An X-ray and Neutron-Diffraction Investigation of the Magnetic Phase Al$_{0.89}$Mn$_{1.11}$

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X-ray and neutron powder diffraction data show that Al$_{0.89}$Mn$_{1.11}$ is tetragonal, $a = 2.77$, $c = 3.54$ Å, with Al$_{0.03}$Mn$_{0.97}$ at (0, 0, 0) and Al$_{0.86}$Mn$_{0.14}$ at ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$). The manganese magnetic moments of 1.94 Bohr magnetons are along the c-axis, pointing in opposite directions for the two positions. By mechanical deformation the disorder may be increased. These results are shown to be compatible with measured values of the saturation magnetization.

Recently Kono (1958) published a study of the manganese–aluminum system and discussed the structure and properties of a tetragonal ferromagnetic phase with a manganese content of somewhat more than 50 at.%.

This system was investigated independently by Koch, Hokkeling, van der Steeg & De Vos (1960) and from them we obtained the specimens used in the present study.

X-ray work

After a heat treatment described by Koch *et al.* (1960), samples of a composition Al$_{0.89}$Mn$_{1.11}$ appeared from X-ray powder diffraction data to have a primitive tetragonal unit cell with $a = 2.77$ and $c = 3.54$ Å.* The systematic appearance of strong reflexions when the sum of the indices is even and weak ones when it is odd proves a difference in scattering power at 0, 0, 0 and $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$, *i.e.* an ordered structure. As the observed density of 5.16 g.cm^{-3} is in good agreement with the calculated one of 5.17 for 1.11 Mn and 0.89 Al per unit cell, atomic distributions with considerable numbers of unoccupied sites need not be considered. The occupancy of the sites may then be expressed as in Table 1.

Table 1. *Occupancy of positions in unit cell*

	(0, 0, 0)	($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$)	Total
Al	r	$0.89 - r$	0.89
Mn	$1 - r$	$0.11 + r$	1.11

Clearly the disorder parameter r may be chosen in the range 0 to 0.445.

As discussed by Koch *et al.* (1960), the magnetic saturation value of the specimen depends on the

degree of cold work applied to it. For this reason we decided to determine the distribution of Mn and Al over the two sites for two samples having a large difference in magnetic saturation value.

Sample 1 was obtained by sieving a fine-grained fraction out of a hammered and milled specimen.

Sample 2 was obtained by collecting the fine-grained powder loosened from a non-deformed ingot of Mn$_{0.89}$Al$_{1.11}$ when this was used as an electrode in dilute acetic acid. Chemical analysis showed no difference between the two samples, but the magnetic saturation of sample 1 was only 73–76 gauss/g, compared with 96–98 gauss/g for sample 2; the latter value is the same as that found for undeformed rods as used in the neutron-diffraction experiments.

X-ray powder diagrams, taken with a Philips diffractometer, showed rather sharp peaks for sample 2, whereas the peaks obtained with sample 1 were considerably broadened.

Integrated intensities were obtained for a large number of lines for both samples by integrating over the full width of the lines and subtracting background counts as measured over equivalent angular ranges. From these intensities the best fit for r was obtained for both samples by a least-squares treatment. The scattering power of Mn was corrected for anomalous scattering according to the data of Dauben & Templeton (1955). We found $r = 0.13 \pm 0.04$ for sample 1 and $r = 0.00 \pm 0.05$ for sample 2.

We shall see later on that this result agrees with the ratio of the saturation values as calculated from the magnetic structure found in the neutron-diffraction study.

Neutron-diffraction experimental procedure

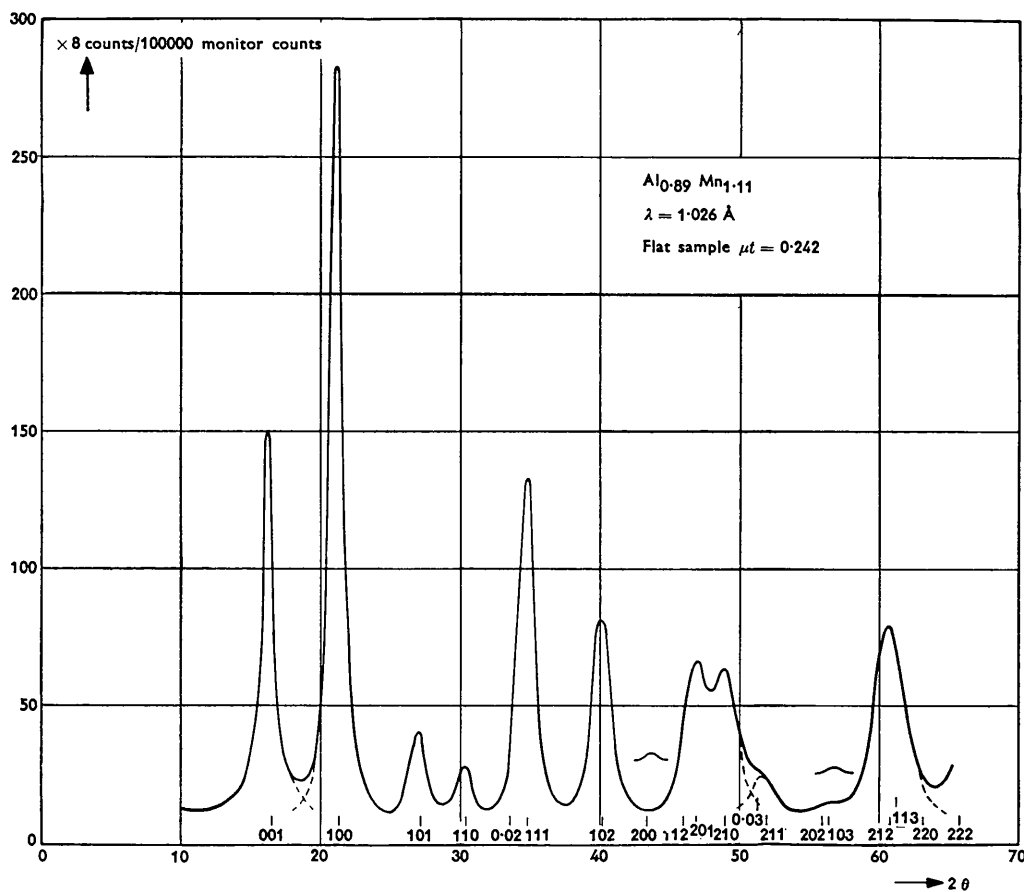In view of the sensitivity of the structure to mechanical deformation the neutron-diffraction data were ob-

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* Kono (1958) in describing essentially the same structure uses a non-primitive cell with an axis $\sqrt{2}$ times as long.

Fig. 1. Neutron diffraction diagram of $Al_{0.89}Mn_{1.11}$. Sample flat, in transmission position, wavelength 1·026 Å, $\mu t = 0.242$. The intensity is given in counts per 12,500 counts in the primary beam monitor.

tained with the alloy as cast, *i.e.* in the form of 50 rods of 3 mm diameter and 70 mm long, heat-treated as described by Koch *et al.* (1960). Fifty of these were stacked together in a close-packed sequence of layers of 17, 16 and 17 rods to form a flat sample, which was then mounted on the neutron diffractometer described by Goedkoop (1957) in the transmission position with the rods perpendicular to the goniometer axis. The wavelength used was $\lambda = 1.026$ Å. Counts were taken at intervals of 0·2° in 2θ. Fig. 1 shows the counting rate with the background subtracted, and with the calculated positions of the reflexions indicated. No other reflexions are seen to occur.

For reasons which will be explained below, it was necessary to measure the diffracted intensities on an absolute scale. This was done by running a flat sample of nickel powder between aluminum windows under identical conditions. The thickness of the nickel layer was chosen equal to the mean outside thickness of the array of rods. The mass per cm² of both samples was obtained by weighing, and the absorption by determining the neutron transmission through each. The last column of Table 2 shows the measured intensities with the estimated error due to counting

statistics only. These intensity values should be compared with those calculated from the equation:

$$I_{hkl} = 10^{24} j_{hkl} \ (\sin 2\theta_{hkl})^{-2}.\exp(-\mu t \sec \theta_{hkl})$$
$$\times \exp -B \ (\sin \theta_{hkl}/\lambda)^2.(F^2_{hkl,\,nucl} + q^2_{hkl}.F^2_{hkl.\,magn}), \quad (1)$$

where j_{hkl} is the multiplicity of reflexion hkl, θ_{hkl} its Bragg angle, and $F_{hkl,nucl}$ and $F_{hkl,magn}$ the nuclear and magnetic structure factors in cm. In the absorption factor, μt was found to be 0·242 from the measurement of the neutron transmission. As usual q_{hkl} is defined as the sine of the angle between spin direction and scattering vector.

Determination of the disorder parameter r from the neutron data

Using Table 1 and the tabulated scattering lengths $b_{Al} = +0.35.10^{-12}$ cm and $b_{Mn} = -0.36.10^{-12}$ cm, one finds for the nuclear structure factors:

for $h+k+l$ even, $F_{hkl,nucl} = -0.09.10^{-12}$ cm ,
for $h+k+l$ odd, $F_{hkl,nucl} = (-0.63 + 1.42r).10^{-12}$ cm.

(2)

Table 2. *Observed and calculated intensities*

hkl	Magn. angle factor q^2	Magn. form factor f	Calculated intensity				Observed intensity*
			Nucl. part	Magn. part		Total	
001	0·00	—	6·56	0·00		6·56	6·70 ± 0·12
100	1·00	0·68	8·00	3·59		11·59	11·66 ± 0·11
101	0·62	0·54	0·22	0·98		1·20	1·32 ± 0·08
110	1·00	0·45	0·09	0·44		0·53	0·73 ± 0·07
002	0·00	—	0·03	0·00	0·03 ⎫	6·68	6·47 ± 0·12
111	0·77	0·34	6·12	0·53	6·65 ⎭		
102	0·29	0·28	4·61	0·10		4·71	4·52 ± 0·10
200	1·00	0·20	0·05	0·05		0·10	0·12 ± 0·06
112	0·45	0·19	0·08	0·03	0·11 ⎫		
201	0·86	0·18	3·45	0·10	3·55 ⎪		
210	1·00	0·15	3·18	0·07	3·25 ⎬	7·79	8·20 ± 0·19
003	0·00	—	0·73	0·00	0·73 ⎪		
211	0·89	0·11	0·12	0·03	0·15 ⎭		
202	—	—	0·05	—	0·05 ⎫	0·11	0·14 ± 0·08
103	—	—	0·05	—	0·05 ⎭		
212	—	—	4·33	—	4·33 ⎫	6·48	6·26 ± 0·12
113	—	—	2·15	—	2·15 ⎭		

* The error indicated in the last column is only that due to counting statistics.

Inspection of the diagram at larger scattering angles, where the magnetic structure factors are essentially zero, shows that in fact the reflections with $h+k+l$ even are barely visible, whereas those with $h+k+l$ odd have quite appreciable intensities. From the latter the disorder parameter r could be determined as well as the coefficient B in the temperature factor. The fourth column in Table 2 shows the nuclear part of the intensities calculated with the values finally adopted for these parameters, $r=0\cdot03$ and $B= 1\cdot34.10^{-16}$ cm².

Determination of the magnetic structure

Since there is manganese in both $(0, 0, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, two possibilities must be considered. In the one the spins in the two positions are parallel, in which case:

for $h+k+l$ even,

$$F_{hkl,\mathrm{magn}} = 1\cdot11 \times 0\cdot539Sf.10^{-12} \text{ cm},$$

for $h+k+l$ odd,

$$F_{hkl,\mathrm{magn}} = (0\cdot89 - 2r) \times 0\cdot539Sf.10^{-12} \text{ cm}, \qquad (3)$$

where S is the manganese spin quantum number and f the magnetic form factor. In the other case they are antiparallel and the above structure factor expressions must be interchanged.

The magnetic structure was mainly determined from the first four reflexions, which are well-resolved and for which the magnetic structure factors should be largest. It is seen from Table 2 that the intensity of the first of these, 001, can be fully accounted for by the nuclear scattering; hence it was concluded that $q_{001} = 0$, which means that the spins are directed along the c-axis. The q's for the other reflexions could now be calculated; their values are given in the second column of Table 2. The third column gives values for the magnetic form factor f calculated

from Pauling & Sherman's screened hydrogenic wave-functions, which have been found to give good agreement for some other manganese compounds (*e.g.* Shull & Wollan, 1956).

Table 3. *Calculation of manganese spin quantum number*

hkl	$h+k+l$	S for spins parallel	S for spins anti-parallel	S for spin $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ non-aligned
100	odd	1·26 ± 0·02	0·95 ± 0·02	1·10 ± 0·02
101	even	0·77 ± 0·03	1·01 ± 0·04	0·89 ± 0·04
110	even	0·88 ± 0·04	1·16 ± 0·06	1·02 ± 0·05
Weighted mean		1·08 ± 0·02	0·97 ± 0·02	1·05 ± 0·02
r.m.s. deviation		0·22	0·06	0·08

For the remaining three of the first four reflexions the magnetic structure factors were now obtained from the difference between the observed and calculated nuclear intensities, using the tabulated q values. Then, using (3) and the tabulated values of f, a value of the spin quantum number S was calculated for each reflexion for both of the two possible relative orientations of the spins. The results are shown in Table 3. It is seen that one obtains much better consistency between the S values calculated for different reflexions if one assumes the spins to be antiparallel, and it was therefore concluded that this is indeed so. This conclusion rests on the assumption of a definite angular dependence of the form factor, but it is easily seen that a highly unusual form factor must be assumed in order to give consistent S values for the parallel spin arrangement.

The agreement could still be improved by allowing the manganese atoms in different crystallographic positions to have different spin quantum numbers. In view of the fact that the two positions have totally different average surroundings this would not be at all

unreasonable. The same phenomenon has in fact been observed in the case of $AlFe_3$ by Nathans, Piggot & Shull (1958) through the use of polarized neutrons. In the present case, where only unpolarized-neutron data for three reflexions are available, it could hardly be significant to consider more than the simplest possibilities. Therefore only one additional model has been worked out, viz. no magnetic alignment of the spin of the Mn atom at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The spin quantum numbers thus calculated are given in the last column of Table 3. They are only slightly less consistent than those in column 4. However the combination with X-ray and magnetic data will be shown further to support the assumption of antiparallel alignment.

Summary of the neutron diffraction results

The final values of the neutron intensities are shown in the penultimate column of Table 2. They are based on the parameter values so far established: disorder parameter $r = 0.03$, spin quantum number $S = 0.97$, antiparallel orientation along the c-axis, Pauling & Sherman's electron distribution of Mn and a temperature factor coefficient $B = 1.34 . 10^{-16}$ cm².

Comparison with the observed intensities shows deviations which on the whole are slightly less than twice the estimated counting errors, which is quite reasonable considering the various other uncertainties. From these deviations one might estimate the error in r to be about 0.01 and in S about 0.02. Further errors might be due to a faulty inter-calibration of the sample and the nickel powder standard. An error here of 10%, which is unlikely, would lead to an error of 0.02 in r and of 0.05 in S.

Absolute determination of the intensities is important in this work; contrary to the X-ray case, because of the almost opposite nuclear scattering lengths of Al and Mn, the reflexions with $h + k + l$ even, which do not depend on the disorder parameter r, are so weak as to be hardly discernible, whereas those with $h + k + l$ odd, which are very sensitive to r, are strong. Of course, r may be determined from the ratio between the nuclear intensities of the two classes of reflexions, but only with a relatively large error. Hence there would remain an equally large error in the normalization of the intensities and therefore also in the determination of the magnetic moment. In short, without an absolute measurement the accuracy of the latter becomes simply equal to the accuracy with which the weak reflexions can be measured, and this, as may be seen from Table 2, is of the order of 50%!

With the parameter values found in this investigation the structure is as follows, a gyromagnetic ratio of 2 being used:

In position (0, 0, 0):

0.03 Al + 0.97 Mn, + 1.88 Bohr magnetons.

In position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$:

0.86 Al + 0.14 Mn, −0.28 Bohr magneton.

Comparison of neutron, X-ray and magnetic data

The value of the disorder parameter r as derived from the neutron intensities is seen to agree with the value quoted earlier from X-ray work on an equivalent sample, confirming that in the undeformed material the one position in the unit cell is almost exclusively occupied by manganese.

The magnetic structure as derived from the neutron diagram may be compared with the saturation magnetization of 97 gauss/g measured in the same sample. It corresponds to 1.47 Bohr magnetons per unit cell, which must be compared with a net moment of 1.60 Bohr magneton found from the neutron data, with the assumed form-factor. This relatively good agreement gives further support to the conclusion that the spins at the two positions in the unit cell are oppositely directed. In fact, the measured saturation magnetization, with $r = 0.03$, leads to spin values per manganese atom of 0.66, 0.89 and 0.76 respectively, depending on whether one assumes the spin at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ to be parallel, antiparallel or non-aligned with respect to that at 0, 0, 0. These values may be compared with 1.08 ± 0.02, 0.97 ± 0.02 and 1.05 ± 0.02 derived for the three cases from the neutron work (Table 3). The errors stated for the neutron work are only the counting errors and considering the other uncertainties involved the agreement for the antiparallel arrangement is as good as one could expect.

The X-ray and saturation data by themselves also support the conclusion of antiparallel alignment since they show that the saturation magnetization decreases rapidly with increasing disorder. Taking $r = 0.13$ for sample 1 and 0.03 for sample 2, the ratio between saturation magnetizations should be

$$\sigma_1/\sigma_2 = (0.89 - 2r_1)/(0.89 - 2r_2) = 0.76 ,$$

whereas the measured ratio is 0.78 ± 0.02. For parallel spins this ratio should obviously not depend on r, whereas with the spins at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ unaligned it would have the value 0.88.

For a full description of the magnetic behaviour we refer to Koch et al. (1960).

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