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## Neutron and X-Ray Diffraction Study of the Low-Temperature Chemical and Magnetic Structure of Alpha-Manganese<sup>†\*</sup>

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The low-temperature chemical and magnetic structures of antiferromagnetic  $\alpha$ -manganese have been investigated. High-resolution neutron powder data indicate that the chemical and the magnetic unit cell are identical in size. An x-ray powder study of 60 reflections at 77 and 4°K indicates no significant changes at low temperature in the atomic coordinates. Fourteen independent magnetic reflections measured at 77, 50, and 4°K were used to determine the signs and magnitudes of the four magnetic moments for a collinear spin model. At 4°K, they are  $1.72 \pm 0.19$ ,  $1.46 \pm 0.08$ ,  $1.11 \pm 0.04$ , and  $0.02 \pm 0.05$  in units of  $\mu_B$  for atoms I, II, III, and IV, respectively. The fit of the observed and calculated magnetic intensities indicates the need for a less restricted model for the magnetic structure. These results are compared with those of other experiments.

### I. INTRODUCTION

The low-temperature allotrope of transition-metal manganese is  $\alpha$ -manganese. Its chemical structure is bcc with 58 atoms per unit cell in the space group  $T_d^3 - \bar{1}43m$ .<sup>1</sup> These atoms are distributed on four different sites. I: two atoms at  $000 + bcc$  with point symmetry  $\bar{4}3m$ ; II: eight atoms at  $x, x, x + bcc$  with point symmetry  $3m$ ; III: 24 atoms at  $x, x, z + bcc$  with point symmetry  $m$ ; IV: 24 atoms at  $x, x, z + bcc$  with point symmetry  $m$ , referred to subsequently as sites I, II, III, and IV, respectively.

In 1953, Shull and Wilkinson<sup>2</sup> established the existence of an ordered antiferromagnetic state in  $\alpha$ -manganese below 100°K from a neutron diffraction study of the powder. The complexity of the chemical structure and the paucity of measurable magnetic reflections made the determina-

tion of a magnetic structure impossible in that investigation. Magnetic diffuse scattering was observed above the Néel transition, providing evidence of residual short-range order between localized moments.

Kasper and Roberts,<sup>3</sup> in 1956, reported the results of another neutron diffraction study of  $\alpha$ -manganese powder. They observed that new coherent diffraction peaks appeared below the transition temperature for odd values of  $h + k + l$ , while the nuclear diffraction peaks remained unchanged. They deduced that the antiferromagnetic ordering was associated with spin reversal under a body-centering translation. The intensities of seven magnetic reflections were then analyzed in terms of a restricted collinear spin model and found to be consistent with either of the two sets of magnetic moments for the four atom types listed in Table I. In their analysis, Kasper and Roberts

assumed that there was zero moment on atom IV and equal moments on atoms I and II. Arrott and Coles<sup>4</sup> suggested that the magnetic peaks in the neutron diffraction data of Kasper and Roberts might be shifted from the positions of integer indexing. Such shifts, if real, would indicate that the unit cell for the magnetic structure was incommensurate with the chemical unit cell; such a magnetic structure could be produced by a spin-density wave of conduction electrons with some or all of the magnetic moments nonlocal in character, as in the case of chromium.

A preliminary communication<sup>5</sup> of the neutron diffraction results presented in this paper confirmed that atoms related by body-centering translations are antiferromagnetic, showed that to a high degree of accuracy the magnetic cell is commensurate with the chemical cell, and presented the magnetic moments on atoms I–IV at 4 °K as given in Table I. In that analysis the collinear model was assumed, i.e., that all magnetic moments in the chemical cell are aligned along the same arbitrary direction and that the magnetic moments in equivalent *crystallographic* symmetry sites are equal.

Kunitomi, Yamada, Nakai, and Fujii<sup>6</sup> in an independent and simultaneous investigation have reported the moments given in Table I for a collinear model at 60 °K. An improved fit of the calculated and observed magnetic intensities was obtained by Kunitomi *et al.* for a noncollinear model for which the moments determined are also listed in Table I (in this model, using the lower magnetic symmetry gives rise to two nonequivalent moments on each of sites III and IV).

In addition to these direct measurements, indirect information is available on the magnetic moments from determinations of the magnetic hyperfine fields. From measurements of the heat capacity of  $\alpha$ -manganese below 0.4 °K, Martin and Heer<sup>7</sup> determined an effective internal field of 74 kG per manganese atom, while nuclear magnetic

resonance investigations below  $T_N$  indicate that a majority of the atom sites have internal fields on the order of 13 kG.<sup>8</sup> It is possible to reconcile these two observations by assuming that sites I and II, which consist of ten atoms per unit cell, have large internal fields while sites III and IV, which consist of 48 atoms per unit cell, have relatively small internal fields.<sup>9</sup> This deduction is consistent with the Mössbauer spectrum of Fe<sup>57</sup> in an alloy of 5-at. % Fe in  $\alpha$ -manganese,<sup>10</sup> which indicated that for the Fe nuclei in sites III and IV the internal magnetic fields are on the order of 10 kG. If the magnitude of the internal field at the nucleus is considered to be a measure of the magnetic moment of the atom, it would follow that atoms I and II would possess relatively large moments and atoms III and IV, relatively small moments. This conclusion appears to be in agreement with the nuclear magnetic resonance spectra observed by Jaccarino and co-workers.<sup>11,12</sup> They conclude that sites I and II have *d*-spin local moments of 2 or 3  $\mu_B$ , while sites III and IV have no appreciable local moment.

The determination of the magnetic structure is dependent on the chemical structure and even relatively small change in the fractional coordinates of the atoms in nonspecial positions affect the fit of the observed and calculated intensities significantly. Previous neutron and x-ray studies<sup>3,13</sup> on limited numbers of nuclear reflections had indicated that no gross changes in the chemical structure take place down to 4 °K, but precise atomic parameters for the low-temperature structure were not available. For this reason a powder x-ray study of the low-temperature chemical structure was undertaken. A single-crystal x-ray study of the atomic and thermal parameters at room temperature will be published elsewhere.<sup>14</sup>

## II. EXPERIMENT

### A. Growth of Single Crystals

Small single crystals up to a few mg in size were grown by vapor deposition.<sup>15</sup> The starting material was pure (99.995%) electrolytic manganese supplied by Johnson, Matthey, and Co. It was rinsed in a 5% solution of HCl in methanol to remove the oxide and was then placed inside the alumina inner crucible of the furnace apparatus shown in Fig. 1. The system was evacuated to a pressure of  $10^{-5}$  Torr. An rf heating unit was used to degas and evaporate the manganese. Because of the high vapor pressure of manganese just above its melting point, about two-thirds of the initial 150-g charge distilled in 2 h in an atmosphere of 50  $\mu$  of hydrogen gas. The distilled manganese condensed on the cooler upper walls of the alumina

TABLE I. Magnetic moments determined in various studies of  $\alpha$ -manganese.

	$\mu_I$	$\mu_{II}$	$\mu_{III}$	$\mu_{IV}$
Kasper and Roberts (A) (at 4.2 °K)	1.54	1.54	-1.54	0.0
(B)	2.50	2.50	-0.85	0.0
Kunitomi <i>et al.</i> (collinear) (at 60 °K) (noncollinear) <sup>a</sup>	1.35	1.32	-0.99	-0.22
	1.90	1.78	-0.50	-0.26
			-0.55	-0.38
Present experiment (at 4.2 °K)	1.72(19) <sup>b</sup>	1.46(8)–1.11(4)		0.02(5)

<sup>a</sup>Absolute values of moments for Mn<sup>2+</sup> magnetic form factor.

<sup>b</sup>Numbers in parenthesis in this and succeeding tables are standard errors.

tion that equivalent magnetic reflections in different quadrants had equal intensities. Fifteen independent nuclear reflections were collected at 300, 77, and 4 °K, and 14 independent magnetic reflections were collected below the Néel temperature (95 °K) at 77, 50, and 4 °K. Background levels were determined by plotting the data, and point counts were totaled to determine the integrated intensities. The size of the crystal (about 1 mm<sup>3</sup>) and the large mosaic spread (25-min peak width) suggested that no corrections for absorption or extinction were necessary; this was confirmed by the good agreement of the nuclear intensities with those calculated from the x-ray data.

### III. RESULTS

#### A. X-Ray Powder Study

The least-squares computer program NUPOWLS<sup>17</sup> was used to refine the atomic parameters and a scale factor from the integrated intensities. The parameters refined are listed in Table II A. The refinement of the room-temperature intensities was used to check the consistency of the experiment and to estimate the precision with which the atomic parameters at low temperatures could be measured. At all three temperatures the refinements on the atomic parameters resulted in no significant changes in atomic parameters. The thermal parameters used in these refinements were calculated using the Debye model from those measured in the room-temperature single-crystal x-ray study. The final observed and calculated structure factors for the atomic parameter refinements are listed in Table III.

#### B. Time-of-Flight Neutron Diffraction on Powder Sample

The results of this experiment are summarized in Fig. 3. Three low-angle magnetic peaks at

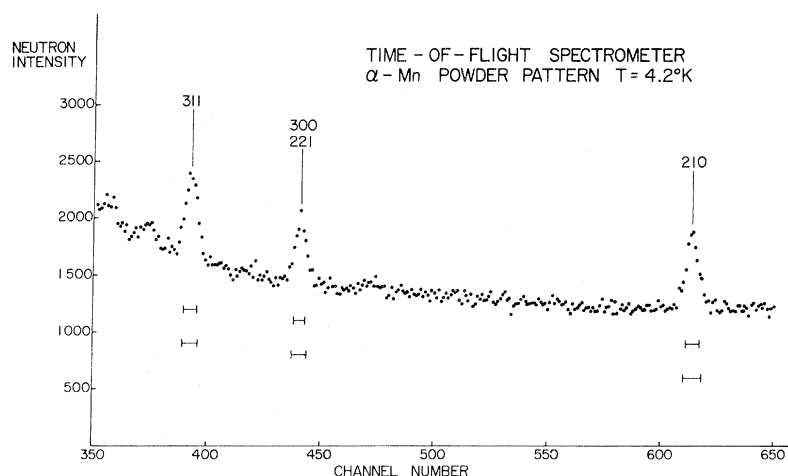


FIG. 3. Portion of the diffraction pattern from the time-of-flight neutron spectrometer.

TABLE II. Atomic coordinates in  $\alpha$ -manganese.

A. X-ray studies				
Atom	Single crystal 300 °K	300 °K	Powder 77 °K	4 °K
II	$x = 0.31787(10)$	0.3171(5)	0.3177(6)	0.3171(6)
III	$x = 0.35706(6)$	0.3578(4)	0.3570(4)	0.3576(5)
	$z = 0.03457(9)$	0.0344(6)	0.0360(6)	0.0352(7)
IV	$x = 0.08958(6)$	0.0903(4)	0.0894(5)	0.0895(4)
	$z = 0.28194(9)$	0.2824(5)	0.2819(6)	0.2818(6)
B. Neutron single-crystal study				
Atom	300 °K	77 °K	4 °K	
II	$x = 0.3175(8)$	0.3175(6)	0.319(1)	
III	$x = 0.3569(5)$	0.3567(5)	0.356(1)	
	$z = 0.0356(6)$	0.034(1)	0.037(1)	
IV	$x = 0.0892(6)$	0.0906(6)	0.089(1)	
	$z = 0.282(1)$	0.281(1)	0.283(1)	
<i>R</i>	3.6%	2.9%	4.3%	

4 °K are shown. Each point corresponds to the number of neutrons counted in a single 8- $\mu$ sec channel. The observed peak positions are at the channel number calculated for the peak from the low-temperature lattice parameter of the *chemical* cell. The upper brackets below the data points indicate the width at half-maximum of the peaks, the brackets below indicate the estimated resolution of the spectrometer. This resolution is approximately four or five times greater than that available to Kasper and Roberts. There is no evidence of broadening or shifting of the magnetic reflections; it is concluded that the chemical and magnetic unit cells are identical in size. The further observation that magnetic reflections appear only for  $h+k+l$  = odd integers confirms the finding of Kasper and Roberts that spins related by a body-centering translation are reversed.

#### C. Single-Crystal Neutron Diffraction Study

The atomic parameters were refined from the nuclear reflections by the least-squares refinement

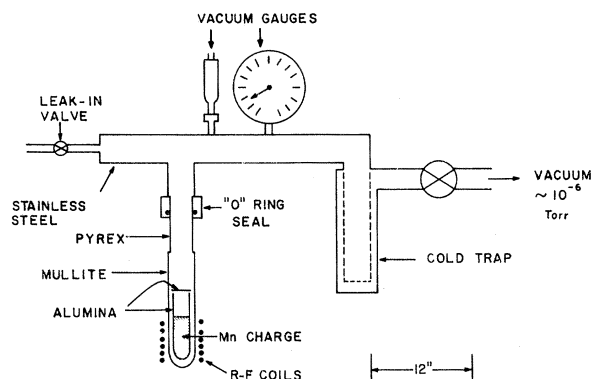


FIG. 1. Apparatus for the growth of single crystals.

crucible. Before cooling, the system was reevacuated to a pressure of  $10^{-5}$  Torr to drive off any absorbed hydrogen. With optimum conditions, the condensate contained regions of loosely packed crystals varying in size up to a few mg. These crystals were bright but showed no smooth-growth faces. Since  $\alpha$ -manganese is very brittle, the single crystals were separated by gently breaking up the condensate and examining likely pieces by means of Laue x-ray photographs. The analysis of the manganese after distillation indicated a purity of 99.9995% with respect to metallic impurities. The oxygen content of a few ppm was small enough to be accounted for by surface oxidation. A similar process has been used by Kunitomi *et al.*<sup>6</sup> to obtain single crystals. The  $\alpha$ -manganese powder used in this study was prepared from manganese distillate produced in the single-crystal-growing process. It was ground in an alumina mortar in an argon atmosphere to a particle size of less than  $35\ \mu$  for x-ray work or  $74\ \mu$  for neutron work.

#### B. X-Ray Study

Approximately 60 reflections were measured at 300, 77, and 4°K. The peaks were recorded on a strip chart, and the integrated intensities were measured by planimeter from the areas. Particular care was taken in estimating background and peak shapes for overlapping peaks. Random deviations in the integrated intensities due to fluctuations in the number of crystallites contributing to a reflection were on the order of 10%, which was large compared to the statistical uncertainty in the counting, the effect of nonlinearities in the chart recorder and area-measuring errors. Uncertainties in the determination of background levels were comparable in size for the weakest peaks to the crystallite fluctuations. The effects of these errors were minimized by proper weighting of the reflections in the refinement program.

#### C. Time-of-Flight Neutron Diffraction on Powder Sample

An accurate determination of the magnetic peak positions and half-widths was made using a time-of-flight powder diffraction instrument at the CP-5 reactor at the ANL. A schematic representation of the apparatus is shown in Fig. 2. A white beam of thermal neutrons is pulsed at the chopper and scattered from the sample. Neutrons detected at a 90° scattering angle are recorded and intensity displayed on a multichannel analyzer as a function of flight time. Peaks in the scattered spectrum correspond to neutrons of wavelengths satisfying the Bragg equation for elastic scattering at the fixed scattering angle by planes of interplanar spacing  $d$ . The value of this instrument in this application is its high resolving power at large values of  $d$ .<sup>16</sup> In the region of interest the sensitivity of the spectrometer to line broadening corresponded to  $\Delta d/d = 0.001$ , while  $d$  could be determined to  $\pm 0.001\ \text{\AA}$ . The sample, consisting of powder encapsulated in a thin-walled aluminum cylinder of  $\frac{1}{2}$  in. diam, was used to record diffraction patterns at room temperature and 4°K.

#### D. Single-Crystal Neutron Diffraction Study

Neutron diffraction measurements were carried out at a two-axis spectrometer at CP-5 at ANL. The measurements were made on a 2.77-mg single crystal of  $\alpha$ -manganese. Two zones were explored: [110] and [100]. The orientation of the crystal was checked by measuring the intensities of the nuclear reflections in different quadrants of the chosen zone. The existence of a random distribution of magnetic domains was established by the observa-

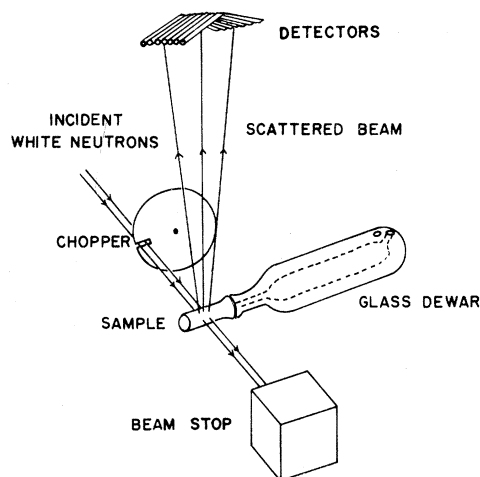


FIG. 2. Schematic representation of a time-of-flight neutron spectrometer.

program NUCLS.<sup>18</sup> The results of the refinements are given in Table II B. No significant changes in

TABLE III. Observed and calculated structure factors  $F_o^2$  and  $F_c^2$  from the x-ray powder study.

T = 300 °K			T = 77 °K			T = 4 °K		
S	$F_o^2$	$F_c^2$	S	$F_o^2$	$F_c^2$	S	$F_o^2$	$F_c^2$
			2	-0	1	2	-0	2
			4	-0	0	4	-0	0
6	18	20	6	20	19	6	20	20
8	21	27	8	28	26	8	23	24
10	3	3	10	5	4	10	5	4
12	25	27	12	29	26	12	29	28
14	39	34	14	45	35	14	41	36
16	206	171	16	205	180	16	162	177
18	3398	3721	18	3559	3836	18	3708	3845
20	6	7	20	11	8	20	13	6
22	786	912	22	809	960	22	760	964
24	317	343	24	320	359	24	312	359
26	510	539	26	533	559	26	527	554
30	36	36	30	34	36	30	32	34
32	13	14	32	13	12	32	13	14
34	27	25	34	32	27	34	29	25
36	35	38	36	40	41	36	44	40
38	48	40	38	57	45	38	57	47
40	8	9	40	11	10	40	12	10
			42	10	8	42	9	8
44	68	75	44	85	82	44	84	84
46	25	25	46	34	25	46	35	28
48	176	194	48	210	206	48	259	210
50	279	269	50	284	291	50	227	298
52	-0	0	52	-0	0	52	-0	0
54	984	842	54	988	918	54	936	923
56	176	141	56	176	156	56	211	154
58	58	79	58	77	90	58	79	86
62	123	126	62	151	141	62	161	143
			64	-0	0	64	-0	0
66	48	46	66	50	50	66	47	51
68	55	53	68	80	61	68	81	64
70	53	44	70	60	50	70	62	51
72	244	248	72	240	276	72	268	279
74	57	44	74	51	55	74	60	54
76	20	21	76	18	25	76	21	26
78	47	39	78	49	44	78	55	46
80	1	2	80	3	3	80	3	2
82	14	19	82	76	82	82	71	85
84	14	19	84	24	22	84	21	22
86	70	72	86	85	81	86	82	80
88	41	37	88	43	45	88	39	46
90	130	135	90	140	152	90	158	152
94	29	24	94	33	28	94	32	28
96	15	13	96	20	15	96	20	15
98	70	57	98	82	65	98	83	71
100	3	1	100	5	0	100	6	1
102	15	17	102	19	19	102	16	19
104	15	19	104	18	22	104	19	23
106	8	8	106	9	11	106	10	11
108	17	17	108	13	20	108	15	22
110	48	51	110	57	65	110	60	65
114	75	77	114	80	90	114	87	92
116	10	9	116	14	13	116	15	12
118	134	95	118	109	116	118	118	119
120	68	58	120	77	67	120	71	68
122	77	73	122	108	89	122	129	90
126	82	86	126	95	103	126	105	107
154	41	44	154	63	57	154	67	58
158	7	8	158	15	13	158	8	12
186	31	26				186	36	35
190	4	4				190	6	5
218	21	17	218	25	26	218	32	26
222	9	9	222	14	12	222	13	13
242	41	28	242	43	41	242	49	42

the atomic parameters at 77 and 4 °K were found, in agreement with the x-ray powder results. The instrumental constant determined from the nuclear reflections at 4 °K on the basis of the accepted scattering amplitude  $b_{Mn} = 0.37 \times 10^{-12}$  cm was used to assign the absolute magnitude of the magnetic moments as found from the intensities of the magnetic reflections.

A collinear spin model for a crystal with a random distribution of magnetic domains was used in the analysis of the magnetic data. The determination of the relative sign and magnitude of the moment on a given symmetry site was made by the computer program NUCLS from the magnetic intensities. The single spherically symmetric  $Mn^{2+}$  magnetic form factor of Hastings, Elliott, and Corliss<sup>19</sup> was used. The results of this refinement are shown in Table IV. In Fig. 4 the results of the magnetic moment refinement have been plotted as a function of temperature. As the moment on atom IV does not differ significantly from zero, it is not clear that any physical significance should be attached to its temperature behavior. The results of the collinear moment determination of Kunitomi, Yamada, Nakai, and Fujii<sup>6</sup> are indicated for comparison. The final observed and calculated values for the nuclear and magnetic structure factors are given in Table V.

The large values of the weighted  $R$  factors, defined by the relation

$$R = \frac{\sum_i w_i (F_o^2 - F_c^2)_i^2}{\sum_i w_i (F_o^2)_i^2},$$

for the magnetic refinements indicate some real discrepancy between the calculated and observed intensities, since the average predicted weighted  $R$  factor for the magnetic reflections is about 7% for statistical deviations and the weighted  $R$  factors for the refinement of nuclear data to the room-temperature structure are about 4%. It is considered significant that the deviations between observed intensities and those calculated using the collinear model are in the same direction and of the same order of magnitude as the deviations observed by Kunitomi *et al.* in the fit of their data to the collinear model.

TABLE IV. Magnetic moments determined for a collinear spin model.

Magnetic moments	77 °K	50 °K	4 °K
$\mu_I$	1.25(9)	1.54(19)	1.72(19)
$\mu_{II}$	0.95(4)	1.14(8)	1.46(8)
$\mu_{III}$	-0.82(2)	-0.97(3)	-1.11(4)
$\mu_{IV}$	-0.04(3)	-0.05(6)	0.02(5)
$R$	14.1%	20.6%	17.7%

## IV. SUMMARY AND DISCUSSION

It has been established by the x-ray powder measurements reported here that the atomic coordinates in  $\alpha$ -manganese at low temperatures do not differ enough from their values at room temperature to affect the calculation of the magnetic structure factors. High-resolution time-of-flight neutron diffraction patterns from the powder indicate that the chemical and magnetic unit cells of antiferromagnetic  $\alpha$ -manganese are identical in size. From the measurement of 14 independent magnetic reflections at three temperatures below the Néel temperature, magnetic moments for the four atom types have been determined assuming a collinear spin arrangement. The fit of the observed and

calculated intensities indicates that a less restricted model is necessary to explain the magnetic structure.

Kunitomi, Yamada, Nakai, and Fujii have proposed a magnetic structure in which the magnetic moments are not collinear. Since their torsion-balance measurements indicate that the magnetic point group is tetragonal, they chose the magnetic space group  $I'42'm'$ .<sup>20</sup> In this model 13 independent parameters, six possible moments, and seven angular variables, are determined from 24 independent reflections. The fit of the calculated and measured intensities is within statistical error for all but one reflection. They point out that the structure so determined is not unique since the ratio of measured reflections to parameters de-

TABLE V. Calculated and observed structure factors  $F_c^2$  and  $F_o^2$  and the uncertainty in the observed structure factors  $\Delta F_o^2$  for the nuclear and magnetic reflection from the single-crystal neutron diffraction study.

Nuclear reflections																	
$T=300^\circ\text{K}$						$T=77^\circ\text{K}$						$T=4^\circ\text{K}$					
$h$	$k$	$l$	$F_c^2$	$F_o^2$	$\Delta F_o^2$	$h$	$k$	$l$	$F_c^2$	$F_o^2$	$\Delta F_o^2$	$h$	$k$	$l$	$F_c^2$	$F_o^2$	$\Delta F_o^2$
2	0	0	0	3	3	2	0	0	1	3	2	2	2	0	48	44	7
2	2	0	39	37	6	2	2	0	39	35	7	3	1	0	7	0	3
3	1	0	3	0	4	3	1	0	2	0	4	2	2	2	96	97	12
2	2	2	95	102	10	2	2	2	90	89	10	4	0	0	1382	1380	40
4	0	0	1319	1254	36	4	0	0	1309	1315	36	3	3	0	5567	5619	77
3	3	0	5301	5363	68	3	3	0	5513	5523	75	4	1	1	5773	5868	74
4	1	1	5533	5492	68	4	1	1	5698	5761	75	4	2	0	24	27	12
4	2	0	19	15	6	4	2	0	21	21	6	3	3	2	2850	2645	61
3	3	2	2728	2763	59	3	3	2	2830	2764	50	4	2	2	1229	1163	46
4	2	2	1176	1201	36	4	2	2	1240	1272	44	5	1	0	426	399	20
5	1	0	423	388	21	5	1	0	441	434	22	4	3	3	166	168	16
4	4	0	143	126	12	4	3	3	140	137	16	5	3	0	22	21	9
4	3	3	141	142	19	5	3	0	2	15	9	6	0	0	41	39	10
5	3	0	4	11	4	6	0	0	45	45	12	4	4	2	279	268	20
6	0	0	38	31	13	4	4	2	262	244	20	6	2	0	83	128	18
4	4	2	241	216	16	6	2	0	78	55	12						
6	2	0	75	126	22	6	2	2	14	33	4						
6	2	2	701	785	50												
Magnetic reflections																	
$T=77^\circ\text{K}$						$T=50^\circ\text{K}$						$T=4^\circ\text{K}$					
$h$	$k$	$l$	$F_c^2$	$F_o^2$	$\Delta F_o^2$	$h$	$k$	$l$	$F_c^2$	$F_o^2$	$\Delta F_o^2$	$h$	$k$	$l$	$F_c^2$	$F_o^2$	$\Delta F_o^2$
1	0	0	1	0	1	1	0	0	2	0	1	1	0	0	4	1	2
1	1	1	82	85	6	2	1	0	229	269	15	1	1	1	193	209	6
2	1	0	159	169	9	3	0	0	109	116	9	2	1	0	297	305	12
3	0	0	80	79	9	2	2	1	98	90	6	3	0	0	108	115	8
2	2	1	71	68	6	3	0	1	205	184	7	2	2	1	153	146	10
3	1	1	145	128	7	3	1	1	44	42	6	3	1	1	278	251	15
3	2	0	32	25	6	3	2	0	81	105	9	3	2	0	70	45	7
3	2	2	56	54	6	3	2	2	71	81	10	3	2	2	125	184	14
4	1	0	49	43	7	4	1	0	6	0	3	4	1	0	93	93	11
3	3	1	5	5	3	3	3	1	53	62	6	3	3	1	7	0	3
5	0	0	37	45	7	5	0	0	42	17	6	5	0	0	106	91	11
4	3	0	30	36	8	4	3	0	17	25	5	4	3	0	53	39	9
5	1	1	12	12	5	5	1	1	8	25	5	5	1	1	21	29	10
3	3	3	6	25	5	3	3	3	21	64	10	3	3	3	11	56	7
5	2	0	14	46	9	5	2	0				5	2	0	33	85	9

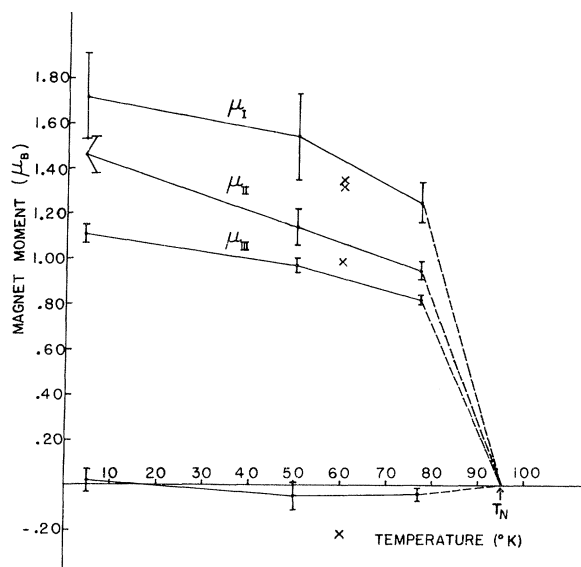


FIG. 4. Magnetic moments determined for the collinear spin model. Lines are drawn between points for clarity. Crosses (x) indicate the results of Kunitomi *et al.* (Ref. 6).

terminated is small.

A difficulty present in all neutron diffraction experiments on  $\alpha$ -manganese is the need to limit the adjustable parameters by assuming that all atoms have the same form factors. Since the different atom types occupy different symmetry sites and volumes in the unit cell, variations in the ionizations of the four atom types may exist. If the 3d shells are affected by these variations, then; as pointed out by Watson and Freeman,<sup>21</sup> the magnetic form factors could be affected. These, in turn, would affect the magnetic moments determined.

In the collinear model at 4 °K, the moments on atoms I, II, III are between 1 and 2  $\mu_B$  while that on atom IV is about 0  $\mu_B$ . For the noncollinear model an extrapolation to 4 °K of the moments de-

termined by Kunitomi *et al.* at 60 °K gives moments between 2 and 2.5  $\mu_B$  for atoms I and II and moments between 0.35 and 0.75  $\mu_B$  for atoms III and IV. Measurements of the internal fields of the four atom sites by others have indicated that large localized moments exist on atoms I and II while small, perhaps nonlocal moments exist on atoms III and IV. These results are consistent with those of the neutron diffraction studies for atoms I and II, but the appreciable moments on atom III for either model and on atom IV for the noncollinear model seem inconsistent with the internal magnetic fields of 10 kG at these sites.

A major difficulty in trying to determine the correct magnetic spin structure for  $\alpha$ -manganese is the averaging of nonequivalent magnetic reflections in a crystal with randomly oriented magnetic domains. If a crystal with a single tetragonal magnetic domain (or significant anisotropies in the domain distribution) could be investigated, the number of independent magnetic reflections would be increased by a factor of 2 over random domain samples. Unsuccessful attempts to produce anisotropies in the domain distribution by cooling the crystals through the Néel transition in the presence of a magnetic field of 30 kG have been carried out in this laboratory.<sup>20</sup> It appears that single crystals of higher perfection whose magnetic domain distributions can be altered will be necessary to define completely the antiferromagnetic structure of  $\alpha$ -manganese.

After the completion of this paper three additional articles<sup>22</sup> by the group at Osaka (Yamada, Tazawa, Kunitomi, and Nakai) have appeared. An elaboration and an extension of the magnetic symmetry, torque, and neutron scattering results previously reported are given. The neutron diffraction study of the magnetic structure has been extended (with Cox and Shirane at Brookhaven) to 4 °K, where the structure is found to be essentially the same as that at 60 °K. The new results presented in these articles are consistent with those previously reported and do not affect the conclusions of this paper.

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## Dielectric Properties of Strontium Titanate at Low Temperature

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The dielectric properties of annealed single crystals of  $\text{SrTiO}_3$  have been measured over the temperature range from 5 to 300 °K. At temperatures below 50 °K, electric double hysteresis loops are observed and associated changes in weak-field permittivity under dc bias have been measured. It is shown that a phenomenological analysis based on the simple Kittel function accounts satisfactorily for many aspects of the dielectric behavior of  $\text{SrTiO}_3$  crystals.

### I. INTRODUCTION

Strontium titanate is of considerable interest as a low-temperature perovskite ferroelectric. The Cochran ferroelectric mode was first observed in this material by infrared<sup>1,2</sup> and by neutron spectrometry.<sup>3</sup> It is well known that a phase transition occurs at about 110 °K, which involves a symmetry change from pseudocubic to tetragonal and is evidenced by the rapid onset of twinning.<sup>4-6</sup> Further evidence is obtained through electron-paramagnetic-resonance<sup>7,8</sup> (EPR) measurements of Fe- and Gd-doped  $\text{SrTiO}_3$ . There is no apparent discontinuity in the dielectric constant<sup>9-11</sup> or its slope at this temperature. Recent measurements by Fleury, Scott, and Worlock<sup>12</sup> and by Shirane and Yamada<sup>13</sup> have shown that the phase change is associated with a "crumpling" of the regular array of oxygen octahedra, in which the individual octahedron rotates about a fourfold axis.

The dielectric constant of  $\text{SrTiO}_3$  follows a Curie-Weiss law with a Curie temperature of 40 °K. Weaver<sup>9</sup> observed weak hysteresis below 62 °K and concluded that  $\text{SrTiO}_3$  goes through a second-order phase transition to a ferroelectric state.

In this paper we present evidence for a possible antiferroelectric phase transition at about 62 °K in carefully annealed single-crystal  $\text{SrTiO}_3$ .

### II. ANNEALING

The procedure used was in many respects similar to that used earlier by Paladino *et al.*<sup>14</sup> Annealing was carried out in a special high-temperature Centorr electric (tungsten) furnace, which was modified for continuous operation with the sample in normal air atmosphere at 1900 °C. The annealing procedure consisted of heating to 1850 °C, maintaining this temperature for 6 h, slow cooling at the rate of 100 °C/h to 1300 °C, then shutting off