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Antiferromagnetic Structure of α-Manganese and a Magnetic Structure Study of β-Manganese*

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Neutron diffraction data have been obtained at 4.2°K and 298°K for both α-Mn and β-Mn. The pattern of moment alignment in the antiferromagnetic state of α-Mn is deduced. Dependent on interatomic distance, both parallel and antiparallel spin couplings are present. Also, for one kind of atom no moment alignment occurs. The magnitudes of the individual moments appear to exceed considerably one Bohr magneton. No coherent magnetic scattering is detectable for β-Mn at 4.2°K. The effect of atomic separation and of atomic arrangement on magnetic structure is discussed.

I. α-MANGANESE

Introduction

IN recent neutron diffraction studies Shull and Wilkinson[1] have shown α-Mn to be antiferromagnetic with a Néel temperature of 100°K. The antiferromagnetic structure gives rise to several new reflections for odd $h+k+l$, in addition to the nuclear peaks of the body-centered atomic arrangement, suggesting that spins of opposite sign are associated with atoms related by the body-centering. The relative intensities of the "magnetic" reflections, however, are such as to exclude a structure with this alignment of spins and with the same moment on each manganese atom. No solution of the magnetic structure was given by Shull and Wilkinson.

In view of our interest in the manganese structures and since we have the means of obtaining neutron diffraction patterns with higher resolution, we have re-examined α-Mn at 4.2°K, 47°K, and 298°K. From this information we have been able to deduce several significant features of the antiferromagnetic structure of α-Mn. We were encouraged to undertake this investigation because of a detailed knowledge of the atomic arrangement in α-Mn. Mr. R. Waterstrat of our Laboratory was in great measure responsible for this knowledge.

Sample Preparation

The material used in this investigation was pure electrolytic manganese. It was deoxidized in dry hydrogen at 1100°C for 24 hours, and then allowed to cool slowly in the furnace to 625°C. At 625°C, the hydrogen was flushed from the furnace with purified argon and the sample was cooled to room temperature in a stream of cold argon. The sample was then crushed in a hardened steel rod mill, which had been flushed with nitrogen to prevent oxidation of the fine particles. The final particle size was 200 mesh.

X-ray diffraction photographs showed only the α-Mn pattern. In particular, no pattern of manganese oxides or of β-Mn could be detected. The a_0 of the 58-atom cubic unit cell was found to be 8.91 A.

Neutron Diffraction Results

The neutron diffraction data were obtained with neutrons of 1.02 A wavelength, monochromatized by reflection from a lead single crystal and collimated by Soller slits, using a BF_3 proportional counter as detector. For the room temperature patterns the fine powder was contained in a flat-cell with glass walls, of dimensions $\frac{1}{2}$ in.$\times 2\frac{3}{4}$ in.$\times 4$ in. The low-temperature patterns were obtained with a double-jacketed vacuum cryostat similar to that described by Erickson.[2] The sample then was contained in an aluminum cylinder, 4 in. long and $1\frac{1}{4}$ in. inner diameter.

The diffracted intensity was recorded at successive angular positions, always for a fixed number of incident neutrons. Integrated intensities were obtained by measuring the areas of the "peaks" in the intensity *versus* angle plots. The room temperature values were put on an absolute basis by reference to the intensities for a nickel standard, but such a procedure could not be followed for the low-temperature data. Here it was assumed that the nuclear structure factors were the same as at room temperature and these were made to set the proper scale for the magnetic intensities.

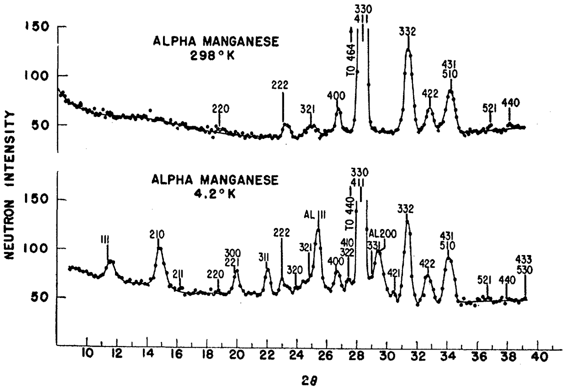

FIG. 1. Neutron diffraction patterns of α-Mn.

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[*] The neutron diffraction work was performed at the Brookhaven National Laboratory Reactor, Upton, New York.

[1] C. G. Shull and M. K. Wilkinson, Revs. Modern Phys. **25**, 100 (1953).

[2] R. A. Erickson, dissertation, Agricultural and Mechanical College of Texas, 1952 (unpublished).

The diffraction patterns at 298°K and 4.2°K are given in Fig. 1. In addition, patterns were obtained also at 47°K. These are similar to those at 4.2°K except that the magnetic intensities are weaker and the peaks are not as sharp. The low-temperature traces contain two Al peaks from the cryostat. Our diffraction data are in agreement with those of Shull and Wilkinson insofar as comparison can be made with the trace reproduced in their article for conditions of lower resolution. It is especially satisfying to obtain the general agreement for the magnetic pattern of the two different specimens as an indication that it is a reproducible characteristic of α-Mn.

The calculated intensities at room temperature (flat-cell container) were made by means of the expression,

$$P_{hkl}=K\frac{\rho'}{\rho}e^{-\mu t\sec\theta}\left(\frac{1}{\sin^2 2\theta}\right)j_{hkl}F_{hkl}^2,$$

where P_{hkl}=integrated power, K=constant instrumental factor evaluated by reference to the Ni standard, ρ'=apparent density of powder, ρ=density of solid, $e^{-\mu t\sec\theta}$=absorption factor, j_{hkl}=multiplicity, and F_{hkl}=structure factor for the (*hkl*) reflection.

The intensities at low temperatures, where a cylindrical sample was used, were computed from

$$P_{hkl}=K'\frac{1}{\sin\theta\sin 2\theta}j_{hkl}F_{hkl}^2.$$

Absorption was found to vary by less than 2 percent over the entire range of study and was taken as constant. The value of K' was established by comparing the observed values to the calculated ones for the nuclear reflections. For the magnetic peaks,

$$|F_{hkl}|^2(\mathrm{mag})=\tfrac{2}{3}\left|\sum p e^{2\pi i(hx_i+ky_i+lz_i)}\right|^2,$$

where p, the magnetic scattering amplitude, is given by $p=\pm 0.539\,Sf_{\mathrm{mag}}\times 10^{-12}$ cm, the sign depending on the atomic site. S is the total spin quantum number and f_{mag} is the magnetic scattering factor.

Nuclear Structure

An attempt was made to ascertain whether the parameters of Bradley and Thewlis[3] were in need of revision. From their work, there are four crystallographically independent sets of atoms in the space group $I\,\bar{4}3m-T_d^3$ as follows:

I 2(a),

II 8(*c*) $x=0.317$,

III 24(*g*) $x=0.356$, $y=0.042$,

IV 24(*g*) $x=0.089$, $y=0.278$.

Despite the limited number of reflections in the neutron diffraction pattern, the inherently greater accuracy of the neutron intensities may allow a more rigorous test of the structure than an x-ray powder diagram. The room temperature intensities, which could be placed on an absolute basis, were examined critically for this purpose. The result of the investigation was only to confirm the parameters of Bradley and Thewlis, at least for the room temperature structure (Table I). The intensity agreement in Table I may not seem to be of the best and a brief discussion may be in order. Special concern was given to the observance of higher intensity for both (222) and (321) than would be calculated. In turn, detailed consideration was given to the possibilities that the discrepancies were due either to impurities or to a change in the structural parameters.

TABLE I. α-Mn neutron intensities 298°K.

$h^2+k^2+l^2$	*hkl*	I_{obs}	A[a] I_{calc}	B[b] I_{calc}
2	110	<3	0.1	0.1
4	200	<3	0.2	0.2
6	211	<3	1.3	1.2
8	220	2	2.0	1.9
10	310	<2	0.5	0.5
12	222	11[c]	2.4	2.3
14	321	8[c]	2.2	2.1
16	400	16	16	15
18	330 411	337	359	337
20	420	<3	1.7	1.6
22	332	97	108	101
24	422	32	41	39
26	431 510	54	59	55
30	521	<5	5.4	5.1
32	440	<5	1.0	0.9

[a] Absolute intensities from comparison with Ni standard.
[b] Intensities normalized on (330, 411).
[c] Includes λ/2 contributions of high-order reflections.

Neither of these possibilities, however, could be established although a portion of the (222) intensity could be due to MnO. In particular, any parameter changes which were in the direction of improving the intensity comparison for (222) and (321) caused large departures from agreement for the strong reflections. It was then recognized that the discrepancy for these two reflections could be well accounted for by the occurrence of λ/2 peaks of higher index reflections, namely those for which $h+k+l=48$ (occurring at same position as 222) and for $h+k+l=54$ (occurring close to 321 position). All of these high-index reflections have very large structure factors and a 1 percent presence of λ/2 would suffice to give the observed intensities. It then seemed that the Bradley and Thewlis parameters were quite good (to ±0.003) and no improvement on them could be made in considering the room temperature data.

On the other hand, the observed nuclear intensities at the low temperatures (Table II) were not in as good agreement with the values calculated with the Bradley and Thewlis parameters and it was found possible to improve the agreement by adjusting the parameters of

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[3] A. J. Bradley and J. Thewlis, Proc. Roy. Soc. (London) **A115**, 456 (1927).

atom IV. It would be difficult, however, to argue that such a change is really called for. The main concern with the nuclear structure here is in establishing a proper scaling of the magnetic intensities. In that respect, there would be less than 10 percent change on the magnetic intensities whether the nuclear intensity values used were those calculated from the Bradley and Thewlis parameters or those corresponding to a set of parameters giving better agreement for the nuclear intensities. Furthermore, the largest peak, for $h+k+l=18$, is quite insensitive to possible parameter variations and more weighting was given it in deducing the scale factor. Accordingly, all calculated intensities reported are with the literature parameter values of α-Mn.

Magnetic Structure

In attempting to account for the magnetic intensities on the basis of an antiferromagnetic arrangement, it becomes evident that it is not possible that the same moment is to be associated with each atom of the unit cell. In the first instance, in order to obtain as much intensity as is observed for reflections with $h+k+l$ odd, it is necessary to have the conditions predominate that (a) atoms related by the body-centering have their spins antiparallel and (b) that atoms in crystallographically equivalent positions (without the body-centering condition) have their spins parallel. If these conditions apply completely, then there are eight different ways of arranging up and down spins on the four independent groups of atoms. Table III gives the calculated intensities for these eight models, and it can be seen that there is violent disagreement with the observed intensities for each case. It does not appear possible to improve the situation by variations of any of the models. Accordingly, it is necessary to consider models with unequal spins for different atoms.

TABLE II. α-Mn neutron intensities at 4.2 and 47°K.

Nuclear reflections

N	hkl	4.2°K I_{obs}	47°K I_{obs}	I_{calc}
2	110	<3	<3	0.1
4	200	<3	<3	0.2
6	211	<3	<3	1.1
8	220	2	2	1.6
10	310	<2	<2	0.4
12	222	10[a]	7[a]	1.9
14	321	[b]	[b]	1.8
16	400	15	13	13
18	330 411	290	290	290
20	420	[b]	[b]	1.4
22	332	69	76	87
24	422	27	30	33
26	431 510	53	52	47
30	521	<5	<5	4.3
32	440	<5	<5	0.8

Magnetic reflections

N	hkl	I_{obs}	I_{calc} A[c]	I_{calc} B[d]
1	100	<3	1	1
3	111	22	21	23
5	210	46	45	48
9	300 221	20	23	18
11	311	20	21	17
13	320	5	4	5
17	410 322	7	7	9
19	331	[b]	1	0
21	421	4	2	3

[a] Includes $\lambda/2$ contributions of high-order reflections.
[b] Obscured by aluminum peak.
[c] A—1.54 μ_B for I, II, III.
[d] B—2.50 μ_B for I and II, 0.85 μ_B for III.

TABLE III. Magnetic intensities for α-Mn, assuming equal moment on every atom.

hkl	I_{obs}	A	B	C	D	E	F	G	H
100	<3	30	95	67	91	50	32	150	9
111	22	49	28	28	13	6	42	14	42
210	46	5	2	6	19	39	0.3	0.1	17
300 221	20	26	26	21	9	7	30	16	24
311	20	5	1	11	12	14	5	8	7
320	5	0.3	0.1	1	7	3	3	2	0.1
410 322	7	3	4	9	1	3	6	5	3
331	[a]	1	0.3	0.1	1	0.3	1	1	1
421	4	6	8	1	7	5	1	8	3

The spin alignment for the four kinds of atoms in the asymmetric unit is as follows:

	I	II	III	IV
A	↑	↑	↑	↑
B	↑	↑	↑	↓
C	↑	↑	↓	↑
D	↑	↓	↑	↑
E	↑	↑	↓	↓
F	↑	↓	↑	↓
G	↑	↓	↓	↑
H	↑	↓	↓	↓

[a] Obscured by aluminum peak.

A second major point about the magnetic intensities is that they are not compatible with the results of the paramagnetic diffuse scattering analysis of Shull and Wilkinson.[1] From their studies above the Néel temperature, they obtained a differential cross section of 0.060 $\times 10^{-24}$ cm^2/sterradian atom from which a value of the moment was determined by the Halpern-Johnson relation[4]:

$$d\sigma = 0.194 \times 10^{-24} S(S+1)\,\mathrm{cm}^2.$$

The value deduced for S is 0.25 and hence a magnetic moment of 0.5 Bohr magneton per Mn atom. This value has subsequently been generally quoted for the moment of an atom in α-Mn. Shull and Wilkinson suggest the possibility that this number is an average value and that there may be a fraction (4/10) of the atoms with 1 μ_B and the rest (6/10) with no moment. Still other methods of distributing unequal moments may be made, but it is clear that any set of numbers deduced from the paramagnetic scattering analysis will not be able to account for the amount of coherent scattering actually observed below the Néel temperature. For

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[4] O. Halpern and M. H. Johnson, Phys. Rev. 55, 898 (1939).

example, the intensity of the largest magnetic peak (210) is 46 units after proper scaling, but the maximum value subject to the paramagnetic analysis would be only 10. The disparity is actually greater when one considers models which give reasonable relative magnetic intensity agreement. The discrepancy may be better appreciated from a consideration of the number of Bohr magnetons per unit cell. For 58 atoms with 0.5 Bohr magneton each there are then 29 μ_B/unit cell. If 40 percent of the atoms have 1 μ_B, the rest no moment, there would be 23.2 μ_B/unit cell. More unequal weightings would further reduce the number per unit cell. On the other hand for any reasonable fit of intensities, we have found it necessary to consider models with at least 50 μ_B/unit cell. The apparent dilemma would appear to exist in the information reported by Shull and Wilkinson.[5]

An extensive trial and error exploration of models did not lead to a unique solution but allowed two general conclusions to be reached; (1) no successful fit of intensities could be made if any appreciable moment was associated with atom IV, (2) all acceptable models involve equal moments on atoms I and II and furthermore correspond physically to the situation of predominantly antiparallel spin alignment of nearest neighbors. Conclusion (1) may be appreciated by considering the structure factor contributions of the four different kinds of atoms to the unobserved (100) peak. These are $A_{\rm I}=1.827$, $A_{\rm II}=-2.987$, $A_{\rm III}=-1.980$, $A_{\rm IV}=11.100$, with $F_{100}=n_{\rm I}A_{\rm I}\pm n_{\rm II}A_{\rm II}\pm n_{\rm III}A_{\rm III}\pm n_{\rm IV}A_{\rm IV}$, where n represents the number of unpaired spins. Conservatively F_{100} could not exceed 2 intensity units in magnitude and fail to be detected. The resulting restrictions on the choice of values of n are such as to give violent disagreement in the intensity comparison if $n_{\rm IV}$ is made at all appreciable. The only reasonable models found were those for which $n_{\rm IV}$ was made zero.

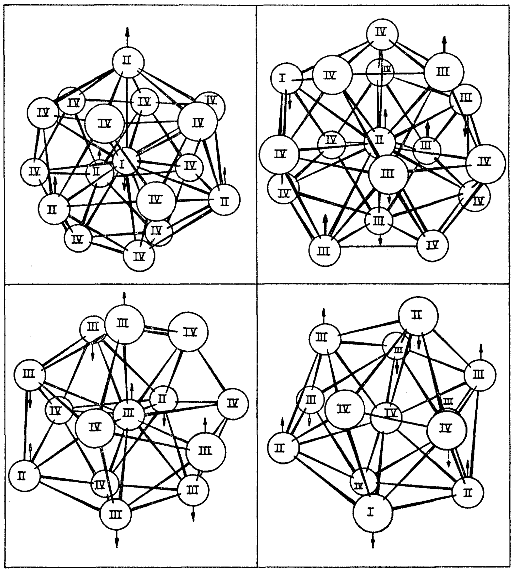

FIG. 2. The coordination of neighboring atoms about each of the four kinds of atoms in α-Mn, with a designation of the moment alignment. The coordination figures about I and II are similar to those about the large atom, A, in the Laves-type phases, AB_2. The coordination about atom IV produces a distorted icosahedron.

TABLE IV. Space group $I\bar{4}3m-T_d^3$.

	(000)+	$(\frac{1}{2}\frac{1}{2}\frac{1}{2})$+
I2(a) 000	1(a)↑	1(a)↓
II8(c)$x=0.317$	4(c)↑	4(c)↓
III24(g)$x=0.356$, $y=0.042$	12(g)↓	12(g)↑
IV 24(g)$x=0.089$, $y=0.278$	no moment alignment	

It is not possible nor desirable to reproduce the calculations for the numerous models that have been tested. Instead, we include in Table II the intensities for the two best models in one of which the same moment (1.54 μ_B) is associated with each atom except IV. All acceptable models have the common feature of equal moments on atoms I and II and a two-parameter problem could be formulated as follows:

$$F_{hkl}^2/p^2=(A_{\rm I}+A_{\rm II}-xA_{\rm III})^2+(B_{\rm I}+B_{\rm II}-xB_{\rm III})^2,$$

where p is the moment of I and II and x is the fraction of that moment to be associated with III. The value of x was determined first from the best relative fit of intensities and p was evaluated as the number placing the intensities on the proper scale.

The arrangement of spins for the acceptable models can be described, in terms of the standard designation for the crystal structure, as follows in Table IV.

The magnetic form factor[6] of Mn^{++} was used for all calculations. Other form factors in the literature were found to be less satisfactory.

Discussion of the Magnetic Structure

With regard to the main findings of our investigation—the pattern of spin alignment and the absence of a moment on atom IV—we believe these to be reasonable and understandable on the basis of the geometrical arrangement of atoms in the α-Mn structure.

It is too difficult to depict the arrangement of spins by means of a unit cell diagram but an adequate representation may be made with coordination figures of nearest neighbors for each kind of atom. We wish to discuss the scheme of spin laignment by reference to such figures which are reproduced in Figs. 2 and 3.

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[5] A private communication from C. G. Shull and M. K. Wilkinson suggests a possible solution to this dilemma. A recent theoretical treatment of neutron scattering by G. T. Trammel (unpublished) indicates that the observed difference in diffuse scattering between high and low temperatures should be proportional to S^2 rather than $S(S+1)$ as in the Halpern and Johnson[4] relation. With the S^2 dependence and either model A or B of Table II one would calculate a value of 0.067 barn/steradian in excellent agreement with the value of 0.060 barn/steradian measured by Shull and Wilkinson. If this interpretation is correct, then the proposal of a statistical distribution of the moments of atom III would have to be abandoned.

[6] Shull, Strauser, and Wollan, Phys. Rev. **83**, 335 (1951).

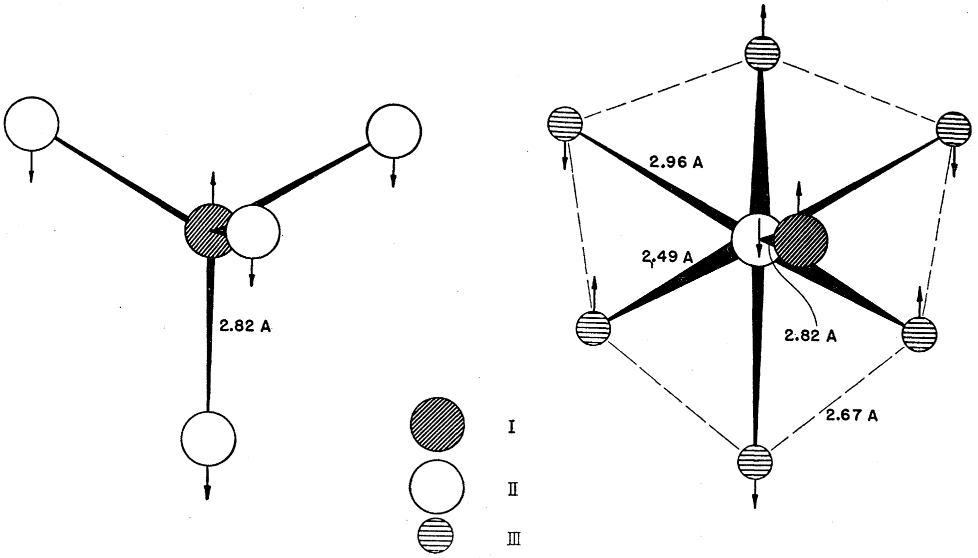

FIG. 3. Schematic representation of the moment alignment in the antiferromagnetic structure of α-Mn.

Atom I (at the origin or body-center of the unit cell) is seen to have its spin antiparallel to four spins (atoms II) surrounding it in the form of a regular tetrahedron and at a distance of 2.82 A. In turn, the spin of atom II is antiparallel to 4 spins at the corners of a distorted tetrahedron, made up of atom I (at 2.82 A) and three atoms of type III with a separation of 2.49 A. In addition there are three atoms of type III with parallel spin surrounding a type II atom, but at a distance of 2.96 A. Finally, a type III atom has an addition to its two neighbors of type II (one at 2.49 A and one at 2.96 A), six other type III atoms (all at a distance of 2.67 A), four of which are antiparallel and two of which are parallel. The scheme of the magnetic structure is given completely by the two schematic diagrams of Fig. 3. The full antiferromagnetic structure can be constructed by focussing attention on atoms I and II, and specifying their moment orientations as well as those of atom III in the manner depicted.

Except for the coordination about atom III, it would be true that antiparallel spin alignment is favored unless the interatomic separation is considerably larger than normal. This is in keeping with the generally recognized behavior of the exchange energy with distance and a survey of Mn alloys indicates that for Mn the change of sign of the exchange energy occurs at a distance of about 2.85 A.[7] We wish to point out that the apparent lack of consistency in considering the surroundings of atom III would be removed by the interpretation that not all such atoms locally are lined up, but only a fraction of them are aligned in a statistical manner from one unit cell to another. More specifically, the tetrahedral surroundings about atom I can be approximated in two ways for atom II; (a) by atom I with the three atoms of type III (antiparallel) at 2.49 A, or (b) by atom I with the three atoms of type III (parallel) at 2.96 A. It may be that locally about a specific atom II, one or the other tetrahedral spin configuration may be assumed, but not both. On the average, however, each atom of type III is then lined up for $\frac{1}{2}$ of the unit cells. The magnitude of the moment deduced from our structural analysis would then be only $\frac{1}{2}$ of the actual value of this atom type.

The absence of oriented spins on atoms IV does not appear strange on the geometrical basis. Considering the groupings of these atoms only, it is not possible to orient their spins in a consistent manner unless they were all parallel, a situation which would not seem likely because of the shortness of the distances (2.24 to 2.37 A). An alternative explanation may be made on the basis of these abnormally short distances, since it may be anticipated that at sufficiently small separations because of the large Fermi energies attendant with a net moment, there will be no net moment.[8]

Unfortunately, the exact values of the moments cannot be specified. In accord with our interpretation, however, the following two assignments of moments may be made for the two models that give best intensity agreement:

$$A\left\{\begin{array}{ll}\text{I} & 1.54\,\mu_B\\ \text{II} & 1.54\,\mu_B\\ \text{III} & 3.08\,\mu_B\end{array}\right. \qquad B\left\{\begin{array}{ll}\text{I} & 2.50\,\mu_B\\ \text{II} & 2.50\,\mu_B\\ \text{III} & 1.70\,\mu_B\end{array}\right.$$

Despite this ambiguity it is clear that there are individual moments considerably larger than 0.5 μ_B and that the number of Bohr magnetons per unit cell is substantially greater than that indicated by the paramagnetic diffuse analysis. There seems to be no hope of specifying the individual moments exactly without single-crystal experiments, a prospect which is not very bright at present because of the lack of such crystals.

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[7] R. Forrer, Ann. phys. (12) **7**, 605 (1952).

[8] This was pointed out to us by Dr. C. P. Bean of our Laboratory.

It is, of course, not possible to specify the spin directions from the powder data. For a cubic or pseudocubic structure the averaging of intensities for planes of the same form would give the same result for any choice of direction.

II. β-MANGANESE

Introduction

In view of the complexity of the crystal structure of α-Mn and the consequent difficulties in determining its antiferromagnetic structure, it seemed worthwhile to us to investigate the possibliity of magnetic structures in the simpler β-Mn modification. No pertinent magnetic measurements for β-Mn could be found in the literature and it was decided to obtain the neutron diffraction pattern at 4.2°K, the lowest temperature readily obtainable by us. It was ascertained by direct measurement at high magnetic fields[9] that β-Mn is not ferromagnetic (within 0.2 Bohr magneton) at this temperature and hence only antiferromagnetic structures were contemplated. Also, a room temperature diffraction pattern of the specimen was recorded.

Experimental

The starting material was pure electrolytic manganese. This material was melted under one atmosphere of argon and cast in a copper mold. The ingot was heated in hydrogen at 850°C for one hour and then quenched in cold water. An x-ray diffraction pattern of the quenched ingot showed no lines other than those of β-Mn; however, peaks due to oxides of manganese were observed in the neutron diffraction patterns obtained at a later time. The sample was crushed to 200 mesh in a hardened steel rod mill to provide suitable powder for neutron diffraction work.

The neutron diffraction measurements were made in a manner similar to that used for α-Mn. The room temperature data were obtained with the powder in a flat cell but a cylindrical sample container was used in the low-temperature cryostat for the measurements at 4.2°K. The intensities reported are not on an absolute basis, but are on an arbitrary scale and normalized on the large peak for the combined reflections (300) and (221).

The diffraction patterns are shown in Fig. 4, and the integrated intensities are given in Table V. At 4.2°K, the counting times were considerably longer and these data should be more reliable than those at room temperature.

Discussion

The structure of β-Mn is given as follows[10]:

Cubic, $a_0=6.30$ A,
Space group $P4_132-O_7$,
$z=20$,
8 atoms (I) at 8(c), $x=0.061$,
12 atoms (II) at 12(d), $x=0.206$.

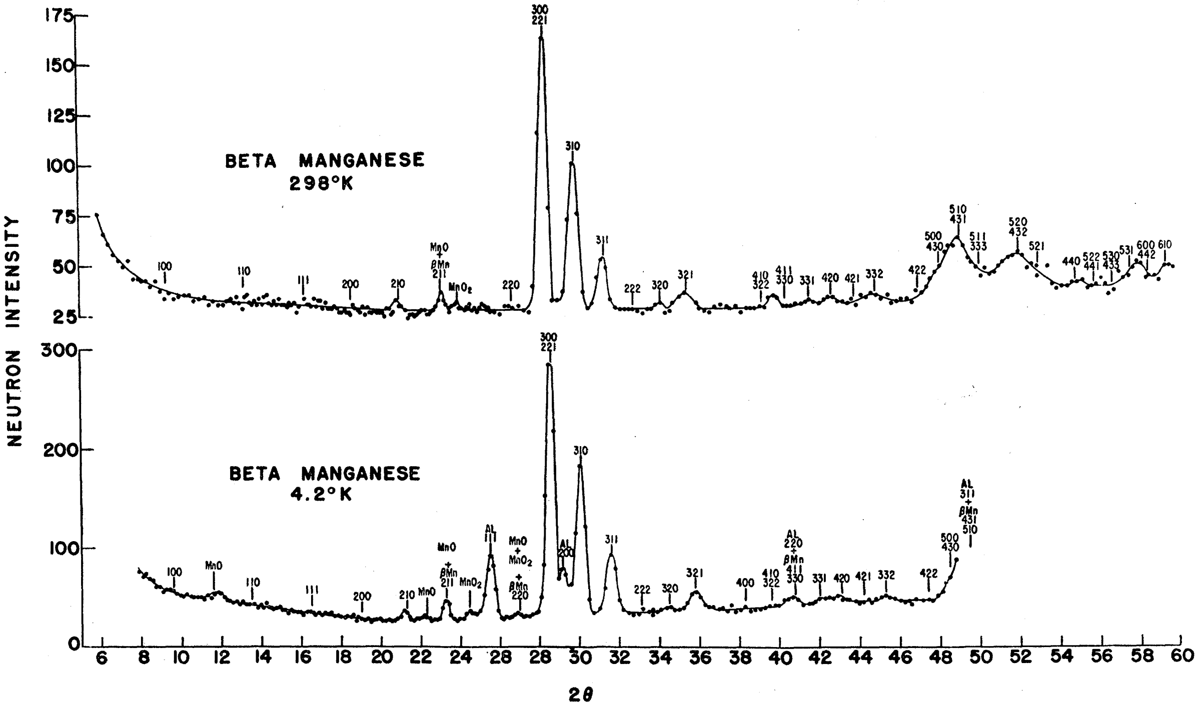

FIG. 4. Neutron diffraction patterns of β-Mn.

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[9] These measurements were made by Dr. C. P. Bean and Dr. I. Jacobs of our Laboratory.

[10] G. D. Preston, Phil. Mag. **5**, 1198 (1928).

TABLE V. Neutron diffraction intensities of β-manganese.

	298°K		4.2°K		Antiferro-magnetic model magnetic intensity
hkl	I_{obs}	I_{calc}	I_{obs}	I_{calc}	I_{calc}
100	<5	0	<3	0	0
110	<5	2	<3	2	0
111	<5	3	<3	3	7
200	<5	0	<3	0	5
210	4	9	12	10	6
211	14[a]	2	14[a]	2	1
220	<5	2	4	2	0
300 221	275	275	275	275	0.2
310	169	166	208	165	0.1
311	65	78	81	77	0.1
222	<5	0	<4	0	0.1
320	6	2	5	2	0.1
321	27	30	34	30	0.6
400	<5	0	<4	0	0
322 410	<5	4	5	4	0
330 411	10	29	20	28	0.1

[a] Includes MnO and MnO_2.

No departure from this structure could be determined from the neutron diffraction intensities, although these are insufficient in number and accuracy for percise parameter evaluation. All calculated intensities were made with the parameters given above.

The comparison of the patterns at the two temperatures indicates little, if any, change due to temperature. In particular, no evidence for an antiferromagnetic structure at 4.2°K is readily discernible. Since the magnitude of magnetic intensity might be quite small if moments of the order of 1 μ_B were involved, it is necessary to consider the experimental situation quantitatively in relation to the effects expected from possible models. For this reason, the portion of the pattern up to 30°(2θ) was scanned several times with longer counting periods than usual. These data allow a conservative estimate of 3 intensity units as the maximum intensity that would fail to be detected for the first four reflections, as indicated in Table V.

There are numerous models if it is assumed that each atom has the same moment and if the balancing of opposite moments is done with no regard for physical reasonableness but only in accord with crystallographic symmetry. In general, these models call for a significantly large intensity for at least one of the first four unobserved reflections if the value of the individual moment is 1 Bohr magneton. The model most favorable in this respect was one for which the intensity of (111) was 11 units (if 1 μ_B per atom is assumed). Comparing this number to the value of 3 which is not to be exceeded we would conclude that the individual moment could not exceed 0.5 Bohr magneton. None of these models, however, appear to have physical significance in that there is no correlation of kind of atom or distance with the pattern of moment alignment. The difficulty arises from the nature of the arrangement of atoms II. As with atoms IV of the α-Mn structure, it is not possible to assign opposite moments in a physically consistent manner to the atoms of type II (β-Mn). Consequently, it would not be surprising if no rigid pattern of moment alignment occurred here.

On the other hand, the spatial arrangement of atoms I is such as to conform readily to an antiferromagnetic structure involving these atoms only. Each atom I has three neighbors of the same kind at 2.37 A, with no bond between any pair of these neighbors. It is possible then, to assign opposing moments to each of the three neighbors of any atom I. This assignment would correspond to the following crystallographic description:

$$\left\uparrow\begin{array}{l} xxx \\ \frac{1}{2}+x,\ \frac{1}{2}-x,\ \bar{x} \\ \bar{x},\ \frac{1}{2}+x,\ \frac{1}{2}-x \\ \frac{1}{2}-x,\ \bar{x},\ \frac{1}{2}+x \end{array}\right. \qquad \left\downarrow\begin{array}{l} \frac{3}{4}-x,\ \frac{3}{4}-x,\ \frac{3}{4}-x \\ \frac{1}{4}-x,\ \frac{3}{4}+x,\ \frac{1}{4}+x \\ \frac{1}{4}+x,\ \frac{1}{4}-x,\ \frac{3}{4}+x \\ \frac{3}{4}+x,\ \frac{1}{4}+x,\ \frac{1}{4}-x \end{array}\right.$$
$$\text{with } x=0.061.$$

The calculated intensities for this model with a moment of 1 μ_B are given in the last column of Table V. The magnitudes of these intensities are small and hence it is not possible to exclude such a model with a small value of the moment. Thus, with (111) calculated to be 7 units and with the condition it should not be greater than 3, it can be deduced that for this model the individual moment cannot be larger than $\sqrt{(3/7)}$ or 0.66 μ_B. Since there is no evidence of α-Mn, or for other Mn alloys, that moments less than 1 μ_B occur, this result may be interpreted as an indication of absence of moment alignment on atoms I also. While the geometry is favorable for the antiferromagnetic arrangement considered here, the shortness of the distances (2.37 A) may exclude the presence of a net moment. All coupled spins in α-Mn are at distances larger than 2.37 A.

It would be possible to test whether β-Mn is paramagnetic at 4.2°K and whether the paramagnetism is the same as at room temperature by a study of the diffuse scattering. Unfortunately, our data are not suitable for any quantitative assessment of the diffuse scattering. It does appear, however, that there is no significant decrease in background in lowering the temperature from 298°K to 4.2°K, and that this background may be largely the result of paramagnetic scattering. Susceptibility measurements at liquid helium temperatures would also be helpful in deciding on the magnetic state of β-Mn.

CONCLUSION

This study of the two highly complex structures emphasizes the importance of two factors in determining the magnetic structure: (1) the effect of interatomic spacing on the exchange interaction, and hence the mode of spin alignment; (2) the geometry of the atomic arrangement. With regard to the first factor, it appears that for very small separations of Mn atoms ($\leq$2.37 A) there is no tendency for spin coupling, that for intermediate ranges of distances (2.49 to 2.82 A) the coupling is antiparallel and for the long distances (≥ 2.96 A) parallel spin coupling occurs. If a group of atoms occurs in a spatial arrangement such that no physically consistent assignment of moments can be made, it seems that no moment alignment among these atoms will occur. Not only the antiferromagnetic structure of α-Mn but the absence of a magnetic structure for β-Mn are understandable on the basis of these statements.

While it is not possible to specify exactly the magnitude of the moments of the respective atoms in α-Mn, it is established that they are well above the value of 0.5 μ_B that is given in the literature.

No significant deviation from the accepted crystal structure descriptions of both α- and β-Mn could be detected in the neutron diffraction results.

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Galvanomagnetic Effects in Bismuth*

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Conductivity, Hall effect, and magnetoresistance in single crystals of pure and tin-doped bismuth have been measured as functions of temperature between 80 and 300°K and as functions of magnetic field up to 2000 oersted. A simple many-valley model for the band structure of bismuth is proposed, and explicit expressions for the galvanomagnetic effects are derived. Numerical values are obtained for the number of conduction electrons and holes, their mobilities, and the overlap of valence and conduction bands.

I. INTRODUCTION

THE galvanomagnetic effects in single crystals of bismuth have been studied extensively.[1–6] An attempt to explain the observed facts in terms of band structure has been made by Jones.[7] This author calculated the galvanomagnetic effects on the assumption that the band structure of bismuth can be approximated by a simple model. However, the model adopted by Jones leads to results which are partially at variance with experiment. For instance, the longitudinal magnetoresistance in the direction of any of the crystallographic axes is calculated to be zero, while experimentally the longitudinal effect is of the same order of magnitude as the transverse effect. The theory is also unable to explain the pronounced anisotropy of the transverse effects at strong magnetic fields. In this paper we will show that a somewhat different model leads to much better agreement between calculated and experimental values.

Measurements of galvanomagnetic effects in different crystallographic directions in weak magnetic fields and at temperatures between 80 and 300°K have been carried out, as the data available in the literature were considered to be insufficient for a satisfactory test of the theory. We have also measured the galvanomagnetic effects in tin-doped bismuth. Thomson[8,9] has reported that small additions of tin to bismuth act in many ways analogously to the addition of acceptor elements to semiconductors, and it should thus be possible to obtain from these measurements more direct information as to the relative contributions of the valence and the conduction bands to the conductivity.

II. EXPERIMENTAL

Single crystals of bismuth were prepared from spectroscopically pure bismuth, supplied by Johnson and Mathey, specified to be better than 99.996% pure. The method used in growing the single crystals follows closely one of the techniques described by Kapitza.[10] The single crystals obtained had the shape of rods with nearly circular cross section of diameter between 1 and 2 mm. Rods of any specified crystallographic direction

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[1] P. Kapitza, Proc. Roy. Soc. (London) **A119**, 358 (1928).

[2] O. Steirstadt, Z. Physik **95**, 355 (1935).

[3] de Haas, Blom, and Schubnikov, Physica **2**, 907 (1935).

[4] A. N. Gerritzen and W. J. de Haas, Physica **8**, 802 (1940).

[5] Gerritzen, de Haas, and van der Star, Physica **9**, 241 (1942).

[6] Y. Tanabe, Science Repts. Insts. Tohoku Univ. **A2**, 341 (1950).

[7] H. Jones, Proc. Roy. Soc. (London) **A155**, 653 (1936).

[8] N. Thomson, Proc. Roy. Soc. (London) **A155**, 111 (1936).

[9] N. Thomson, Proc. Roy. Soc. (London) **A164**, 24 (1938).

[10] An adaptation of the "plate furnace" method described in reference 1 was used.