Magnetic Structure of Mn_4N†

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The magnetic structure of Mn_4N has been determined by neutron diffraction from powders. The cubic unit cell has Mn at the corner and face centers and N at the body center. Standard diffraction techniques led to four possible models and it was necessary to perform polarized neutron beam experiments to resolve this ambiguity. The structure is ferrimagnetic with a corner moment of $3.5\mu_B$ antiparallel to the three face center moments of $0.7_7\mu_B$.

I. INTRODUCTION

SEVERAL studies have been made on the preparation, structure, and magnetic properties of the transition metal nitrides.[1–9] The nitrides with composition T_4N have a simple structure composed of metal atoms at the points of a face centered cubic lattice with nitrogen at the body-center position of the unit cell. Such compounds have been prepared with T equal to Mn, Ni, and Fe and with partial substitution of these metals by Ni, Zn, Cu, and Pt. Several models have been proposed for the magnetic structure of these compounds. Frazer[9] showed that the neutron diffraction data for Fe_4N could be explained by a model proposed by Wiener and Berger[3] in which nitrogen was assumed to be an electron donor to the 3-*d* shell of the face-center atoms. The Fe moments (of $3\mu_B$ and $2\mu_B$ for the corner and face-centered atoms, respectively) are aligned ferromagnetically to give the total moment of 9 Bohr magnetons per unit cell. However, Mn_4N has a total moment of $1.2\mu_B$ per unit cell.[5] To explain this low value, various models, shown in Table I, have been proposed, all of which assume a ferrimagnetic arrangement of the individual moments. A neutron diffraction study was made in an attempt to determine the magnetic structure of this compound directly.

II. SAMPLE PREPARATION

The Mn_4N powder was prepared by following the procedure of Mah.[10] Nitrogen gas was passed for 24 to 36 hr over approximately 15 g of Mn powder heated to 1000°C. X-ray examination of the inner and outer portions of the resultant slugs did not reveal any differences, both showing the presence of the ζ phase, Mn_2N. A pure sample of Mn_4N was not obtained although one run showed only faint traces of Mn_2N. All runs showed a lattice constant for Mn_4N of 3.865 ± 0.002 A. Since the quantity of the best product was not sufficient for the diffraction analysis, several of the better preparations were combined and ground to 300 mesh to give the final sample. Chemical analysis of this sample gave a Mn/N ratio of 4/1.06. Since the diffraction lines of Mn_2N are visible on the x-ray photographs, it seems probable that at least a large part of the excess nitrogen is due to the presence of this phase. The magnetic measurements of the "pure" sample gave a moment per unit cell of $0.85\mu_B$ at 298°K and $1.17\mu_B$ at 77°K. However, the values from the diffraction sample were lower, 0.72 and $0.98\mu_B$ respectively (minimum values uncorrected for impurities). The measurements were made with an applied field of 12 000 oersteds. An extrapolation of these moments to infinite field and 0°K would increase them so that the $1.20\mu_B$ value of Juza and Puff[5] would fall between them. Although the saturation moment was used in the calculation of the individual atomic moments during the course of the structure determination, the results were not very sensitive to the value used. Since a 10% variation produced a change of less than $0.03\mu_B$ in the individual moments, the values for the pure sample were used in the final calculations.

The blocks used for the polarized neutron experiments were made by treating pressed powder, 1 in.

TABLE I. Models proposed for Mn_4N. Atomic moments in Bohr magnetons for the atoms with coordinates as given in the table.

	Mn_1 (000)	Mn_2 $(\frac{1}{2}, \frac{1}{2}, 0)$	Mn_3 $(\frac{1}{2}, 0, \frac{1}{2})$	Mn_4 $(0, \frac{1}{2}, \frac{1}{2})$
Wiener and Berger[3]	+4	+3	−3	−3
Guillaud[2]	−5	+2	+2	+2
Juza and Puff[6]	+3.2	+2	−2	−2

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* Diffraction experiments conducted while a Guest Scientist at Brookhaven National Laboratory.

[1] C. Guillaud and J. Wyart, Compt. rend. **222**, 71 (1946).
[2] C. P. Guillaud, Revs. Modern Phys. **25**, 119 (1953).
[3] G. W. Wiener and J. A. Berger, J. Metals **7**, 360 (1955).
[4] V. Zwicker, Z. Metallkund **42**, 274 (1951).
[5] R. Juza, H. Puff, and F. Wagenknecht, Z. Electrochem. **61**, 804 (1957).
[6] R. Juza and H. Puff, Z. Electrochem. **61**, 810 (1957).
[7] N. Terao and A. Bughezan, J. Phys. Soc. Japan **14**, 139 (1959).
[8] J. B. Goodenough, A. Wold, and A. Arnott, J. Appl. Phys. **31**, (1960).
[9] B. C. Frazer, Phys. Rev. **112**, 751 (1958).
[10] A. D. Mah, J. Am. Chem. Soc. **80**, 2954 (1958).

$\times 1$ in.$\times\frac{1}{4}$ in, for 48 hr with N_2. The product was a solid block which could be cut with a diamond saw to obtain the desired sample size.

III. DETERMINATION OF THE STRUCTURE

A. Unpolarized Neutron Experiments

Powder diffraction patterns were obtained at room and liquid nitrogen temperatures. For the former, the powder was encased in a $\frac{7}{8}$-in. diameter, thin-walled silica cylinder. The low-temperature patterns were taken with the powder in a flat, $\frac{1}{4}$-in, thin walled Al sample holder. The first three peaks were also scanned at 77°K with a magnetic field of 6200 oersteds applied parallel to the scattering vector. The low-temperature runs are shown in Fig. 1. The observed intensities are given in Table II after correction for the appropriate Lorentz factors. No absorption corrections were made. The (111) peak, which consists primarily (99.6%) of nuclear scattering, was used to scale the room temperature measurements. An average scale factor was used for

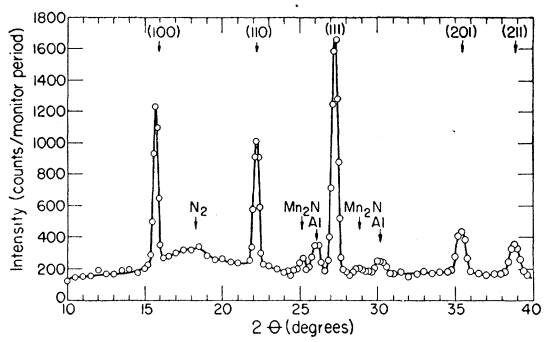

FIG. 1. Neutron diffraction pattern of Mn_4N powder at 77°K. $\lambda = 1.05$ A.

the 77°K data. The calculated nuclear scattering intensity is also given in the table. The nuclear scattering lengths of -0.36×10^{-12} cm for b_{Mn} and 0.94×10^{-12} for b_N were taken from the compilation of Shull and Wollan.[11]

Two assumptions were made in deriving the magnetic structure. These were:

(1) Only one magnetic axial direction is present, i.e., Yafet-Kittel angles were not considered.
(2) The moments of the three face-centered Mn atoms are equal in magnitude. This assumption will be examined later.

From the data, it is immediately obvious that the magnetic moments must be aligned ferrimagnetically since a ferromagnetic arrangement cannot result in a large magnetic contribution to the (100) and (110) maxima if the total moment is kept small. These two

[11] C. G. Shull and E. O. Wollan in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1956), Vol. 2.

TABLE II. Intensity data for Mn_4N. Observed intensities corrected for the appropriate Lorentz factors. Scaled to (111) with an average scale factor used for the 77°K data. $\lambda = 1.05$ A.

hkl	300°K	77°K No field	77°K Magnetic field	I_{nuc}(calc)
100	7.66	8.27	4.82	5.28
110	13.9	14.7	9.9	10.6
111	45.5	46.1	44.7	45.3
200	1.7			1.5
210	20.9	20.7		21.1
211	20.3	18.8		21.1
221\ 300/	21.8			26.4
301	16.3			
311	122			141

peaks, which are the only ones with large magnetic intensities, were used to derive the magnetic moments. There are other peaks with the same structure factors, but the rapid angular fall off of the magnetic form factor almost eliminates their magnetic intensity components.

Examination of the possible models showed two types of configurational symmetry (as defined by Shirane[12]): cubic with the three face-center moments antiparallel to the corner moment, and tetragonal with the two face-center moments at $z=\frac{1}{2}$ antiparallel to the one at $z=0$. The magnetic structure amplitudes for the two types of symmetry are shown in Table III. The nuclear scattering factor is the same for both. The numbering scheme is given in Table I. The p_i are the atomic magnetic scattering factors which are related to the magnetic moment μ_i by a constant and a magnetic form factor.[13] The Mn^{+2} form factor curve was used in the calculations. The structure-dependent portion of the intensity is given by:

$$I=\sum j_i(F_{inuc}{}^2+\langle q^2\rangle_i F_{imag}{}^2),$$

where i refers to the nonequivalent reflection at a given angle; j_i=multiplicity; $\langle q^2\rangle_i$ the average value of $\sin^2\alpha$ for the ith reflection where α is the angle between the scattering and magnetic vectors; and F_i=structure factor for the ith reflection.

In the case of cubic models, $\langle q^2\rangle$ is equal to $\frac{2}{3}$, independent of the magnetic axis, and all (100) reflections are equivalent, as are all (110). Therefore, the only

TABLE III. Structure factors for Mn_4N. Derived with assumptions mentioned in text. Summations to be made over all Mn.

Indices	F_{nuc}	F_{mag} Cubic	F_{mag} Tetragonal
All even	$4b_{Mn}+b_N$	$\sum p_i$	$\sum p_i$
All odd	$4b_{Mn}-b_N$	$\sum p_i$	$\sum p_i$
Mixed $h+k$ even	$\pm b_N$	p_1-p_2	p_1+3p_2
Mixed $h+k$ odd	$\pm b_N$	p_1-p_2	$\sum p_i$

[12] G. Shirane, Acta Cryst. **12**, 282 (1959).

[13] For convenience, the algebraic sign of p_i and μ_i is assumed to be positive if the spin direction is parallel to the net moment of the unit cell, and negative if antiparallel.

TABLE IV. Models from powder diffraction data. Magnetic moments given in Bohr magnetons. Positive direction defined as direction of net moment.

Model	300°K		77°K	
	μ_1	μ_3	μ_1	μ_3
Cubic I	2.9	-0.6_8	3.5	-0.7_7
Cubic II	-2.6	1.1	-2.9	1.4
Tetragonal I	2.1	-1.3	2.7	-1.5
Tetragonal II	-0.8_8	1.7	-0.9_1	2.1

parameter, p_1-p_2, or equivalently, $\mu_1-\mu_2$, can be calculated directly from both the (100) and (110) magnetic scattering. This gave $4.2_9\mu_B$ (an average of 4.3_3 and $4.2_5\mu_B$) at 77°K for the absolute sum of the corner and one face-center moment. In order to calculate the value of the individual moments, the value of $\sum \mu_i$ (or some other function of the μ_i's) is needed. While this is available from the reflections with h, k, and l all even or all odd, the magnetic contribution to these reflections is very small and difficult to determine accurately. Therefore, the measured saturation moment ($1.17\mu_B$ at 77°K) was combined with the foregoing result to solve for the atomic moments. However, defining the direction of the net moment as positive, $\mu_1-\mu_2$, which has the same sign as the (100) structure factor, can be either negative or positive. These possibilities lead to the two solutions shown in Table IV. The moments obtained by assuming a positive sign are numbered I, and those from a negative sign, II. The results of a similar analysis of the room temperature data are also shown.

In the case of the tetragonal model, the determination of the moments is not as direct as for the cubic symmetry. All of the reflections at a given angle are not equivalent, and not only the magnetic structure factor but also the $\langle q^2\rangle_i$ values are different. However, for the $h+k$ odd reflections, the magnetic structure factor can be calculated from the saturation magnetization and is very small. Although $\langle q^2\rangle_i$ is a function of the orientation of the magnetic axis, by assuming a median $\langle q^2\rangle$ (values range from $\frac{1}{2}$ to 1), approximations can be made for the magnetic scattering by (100) and (101) tetragonal planes. The relatively small intensities so obtained can be subtracted from the total magnetic intensities to give reliable values for the large (001) and (110) magnetic scattering. One can then calculate $\mu_1+3\mu_2$ as a function of the angle ϕ between the magnetic axis and the c axis. This dependence is shown in Fig. 2. It is evident from the figure that the magnetic axis must make about the same angle with the tetragonal c axis as [111]. At 300°K $\mu_1+3\mu_2$ is equal to 6.0_5, and 7.2_3 at 77°K. As before, this leads to two sets of possible atomic moments. These are shown in Table IV. Tetragonal model I was derived assuming a positive structure factor for (001).

Thus, there are four models which satisfy the neutron powder diffraction data. None of them are in good agreement with models which have been proposed previously. Tetragonal I is similar to that of Juza and Puff[5] but the moments are lower: 2.7 and $1.5\mu_B$ as compared to their 3.2 and $2\mu_B$.

B. Polarized Neutron Experiments

It was possible to choose between the four models by the use of polarized neutrons. This technique has been described previously[14,15] and only the pertinent relationships will be given here.

The magnetic and nuclear scattering amplitudes interact coherently in the diffraction of polarized neutrons. With a magnetic field applied perpendicular to the scattering vector to align the atomic moments, the neutron polarization directions parallel or antiparallel to the field give a total structure factor of

$$F=F_{\text{nuc}}\pm F_{\text{mag}},$$

where the negative sign applies to the antiparallel case.

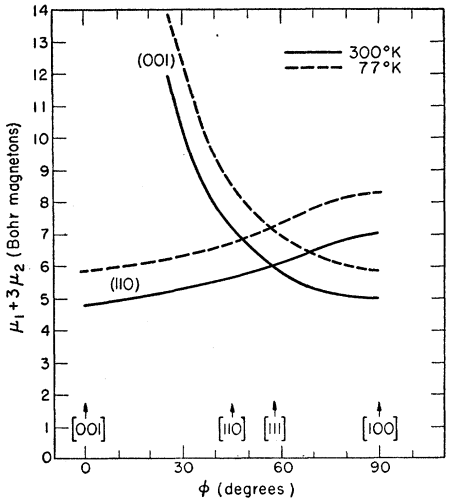

FIG. 2. The value of $\mu_1+3\mu_2$ as a function of the angle ϕ between the c axis and magnetic axis if a tetragonal model is assumed.

Thus from qualitative considerations of the change in intensity with change of polarization direction, the direction of net magnetization relative to the direction of the corner moment can be determined, i.e., a choice can be made between Type I and Type II models. The difference between a cubic and tetragonal model can be distinguished only by a quantitative study. The observed intensity is affected by the initial degree of polarization, by depolarization in the sample, and by the "flipping efficiency" of the rf field in reversing the direction of polarization. For antiparallel polarization the structure dependent part of the intensity is given by:

[14] R. Nathans, C. G. Shull, G. Shirane, and A. Andresen, J. Phys. Chem. Solids **10**, 138 (1959).
[15] C. G. Shull, E. O. Wollan, and W. C. Koehler, Phys. Rev. **84**, 912 (1951).

$$I \text{ (antiparallel)} = \sum_i j_i \left\{ 0.95\phi \left(\frac{D+1}{2} \right) (Fi_{\text{nuc}} - Fi_{\text{mag}})^2 + \left[1 - 0.95 \left(\frac{D+1}{2} \right) \right] [Fi_{\text{nuc}}^2 + Fi_{\text{mag}}^2] \right\},$$

where 0.95 = initial polarization, ϕ = flipping efficiency, and D = depolarization factor, For parallel orientation, ϕ is dropped and the difference in F's is replaced by their sum. The second term is small and is significant only for the smaller of each intensity pair.

In order to minimize depolarization of the beam, a small sintered block, $\frac{1}{8} \times \frac{1}{4} \times \frac{3}{4}$ in.^{3}, was used as a sample. The depolarization factor and flipping efficiency were determined as 0.96 and 0.99 respectively by analyzing the transmitted beam with a Co single crystal. Because of the small sample, the diffracted intensity was very low, particularly for the smaller of each pair of intensities. Therefore, it was necessary to determine the intensities by setting the counter at the peak maximum instead of scanning. Background was measured by moving the counter 1.5 to 2.0° off peak. The experiments were conducted at room temperature with results as shown in Table V.

TABLE V. Polarized neutron diffraction intensities for Mn_4N. Measured on sintered block at room temperature. The starred observed intensities are to be compared with the calculated small intensities.

hkl	Observed intensity		Calculated ratio		Calculated small intensity	
	Parallel	Anti-parallel	Cubic	Tetragonal	Cubic	Tetragonal
100	16*	417	0.045	0.20	19	83
110	355	17*	14	4.5	25	79
111	257*	310	0.82	0.82	254	254

The observed intensity for (100) is small for parallel and large for antiparallel polarization.[16] Since the nuclear structure factor is always negative for this reflection, the magnetic structure factor must be positive. Therefore, the Type II models are eliminated leaving two possible models, one cubic and one tetragonal. A similar analysis for the (110) reflection produces the same conclusion. The ratio of intensities to be expected for each model is shown in Table V. Since the lower of each pair of observed intensities is so small, their ratio is extremely sensitive to errors. The calculated ratios have been used with the observed large intensity to obtain the calculated small intensity given in Table V. Only the cubic model is seen to agree with the observed (starred) values.

The question arises as to whether the data could be in error sufficiently to enable it to fit the tetragonal model. To obtain agreement, the values used for the initial polarization, the depolarization factor, and the flipping efficiency would have to be increased. However, since all these factors are very close to their maximum value of one, it is not possible to obtain a significant change. Another potential source of error is in the measurement of the background. The smaller of each intensity pair is very close to background which is approximately 100 in each case. If the true background was smaller, it could cause the required decrease in the intensity ratio. However, the background, measured without a sample, was 70. Even with this minimum value, the intensity would not increase sufficiently to give agreement with the tetragonal model.

There is one process by which the tetragonal model could give the observed high ratio. A large change in intensity with change in polarization direction requires all the reflections at a given angle to have a large magnetic contribution. However, in a powder composed of randomly oriented tetragonal crystallites, two-thirds of the reflections of the form (100) or (110) have $h+k$ odd. These have a small magnetic component and thus limit the intensity ratio. Since the sample used was sintered and composed of crystals which are crystallographically cubic, preferred orientation in the usual sense should have no effect. However, it is conceivable that upon application of a magnetic field perpendicular to the scattering vector a rearrangement of the magnetic spin alignment occurred such that all of the reflections were converted to the form $h+k$ even. This possibility was tested by use of a perpendicular magnetic field with unpolarized neutrons. In this experiment, the tetragonal model predicted large increases in intensity upon application of the magnetic field, whereas the only change expected for the cubic model was that $\langle q^2 \rangle$ would increase from $\frac{2}{3}$ to 1. The intensity changes calculated for the (100) reflection for the tetragonal and cubic models were increases of 62% and 15.5% respectively. The experimentally observed change was 15.2 $\pm$1.8%, leading to the conclusion that the cubic model was correct.

As mentioned initially, in deriving the structure, it was assumed that the three face-centered Mn atoms had equal moments. This seemed reasonable in view of the chemical similarity of the environments of these atoms. However, with a tetragonal model, there is at least a formal difference in environment between the Mn at $z=0$ and the two at $z=\frac{1}{2}$. Therefore, this assumption was examined.

A calculation was made assuming that only two of the face-centered moments were equal. Since the resulting symmetry is tetragonal, the equations were a function of the orientation of the magnetic axis. Solutions were obtained by assuming various orientations. In each case the results were similar, one solution being close to the cubic model while the others were in disagreement with the polarized neutron experiments. The

[16] Here, as in Table V, the designation (100) is meant to include both the (100) and (001) type reflections when tetragonal symmetry is considered.

largest deviations from cubic symmetry that were still compatible with the polarized beam data occurred at the two extreme cases of magnetic axis orientation, the magnetic axis making a 0° or 90° angle with the c axis. For the 90° orientation the moments were 3.6, -0.8_3, -0.8_3, and $-0.6_7\mu_B$ while for 0° they were 3.5, -0.7_4, -0.7_4, and $-0.8_5\mu_B$. Since a change of less than 5% in either the (100) or (110) magnetic intensity would re-establish the cubic symmetry, these deviations were not considered significant.

IV. DISCUSSION

On the basis of the foregoing analysis, it is concluded that the magnetic structure of Mn_4N is cubic with moments of about $0.8\mu_B$ for each of the face-center Mn atoms, and a moment of about $3.5\mu_B$ for the corner Mn. The face-center moments are all antiparallel to the corner moment. The nearest neighbors of the corner Mn are twelve antiparallel face center Mn at 2.72 A, eight N at 3.33 A, and six parallel Mn at 3.86 A. The nearest neighbors of the face center Mn are two N at 1.93 A, eight parallel face center Mn at 2.72 A, and four antiparallel corner Mn at 2.72 A.

This magnetic structure does not agree with any of the previously proposed models. The cubic antiparallel spin configuration is the same as that of Guillaud,[2] but the moment magnitudes are significantly smaller than those of his model. The corner Mn moment of $3.5\mu_B$ agrees fairly well with the moment of $3.2\mu_B$ proposed for this site by Juza and Puff,[6] but their face-center moments are too large, and their spin configuration is tetragonal. Juza and Puff assumed that the corner Mn, not being bonded with the body center N, would be in the same state as in manganese metal, for which they assumed an electronic assignment of $3d^{6.8}4s^{0.2}$. The corner moment of $3.2\mu_B$ was derived from this by applying Hund's rule of maximum multiplicity. The face-center moment of $2\mu_B$ was derived, in effect, by applying Hund's rule to a $3d^8$ configuration. The extra electron came from nitrogen $2p$ in bonding.

It is clear that the small moment of $0.8\mu_B$ obtained for the face-center Mn atoms in the present study cannot be interpreted by a straightforward application of Hund's rule to some reasonable electronic configuration. While this is a somewhat unexpected result, since Hund's rule does seem to be applicable in the case of the closely related Fe_4N structure,[9] it is perhaps explicable in terms of the anomalous behavior observed for Mn in its various metallic phases and in certain compounds.[17–19] As will be shown below, Hund's rule appears to be applicable in the case of the corner moment of $3.5\mu_B$.

In a neutron diffraction study of the Cu-Mn alloy system Bacon *et al.*[18] found a moment of $2.4\mu_B$ for Mn in the antiferromagnetic face centered tetragonal γ-Mn structure. Using the band structure concept, this moment was accounted for by assuming a $3d^64s$ configuration with $4.2\uparrow d$ and $1.8\downarrow d$ electrons. A similar approach can be used to account for the observed moments in Mn_4N if reasonable outer electron configurations can be assumed for the two different Mn atoms in the structure. The corner Mn probably is in very nearly the same state as metallic Mn, as was assumed by Juza and Puff. Taking this to be $3d^{6.4}4s^{0.6}$ (after Bozorth[20]), one obtains $5.0\uparrow d$ and $1.5\downarrow d$ electrons. Thus, in this case, it appears that Hund's rule can be used. The face-center Mn atoms are assumed to "gain" an electron by bonding with nitrogen. This assumption, which also was made by Juza and Puff, is supported by the Fe_4N results,[9] and by the magnetic measurements of Wiener and Berger[3] on Fe_3PtN and Fe_3NiN. The assumed electronic configuration is then $3d^{7.4}4s^{0.6}$, which leads to $4.1\downarrow d$ and $3.3\uparrow d$ electrons.

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[19] L. Pauling, *Nature of Chemical Bond* (Cornell University Press, Ithaca, New York, 1958), pp. 186, 415.
[20] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1951), p. 436.