1.9}Cr_{0.1}Sb$ at 50°C, and $Mn_2Sb_{0.7}As_{0.3}$ at 150°C; (B), antiferromagnetic state at room temperature of Mn_2As, $Mn_{1.9}Cr_{0.1}Sb$, and $Mn_2Sb_{0.7}As_{0.3}$. Closed circles denote Mn(I) layers; open circles denote Mn(II) layers. Braces indicate three-layer sets. Arrow c gives direction of tetragonal axis.

$Mn_2Sb_{0.7}As_{0.3}$

Neutron diffraction measurements on a powder specimen were made at room temperature and at 150°C. At room temperature the magnetic structure is the antiferromagnetic structure of Fig. 1(B) and at 150°C it is the ferrimagnetic structure of Fig. 1(A) in exact analogy to the $Mn_{1.9}Cr_{0.1}Sb$ system. The intensities of the $00\frac{3}{2}$ and $10\frac{1}{2}$ reflections are shown in Table I. X-ray powder data give $a=4.02$ A, $c=6.44$ A for $Mn_2Sb_{0.7}As_{0.3}$ at room temperature. Assuming that the z parameter for Mn(II) is 0.295 as it is in Mn_2Sb[8] the Mn(I) and Mn(II) moments were found to be 2.3 and 2.8 Bohr magnetons respectively in the room-temperature antiferromagnetic state (see Table II).

The ferrimagnetic and antiferromagnetic structures of the Mn_2Sb (or Mn_2As) crystal structure involve ferromagnetic or antiferromagnetic ordering of ferrimagnetic layers as shown in Fig. 1. These are the ferri and anti 2 structures suggested by Yuzuri and Yamada.[5] Within a layer the Mn(I), moments are always antiparallel to the Mn(II) moments. Partial substitution of As into Mn_2Sb increases the Mn(I) moment but causes little change in the Mn(II) moment; conversely substitution of Cr for Mn decreases the Mn(II) moment.

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[8] L. Heaton and N. S. Gingrich, Acta. Cryst. **8**, 207 (1955).