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The Crystal Structure of Mn_2Sb

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The crystal structure of Mn_2Sb has been re-examined. Rotation and Laue patterns from small fragments and patterns using powdered samples confirmed the published tetragonal structure with $a = 4{\cdot}08$, $c = 6{\cdot}56$ Å. Large single crystals were grown to make possible a study of reflections from $00l$, $h00$ and $hh0$ planes. Revised values of parameters are $z_{Mn} = 0{\cdot}295$ and $z_{Sb} = -0{\cdot}280$. From 100° K. to 500° K., the Debye characteristic temperature for reflections from the $00l$ planes is $3{\cdot}0 \times 10^2$ °K. and for reflections from the $h00$ planes is $2{\cdot}8 \times 10^2$ °K. Above 500° K. the intensities fall off more rapidly than expected. At room temperature the expansion coefficient along the c axis is $1{\cdot}4 \times 10^{-5}$/°C. and along the a axis is $4{\cdot}0 \times 10^{-5}$/°C.

Introduction

The compound Mn_2Sb has been studied largely because of its interesting magnetic properties. Heusler (1903–4), Wedekind (1909) and Honda & Ishiwara (1917) contributed to the early studies on this material and recent results are reported by Guillaud (1946), Serres (1947), Néel (1948) and others (e.g. Guillaud, Bertrand & Vautier, 1949), including work on both powdered samples and single crystals whose structure is given by Halla & Nowotny (1936) as tetragonal. Above 240° K. the direction of easy magnetization is along the c axis and below 240° K. it is perpendicular to that axis. The moment at saturation due to the manganese atoms is given as 0·936 Bohr magneton, which is believed to be due to a spin moment of one Bohr magneton reduced slightly by the orbital moment of the $3d^7$ ion. Since manganese atoms occupy two crystallographically different sites in this crystal, it has been postulated that $3d^5$ ions of 5 Bohr magnetons and $3d^7$ ions of 3 Bohr magnetons are mixed in equal amounts and oriented antiparallel, for which case the resultant saturation moment will be one Bohr magneton per manganese atom. Above the ferromagnetic Curie point, 277° C., the reciprocal of the magnetic susceptibility, plotted as a function of temperature, shows a curve strongly concave toward the temperature axis instead of the more usual straight-line relationship.

Using X-ray data from powder, Laue and rotation patterns, Halla & Nowotny (1936) concluded that the tetragonal cell had lattice constants $c = 6{\cdot}56$, $a = 4{\cdot}08$ Å, with two molecules per unit cell, and that the space group is D^7_{4h}–$P4/nmm$. Two Mn_I atoms were located at 0, 0, 0; $\frac{1}{2}, \frac{1}{2}, 0$; two Mn_{II} atoms at $0, \frac{1}{2}, z$; $\frac{1}{2}, 0, \bar{z}$; and two Sb atoms at $0, \frac{1}{2}, z$; $\frac{1}{2}, 0, \bar{z}$. It is stated that for Mn, $z = 0{\cdot}27$ and for Sb, $z = -0{\cdot}30$, exactly the same parameters reported earlier for Cu_2Sb (Howells & Morris-Jones, 1930).

In the course of work with neutron diffraction to determine the magnetic structure of Mn_2Sb, Gingrich, Shull & Wilkinson (1953) found evidence that the parameters given by Halla & Nowotny might not be correct; hence the present work was undertaken to investigate the chemical structure more completely, using X-rays.

Results

First attempts used powdered samples, some made at the Oak Ridge National Laboratory and others made at Missouri. With chromium radiation as many as 32 lines were obtained, but even the best patterns proved to be inadequate for precise parameter determination, perhaps largely because of preferred orientation and strong absorption and fluorescence effects. For example, the 001 reflection was never observed by this method although special attention was given to try to bring it out. Nevertheless, analysis of these powder patterns led to average values of

$$a = 4{\cdot}078,\ c = 6{\cdot}557\ \text{Å},$$

in good confirmation of the earlier work. A thin flake of crystal provided an adequate sample for a Laue pattern, whose symmetry and gnomonic projection confirmed that the face of the flake was parallel to the $00l$ planes and that, within the precision of this determination, c/a was the same as given by Halla & Nowotny. Another crystal fragment used for rotation patterns was rotated about the (370) axis, giving a satisfactory pattern of layer lines from which to determine that $c = 6{\cdot}56$ Å and $a = 4{\cdot}08$ Å, in good accord with published values. However, for an accurate determination of parameters it was recognized that reflections from fairly large single-crystal faces were probably necessary.

Following a modification of the method outlined by Guillaud*, progressively larger single crystals were

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* From a reprint sent by C. Guillaud without specification of its origin.

grown in successively improved runs until single-crystal ingots were obtained large enough to prepare reflection faces up to approximately $1{\cdot}5\times2{\cdot}5$ cm. in area. Back-reflection Laue patterns confirmed earlier evidence that natural cleavage is habitually at $00l$ planes. Preparation by cleaving, sawing, grinding and polishing provided faces parallel to $00l$, $h00$ and $hh0$ planes with surfaces of areas large enough to reflect the entire beam. Mo $K\alpha$ radiation, monochromatized by reflection from a rocksalt crystal, was reflected from Mn_2Sb faces, detected photographically in some runs, but more commonly with a Geiger–Müller counter and associated circuits. For other than room temperatures, the crystal was mounted in an evacuated metal chamber provided with entrant and exit windows of thin aluminum, and temperatures of the crystal mounting close to the crystal face (measured with a thermo-couple) ranged from 100° K. to 600° K. through the use of coolants or heaters.

Reflections from the $00l$ face at room temperature were studied from 001 through 0,0,17, giving the observed integrated reflections R_o listed in Table 1.

Table 1

l	R_o	F_o^2	F_c^2
1	0·219	0·017	0·029
2	2·183	0·508	0·700
3	2·929	1·288	1·294
4	2·108	1·088	1·057
5	0·525	0·265	0·299
6	0·005	0·003	0·001
7	1·000	1·000	1·000
8	0·029	0·033	0·012
9	0·109	0·161	0·158
10	0·132	0·255	0·229
11	0·121	0·298	0·274
12	0·022	0·067	0·055
13	0·000	—	0·0004
14	0·068	0·284	0·246
15	0·006	0·026	0·011
16	0·008	0·035	0·038
17	0·024	0·085	0·046

With a background counting rate of about 80 counts per min., the highest counting rate for 003 was 17,000 counts per min. and for 0,0,17 with α_1 and α_2 completely resolved, it was 300 counts per min.; while for 0,0,13 no reflection could be detected. Corrections for geometrical factors, for polarization and for temperature, using $3{\cdot}0\times10^2$ °K. (see below) for the Debye characteristic temperature, gave F^2 values which led to tentative parameters that were reasonably satisfactory for reflections higher than 004, but for the high-intensity lower-order reflections considerable discrepancies persisted. An arbitrary extinction correction* using $a=0{\cdot}15$ in the relation $R_{\text{corr.}}=R_o/(1-aR_o)$, where R_o is the observed integrated reflection and $R_{\text{corr.}}$ is the corrected value, gave the observed F^2 values listed in Table 1 normalized to $F_{007}^2=1{\cdot}000$. Least-squares analysis led to parameters $z_{\text{Mn}}=0{\cdot}295$ and $z_{\text{Sb}}=-0{\cdot}280$, and F^2 values calculated with these parameters are listed in Table 1. If, as a measure of the comparison between observed and calculated values, a factor R is computed according to the relation $R=\Sigma(|F_o|-|F_c|)\div\Sigma|F_o|$, this factor turns out to be 0·08, a value that tends to give confidence in the correctness of the above parameters.

Reflections from the $h00$ face are shown in Fig. 1.

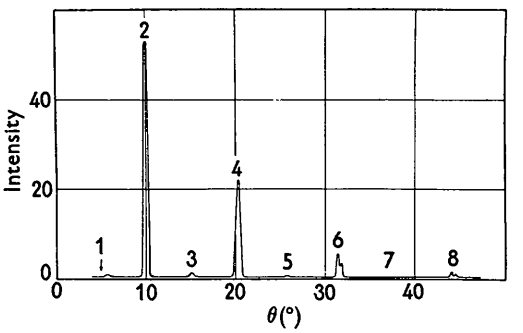

Fig. 1. Observed intensities versus angle for $h00$ reflections from Mn_2Sb.

Integrated reflections for h even were corrected as before, except that the Debye characteristic temperature was $2{\cdot}8\times10^2$ °K. (see below) and in the extinction correction, $a=0{\cdot}17$. Table 2 lists the observed integrated reflection R_o, the observed F^2 values determined this way, and the corresponding values calculated with the parameters given above.

Table 2

h	R_o	F_o^2	F_c^2
2	3·113	1·99	1·97
4	1·000	1·00	1·00
6	0·244	0·530	0·538
8	0·078	0·359	0·309

In this series of reflections those for h odd should not appear, but there are weak reflections at or near the positions for 100, 300 and 500. Careful measurement showed that while the 100, if present, should appear at 4° 59′ the extraneous reflection appeared at 5°39′ and was broader than other reflections; it persisted in about its same relative amount at low temperatures and also with markedly reduced X-ray tube voltage. The other two extraneous reflections with somewhat greater width than regular reflections appeared closer to calculated positions, and they too persisted under a variety of conditions though their weak intensities made accurate measurements difficult.

Reflections from the $hh0$ face were observed for $h=1$, 2, 3 and 4. Their intensities agreed satisfactorily with calculated values using the above parameters, and no extraneous reflections were found in the angular range covered by these reflections.

The effect of temperature on the integrated reflec-

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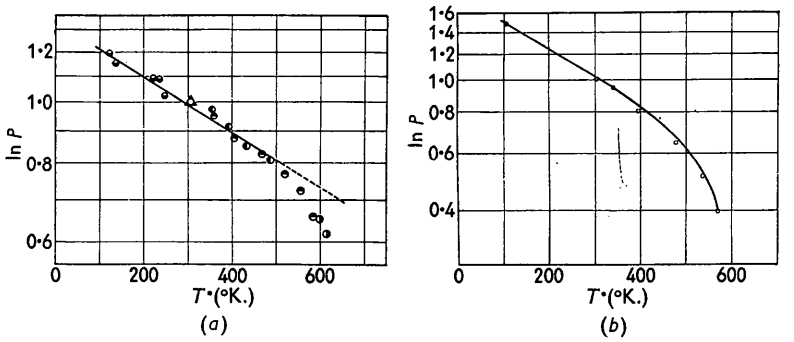

Fig. 2. Logarithm of integrated reflection versus T^* (*a*) for 007 reflection, (*b*) for 600 reflection from Mn_2Sb.

tion was investigated for several sets of planes. Fig. 2(*a*) shows a plot of the logarithm of the integrated reflection from 007 planes at several temperatures ranging from 98° K. to 610° K. The abscissa is $T^* = T(\varphi(x)+\frac{1}{4}x)$, where T is the absolute temperature, $x = \Theta/T$, and $\varphi(x)$ is a function that appears in the expression e^{-2M}, where

$$M = \frac{6h^2}{mk}\frac{T}{\Theta^2}(\varphi(x)+\tfrac{1}{4}x)(\sin^2\theta)/\lambda^2,$$

and m is taken as the average of two Mn atoms and one Sb atom, or 77 atomic mass units. From the slope of the straight-line portion of this curve, it is found that $\Theta = 3{\cdot}0\times10^2$ °K., which is applicable for atomic displacements along the *c* axis. Similar determinations for the 600 reflections in Fig. 2(*b*) lead to $\Theta = 2{\cdot}8\times10^2$ °K. for the straight-line portion of the curve. Fig. 3 presents the variations of lattice constants *a* and *c* with temperature, giving values of the expansion coefficients at room temperature of $4{\cdot}0\times10^{-5}$/°C. for *a* and $1{\cdot}4\times10^{-5}$/°C. for *c*.

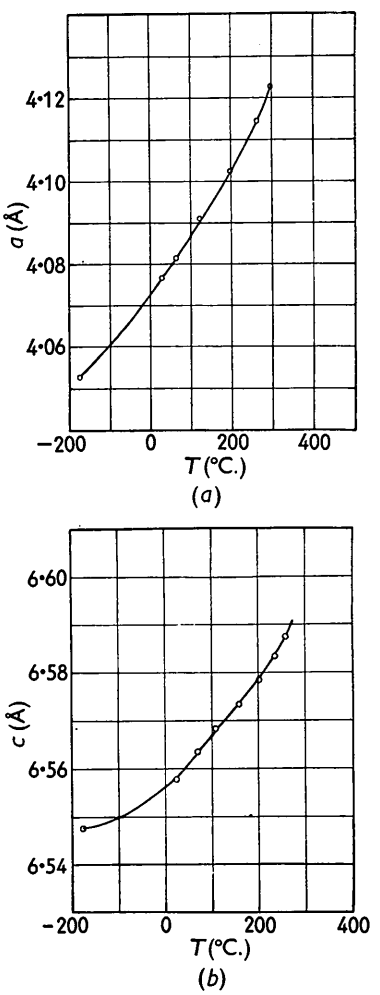

Fig. 3. Variation with temperature of (*a*) the *a* axis, (*b*) the *c* axis in Mn_2Sb.

Discussion

The lattice constants *a* and *c*, as obtained by Halla & Nowotny, have been confirmed from Laue, rotation and powder patterns, perhaps with some improvement in the precision of measurement. However, reflections from large single-crystal faces disclose marked discrepancies between intensities observed and calculated from published values of parameters. Since the parameters are along the *c* axis, reflections from 00*l* planes are well-suited for their determination. Analysis of this series of reflections leads to the values $z_{Mn} = 0{\cdot}295$ instead of the published value 0·27, and $z_{Sb} = -0{\cdot}280$ instead of the published value −0·30. Of the many differences between F^2 values observed and calculated with published parameters, those for 006 and 0,0,13 are outstanding, for the observed values are exceedingly weak or undetectable and the calculated values are much larger than for many reflections which have been observed with considerable intensities. While it is true that a few of the high-intensity reflections could be brought into agreement only with the introduction of an arbitrary extinction correction, this correction had negligible effect on all the higher orders, and parameter calculations made by ignoring the three most intense reflections gave parameters essentially as given here.

Of the other two series of reflections, the *hh*0 series was approximately as expected on a relative basis within the series and inter-comparisons with the 00*l*

series gave closer agreement than was expected. The $h00$ series with corrections for temperature and extinction appear to be quite satisfactory except for very weak reflections at or near positions corresponding to 100, 300 and 500 reflections, which should be absent. If the 100 reflection were present, it should appear at 4° 59′ but the weak extra reflection is found at 5° 39′, an angular separation well outside of experimental error even though the weak reflection seemed to be broader than others and hence cannot be located precisely. If this were due to thermal diffuse scattering, it should show a marked decrease in intensity with decreasing temperature, but at a temperature of −175° C. it persisted in about the same relative amount as at room temperature and hence could not be attributed to thermal diffuse scattering. If it were due to a parasitic reflection of half-wavelength radiation from the monochromatizing crystal, it should diminish in relative intensity as the X-ray tube voltage was lowered, but with the tube operated at 26 kV. instead of the usual 37 kV. the extraneous reflection approximately retained its intensity relative to other reflections and could not be ascribed to this cause. The other two extraneous reflections which were also slightly broader than usual appeared to be close to the positions expected for 300 and 500 reflections respectively, and they also remain unexplained. Another possible origin might be double reflections from planes which happen to be favorably oriented. Initial attempts to explore this possibility were promising, but definite conclusions were not reached. The highest counting rate for the reflection near the 100 position was 0·6% of that for the 200 reflection; for the reflection near 300, it was 1·0%; and for the reflection near 500 it was less than 0·5%. Fully corrected relative values of F^2 show that if $F^2_{200} = 1{\cdot}000$, that for the first weak peak is 0·002, for the second is 0·014 and for the third is 0·006.

In the variation of the integrated reflection with temperature, Fig. 2 shows reasonably good straight-line relationship between ln P versus T^* from 100° K. to about 500° K., giving $\Theta = 3{\cdot}0 \times 10^2$ °K. for 007 planes and $2{\cdot}8 \times 10^2$ °K. for 600 planes. Less extensive runs with other reflections in these series confirmed these values. However, above about 500° K., the intensities fall off more rapidly than at lower temperatures. At times the crystal which had been heated to maximum temperatures was returned to low temperatures where it gave values falling on the straight-line portion of the curves, indicating that the heat treatment did not permanently affect the crystal. If the abnormal drop in intensity were due to a change of parameters, then some of the reflections which are highly parameter-sensitive might change intensity considerably. This was checked qualitatively for the 006 and 0,0,14 with no indication of parameter change. Furthermore, according to the structure determination at room temperature, parameters do not enter into the $h00$ intensities and yet the departure from a straight-line relation sets in at about the same temperature for this series as for the $00l$ series, which is parameter dependent. Without further investigation of this effect it seems necessary to assume a change in the characteristic temperature to account for the curves as shown. An approximate calculation of the r.m.s. atomic displacement leads to a value at room temperature along the c axis of 0·08 Å, and along the a axis of 0·09 Å.

Using the newly determined parameters, each Mn_I atom has four neighbors of type Mn_I at 2·88 Å, four of type Mn_{II} at 2·81 Å and four Sb atoms at 2·75 Å. Each Mn_{II} atom is surrounded by four Mn_I atoms at 2·81 Å, four Sb atoms at 2·89 Å, one Sb atom at 2·79 Å and one Sb atom at 3·77 Å. Each Sb atom has four Mn_I neighbors at 2·75 Å, one Mn_{II} at 3·77 Å, one Mn_{II} at 2·79, and two Mn_{II} at 2·89 Å. The perpendicular distance between planes of Mn_I atoms and puckered planes of Mn_{II} and Sb atoms is 1·87 Å while that between adjacent puckered planes is 2·82 Å. Natural cleavage probably takes place between puckered planes.

It is interesting to note that no abnormal effect upon reflections was observed in the neighborhood of the magnetic transition at 240° K. and that the departure from straight-line relationship between ln P and T sets in at about the ferromagnetic Curie temperature, 277° C.

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