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The Magnetic Structure of $FeSb_2O_4$†

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The magnetic structure of $FeSb_2O_4$ at 4.2°K has been investigated by powder neutron-diffraction techniques. The spin arrangement is noncollinear, consisting of a combination of three different antiferromagnetic modes. The principal mode (A) is one in which the Fe^{2+} moments are parallel within a given (001) layer, with adjacent layers coupled antiparallel, the moments being directed perpendicular to the tetragonal c axis. However, from the data it is not possible to specify the relative directions of the secondary modes (G and C). The value of the resultant moment is approximately $3.8\mu_B$ per Fe^{2+} ion.

INTRODUCTION

A NUMBER of complex oxides isostructural with "red lead" (Pb_3O_4) are known in which the Pb ions in octahedral sites are replaced by $3d$ ions and those in pyramidal sites by Sb ions.[1] The tetragonal crystal structure of one compound of this type, $FeSb_2O_4$, is shown in Fig. 1, in which the nearly regular oxygen octahedra surrounding the Fe ions are seen to form chains along the c axis. The separation between neighboring Fe ions within a chain is only about 3.0 Å, but between those in different chains the separation is much larger, about 6.1 Å in the basal planes. Thus magnetic interactions within a chain might be expected to be relatively strong compared to interactions between chains, and the possibility of unusual magnetic properties at low temperatures arises, as is the case for $CoCl_2\cdot 2H_2O$ for example.[2,3] The present paper describes more fully the results of a neutron-diffraction study of polycrystalline $FeSb_2O_4$ previously reported in brief.[4]

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‡ Operated by the University of Puerto Rico for the U. S. Atomic Energy Commission.
[1] S. Ståhl, Arkiv. Kemi. Min. Geol. **17B**, No. 5 (1943).
[2] H. Kobayashi and T. Haseda, J. Phys. Soc. Japan **19**, 765 (1964).
[3] A. Narath, J. Phys. Soc. Japan **19**, 2244 (1965).
[4] J. A. Gonzalo, D. E. Cox, and G. Shirane, Bull. Am. Phys. Soc. **10**, 353 (1964).

PREPARATION AND CRYSTAL STRUCTURE

The sample was prepared by heating a mixture of powdered reagent grade Fe, Fe_2O_3, and Sb_2O_3 in the correct proportions in a sealed, evacuated silica capsule to 500°C overnight. The product was ground and refired at 600°C. An x-ray powder photograph and diffractometer trace showed only a single tetragonal phase, with unit cell parameters $a=8.62$ Å and $c=5.91$ Å, in reasonable agreement with the published values.[1] The neutron patterns did, however, show that a small amount of Fe_3O_4 was present as an impurity in the sample. The relative amount was estimated to be smaller than 1% by weight, and in cases where there was overlap of peaks, the estimated contribution from Fe_3O_4 was subtracted from the observed $FeSb_2O_4$ intensities.

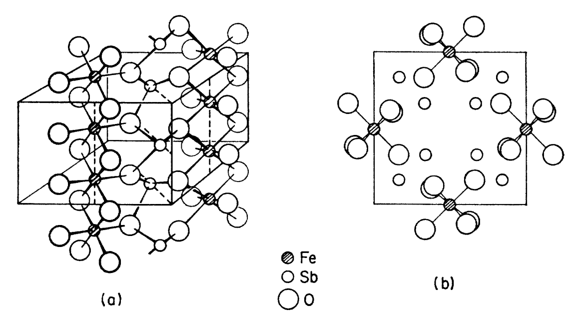

FIG. 1. The crystal structure of $FeSb_2O_4$ at room temperature (a) perspective drawing, (b) projection on (001).

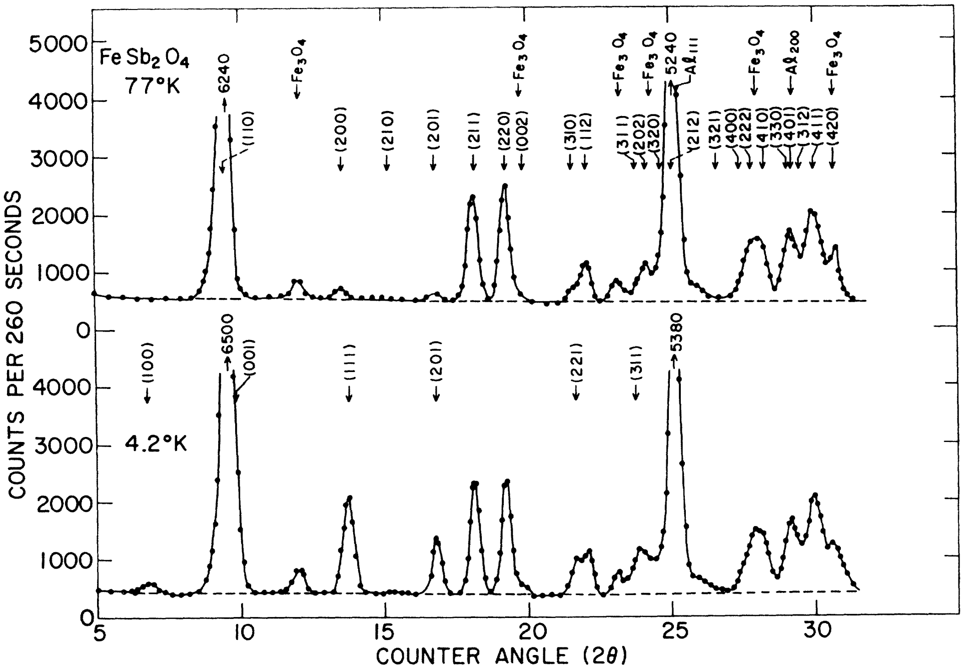

FIG. 2. Neutron-diffraction patterns from $FeSb_2O_4$ at 77°K (top) and 4.2°K (bottom).

The crystallographic space group of $FeSb_2O_4$ is $P4_2/mbc(D_{4h}^{13})$, with atoms in the following special positions:

$$\begin{array}{ll} \text{Fe}4(d) & 0,\tfrac{1}{2},\tfrac{1}{4} \\ \text{Sb}8(h) & x_1,y_1,0 \\ \text{O(I)}8(h) & x_2,y_2,0 \\ \text{O(II)}8(g) & x_3,\ \tfrac{1}{2}+x_3,\ \tfrac{1}{4}. \end{array}$$

The powder x-ray and neutron data collected at room temperature were used in a least-squares refinement of the antimony and oxygen parameters, respectively, and the final values are given in Table I which also lists those of isostructural $ZnSb_2O_4$ in parentheses.[1] Standard errors are in the region of 0.005.

MAGNETIC STRUCTURE

Neutron diffraction patterns were obtained at 77 and 4.2°K (Fig. 2) which show that a magnetic transition occurs at some intermediate temperature. The corresponding difference pattern (Fig. 3) contains a number of additional reflections, all of which can be indexed on the basis of the chemical unit cell. These consist of a set of strong peaks satisfying the reflection condition ($h+k$ even, l odd) together with a few other weak reflections.

Since the magnetic unit cell contains only four Fe^{2+} ions, there are only four collinear models possible, if ferrimagnetic arrangements are disregarded. These four may be labeled A, G, C, and F, in complete analogy with the perovskites.[5,6]

$$\begin{aligned} A&=S_1-S_2+S_3-S_4(h+k \text{ even}, l \text{ odd}),\\ G&=S_1-S_2-S_3+S_4(h+k \text{ odd}, l \text{ odd}),\\ C&=S_1+S_2-S_3-S_4(h+k \text{ odd}, l \text{ even}),\\ F&=S_1+S_2+S_3+S_4(h+k \text{ even}, l \text{ even}). \end{aligned}$$

S_1, S_2, S_3, and S_4 refer to spins at sites $(\frac{1}{2},0,\frac{1}{4})$, $(\frac{1}{2},0,\frac{3}{4})$, $(0,\frac{1}{2},\frac{1}{4})$, and $(0,\frac{1}{2},\frac{3}{4})$, respectively, and the corresponding reflection conditions are stated in parentheses.

From the relative intensities of the reflections in Fig. 3, one can conclude that the magnetic structure is determined chiefly by a configuration of A type. However, the presence of a small (100) peak clearly shows that there is a minor component of C type, and the structure is not collinear. The presence of (101) and (211) indicates yet a third component of G type. These two peaks are subject to considerable uncertainty, as they are combined with the (111) peak of Fe_3O_4 and nuclear (211) of $FeSb_2O_4$, respectively, but they appear

TABLE I. Atomic parameters of $FeSb_2O_4$. Those of $ZnSb_2O_4$ are in parentheses.

	x	y	z
Fe(Zn)	0	0.5	0.25
Sb	0.177(0.175)	0.166(0.167)	0
O(I)	0.104(0.114)	0.643(0.614)	0
O(II)	0.677(0.669)	0.177	0.25

[5] E. O. Wollan and W. C. Koehler, Phys. Rev. **100**, 545 (1955).
[6] E. F. Bertaut, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. III, p. 149.

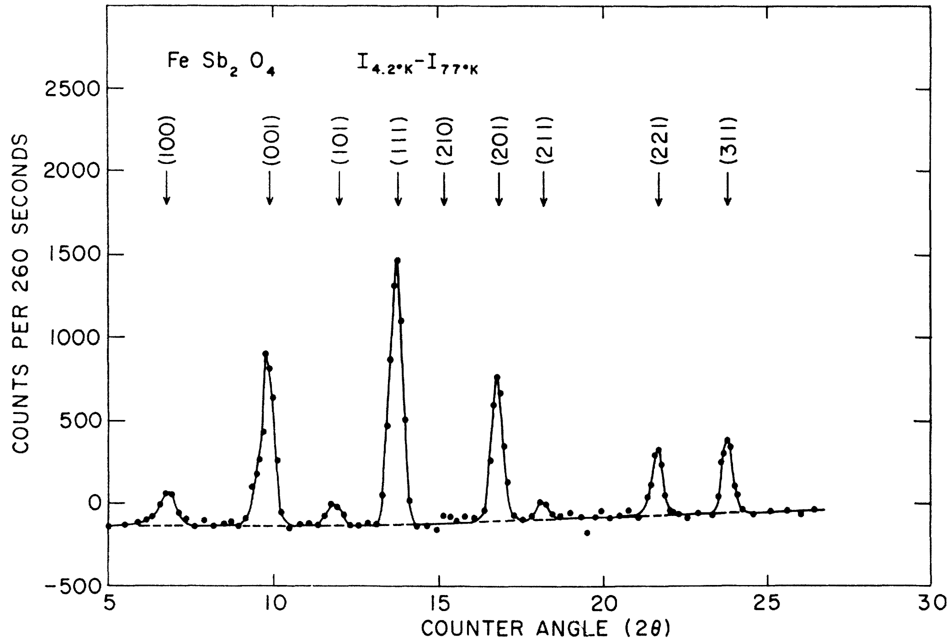

FIG. 3. Neutron-diffraction difference pattern ($I_{4.2°K}-I_{77°K}$) from $FeSb_2O_4$.

to be in excess of counting statistics. A difference pattern from the 77°K and 25°C data gave no indication of any peaks in these positions.

Comparison of observed and calculated magnetic intensities yields the following information. The spin direction of the major component (mode A) is perpendicular to the c axis with a moment of $3.5\pm0.2\mu_B$. However, the data are not sufficiently accurate to enable the directions of the other two components to be specified. Table II lists intensities for the two models $A_xC_yG_z$ and $A_xG_yC_z$, although the components in the basal plane could equally well be in any two orthogonal directions within the plane without affecting the intensities, and Fig. 4 shows the arrangement of moments.

TABLE II. Comparison of calculated and observed nuclear (I_N) and magnetic (I_M) relative intensities for $FeSb_2O_4$ at 77 and 4.2°K. The calculated spherical magnetic form factor for Fe^{2+} has been used.[a] The moments of the C and G modes have been determined from (100) and (101), respectively.

hkl	I_N(calc)[b]	I_M(calc)[c] $A_xC_yG_z$	I_M(calc)[d] $A_xG_yC_z$	$I_{4.2°K}$	$I_{77°K}$
100	···	95	95	95	···
{110	3247	···	···	3751	3230
001	···	519	519		
{Fe_3O_4	···	···	···	209	131
101	···	78	78		
{200	71	···	···	789	73
111	···	721	721		
210	0	28	28	20	<10
201	43	362	362	416	53
211	775	111	40	868	833
{220	941	···	···	946	945
002	3	···	···		
300	···	6	6	<10	···
102	···	19	1	<10	···
{310	93	···	···	578	420
221	···	150	150		
112	386	···	···		

[a] R. E. Watson and A. J. Freeman, Acta Cryst. **14**, 27 (1961).
[b] Calculated with $b_{Fe}=0.952$, $b_{Sb}=0.54$, $b_O=0.577$ ($\times10^{-12}$ cm); $B=0.4$ Å^2. Other parameters as in Table I.
[c] Calculated with $\mu(A_x)=3.52\mu_B$, $\mu(C_y)=0.99\mu_B$, $\mu(G_z)=1.50\mu_B$.
[d] Calculated with $\mu(A_x)=3.52\mu_B$, $\mu(G_y)=0.93\mu_B$, $\mu(C_z)=0.70\mu_B$.

MAGNETIC SYMMETRY

A search for possible magnetic space groups ruled out any of the tetragonal groups. Of the orthorhombic

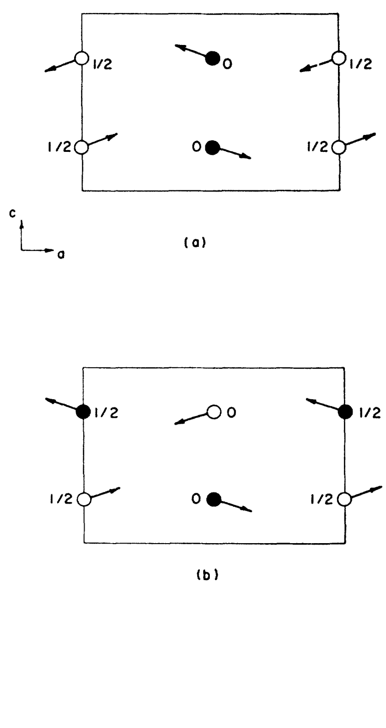

FIG. 4. (a) The $A_xC_yG_z$ and (b) $A_xG_yC_z$ magnetic structures projected on (010). The moments from open and closed circles point, respectively, slightly above and below the plane of the page. Small numerals denote the y parameter of the ions.

TABLE III. Symmetry permitted configurations in some of the Shubnikov groups $Pmc2_1$. The primes denote antisymmetry operations. The unit cell vectors refer to the tetragonal unit cell. The orientation of the orthorhombic cell is defined in the text.

	a	*b*	*c*
$Pmc2_1$	*A*	*G*	*C*
$Pm'c2_1'$	*F*	*C*	*G*
$Pmc'2_1'$	*G*	*A*	*F*
$Pm'c'2_1$	*C*	*F*	*A*

subgroups of $P4_2/mbc$, namely, $Pbam$, $Pba2$, $Pmc2_1$, and $P2_12_12$, the point symmetry of the Fe^{2+} sites confines the spin directions to along an axis or within a plane in all cases except $Pmc2_1$. The symmetry permitted configurations in the set of Shubnikov groups[7] $Pmc2_1$ for those which do not involve an enlarged unit cell are given in Table III. The orthorhombic cell has the orientation $a'=c$, $b'=a$, $c'=b$, where a, b, and c are the tetragonal unit cell vectors, the latter having been used in Table III. The origin is shifted by $(0,\frac{1}{4},0)$, and the Fe^{2+} ions occupy the general positions x,y,z. For $x=\frac{1}{4}$, $y=\frac{1}{4}$, and $z=\frac{1}{2}$, their relative positions are unchanged. From this viewpoint, the model $A_xG_yC_z$ is favored (Shubnikov group $Pmc2_1$, No. 26-66[7]) in which case the components G_y and C_z have moments of $(0.9\pm0.2)\mu_B$ and $(0.7\pm0.2)\mu_B$, respectively.

The crystal structure at 4.2°K should reflect the orthorhombic symmetry, and a diffractometer trace at 4.2°K did in fact reveal that the (hkl) peaks in general and $(h00)$ peaks in particular were visibly broadened, while $(hh0)$ and (hhl) peaks were not. The resolution was not sufficient for the distortion to be measured accurately, but at a rough estimate there is a difference of 0.2% between the original tetragonal a axes. However, this effect was still present well above 77°K, and hence the distortion is not connected with the magnetic transition.

It is interesting to note that in orthorhombic β-$CoSO_4$ the combination of antiferromagnetic modes $A_xG_yC_z$ has been definitely established at 4.2°K.[8,9] The crystal structures of this compound and $FeSb_2O_4$ can be considered analogous to the extent that the $3d$ ions occupy similar sites within chains of oxygen octahedra along the c axes.

[7] N. V. Belov, N. N. Neronova, and T. S. Smirnova, Kristallografiya **2**, 315 (1957) [English transl.: Soviet Phys.—Cryst. **2**, 311 (1957)].

[8] P. J. Brown and B. C. Frazer, Phys. Rev. **129**, 1145 (1963).

[9] R. Ballestracci, E. F. Bertaut, J. Coing-Boyat, A. Delapalme, W. James, R. Lemaire, R. Pauthenet, and G. Roult, J. Appl. Phys. **34**, 1333 (1963).

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Local Antiferromagnetic Order in Single-Crystal MnO above the Néel Temperature*

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This investigation of the spin arrangement in a single crystal of MnO above the Néel temperature ($T_N \simeq 122$°K) has shown that the magnetic neutron scattering in the vicinity of the (111) magnetic peak position consists of diffuse but distinct satellites. The presence of these satellites, which are lined up approximately along a ⟨111⟩ axis of the single crystal, indicates that small regions containing antiphase boundaries and strong antiferromagnetic order exist well above T_N. Applying a model developed for domains in ordered alloys, the average domain size was estimated to be 46 ±5 Å at 133°K. The general features of the scattering indicate that the number of coherent domains in a given region is small, and lead to the preliminary conclusion that the local order in MnO above T_N is inhomogeneous.

I. INTRODUCTION

A RECENT study of diffuse magnetic neutron scattering in powder samples of MnO[1] showed that there is a local coupling above the Néel temperature ($T_N \simeq 122$°K) with spins tending to remain parallel to a {111} plane, and with neighboring planes arranged in an antiferromagnetic fashion. It was also apparent from that study that the directional preference for a {111} layering of the spins diminished as the temperature increased, so that at room temperature the fit of the diffuse data to a (111) model was less satisfactory than at temperatures just above T_N. The local correlations were estimated to extend over regions of 20–50 Å.

The current work on a single crystal of MnO presents a more detailed examination of the neutron spin scattering from this material, and this provides a much better insight into the nature of the local spin order above the critical point. The powder method yields a spherical average of diffuse scattering for each diffraction vector; the single-crystal method, on the other

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