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Long-Range Magnetic Order in MnO

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Neutron diffraction measurements on powder samples confirm that the magnetic moments in MnO are arrayed in ferromagnetic sheets parallel to {111} planes, with neighboring planes coupled in an antiferromagnetic fashion. The long-range order parameter S increases progressively with decreasing temperature below the Néel temperature, but complete order is apparently not reached even at very low temperatures. The magnetic unit cell is rhombohedral, and the rhombohedral angle changes progressively as the temperature is lowered. The change in rhombohedral angle is shown to be related to the long-range order parameter, and it is deduced from this that the distance between antiparallel spins is less than the distance between parallel spins by 0.8%.

I. INTRODUCTION

THE long-range spin order in MnO has been investigated by means of neutron diffraction by Shull, Strauser, and Wollan[1] and by Roth.[2,3] It is agreed that the magnetic unit cell has a cell edge which is twice as large as the chemical cell, and that the magnetic moments are ferromagnetically arranged on {111} planes with neighboring planes coupled in an antiferromagnetic fashion. The structure has the NaCl form above the Néel temperature (which is about 122°K) and becomes rhombohedral below the critical with a rhombohedral angle slightly greater than 90°. Shull *et al.* postulated a spin alignment parallel to the [100] direction. Roth showed that this was inconsistent with his more extensive data and suggested that the spin vector was in the {111} planes, although he was unable to unequivocally assign a direction to the spins in the {111} sheets. The short-range order above the Néel temperature has been measured recently by the present authors[4] and it was shown that the {111} layering is retained on a localized scale above the critical, in regions of about 50 Å dimension.

We confirm the spin arrangement suggested by Roth in this study. In addition, a determination of the long-range order parameter S has been made as a function of temperature. It is shown that the rhombohedral angle also changes with the degree of order, and we use this observation to deduce that the distance between antiparallel spins is about 0.8% shorter than the distance between parallel spins.

II. EXPERIMENTAL RESULTS

MnO powder was prepared by decomposing $MnCO_3$ at 1000°C under a dry hydrogen atmosphere. The powder sample was packed in a cylindrical aluminum holder with a cavity $\frac{3}{4}$ in. in diameter and 2 in. long in a cryostat which could be held at various temperatures down to that of liquid nitrogen. The diffraction experiments were carried out at the MIT nuclear reactor with thermal neutrons monochromated by a {111} reflection from a lead crystal. The mean wavelength used was 1.199 Å. A small half-wavelength contribution was present from the {222} nuclear peak for MnO, since this occurs at the same position as the normal {111} magnetic peak. The nuclear peak was approximately invariant with temperature, and it was possible to make a small correction, where needed, by observations of the half-wavelength peak at temperatures just above the Néel temperature. The diffracted beam was collimated by a Soller slit system and the diffraction angle could be determined within ±1 min of arc.

The powder patterns confirmed the structure determined by Roth. The rhombohedral structure is indicated by the asymmetry in the {222} nuclear reflection shown in Fig. 1. The {222} reflection, with a multi-

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[1] C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. 83 333 (1951).

[2] W. L. Roth, Phys. Rev. **111**, 772 (1958).

[3] W. L. Roth, Phys. Rev. **110**, 1333 (1958).

[4] I. A. Blech and B. L. Averbach, Physics **1**, 31 (1964).

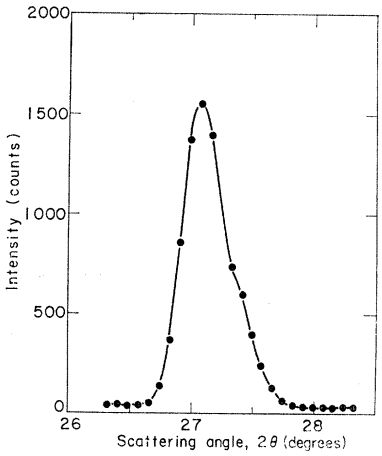

FIG. 1. {222} diffraction peak of MnO at 82°K.

plicity of 2, appears at a slightly larger diffraction angle than the other six planes. The magnetic superstructure peaks appear at the corresponding {111} position, indicating that the magnetic planes have a slightly smaller interplanar distance. For the magnetic MnO cell, containing 32 manganese atoms and 32 oxygen atoms, the structure factors for the nuclear peaks F_n are

$$\begin{aligned} &F_n=0, && h,k,l \text{ mixed},\\ &F_n=32\,(b_{\mathrm{Mn}}+b_0), && h,k,l \text{ even},\\ &F_n=32\,(b_{\mathrm{Mn}}-b_0), && h,k,l \text{ odd}. \end{aligned} \tag{1}$$

The quantities b_{Mn} and b_0 are the nuclear scattering amplitudes for manganese and oxygen, respectively. For the magnetic structure factor F_m we assume that all of the spins are parallel to {111} planes and obtain,

$$\begin{aligned} &F_m=32p, && h,k,l \text{ all odd, with } h+k,k+l,l+h=4n+2,\\ &F_m=0, && \text{otherwise}, \end{aligned} \tag{2}$$

and the total structure factor becomes,

$$F^2=F_n^2+q^2F_m^2, \tag{3}$$

where the magnetic scattering amplitude,[5] $p=(e^2\gamma/mc^2)sf$, with s=spin quantum number, γ=magnetic moment of neutrons in nuclear magnetons, f=magnetic form factor,[6] e=electronic charge (esu), m=electronic mass, c=velocity of light, and q is a factor which depends on the direction of the spins. The values used here are,[6] $b_{\mathrm{Mn}}=-0.37\times10^{-12}$ cm, $b_0=0.577\times10^{-12}$ cm, $p=1.35\times10^{-12}$ cm at $\sin\theta/\lambda=0$.

The positions of the first two magnetic superstructure reflections, θ_{111} and $\theta_{11\bar{3}}$, were used to calculate the cell parameter and rhombohedral angle. These values were consistent with the positions of the other diffraction peaks up to {622}. Only {111} and $\{\bar{1}\bar{1}\bar{1}\}$ planes contribute to the first superstructure reflection,

TABLE I. Cell parameter and rhombohedral angle of MnO.

Temp. (°K)	T/T_c	θ_{111}	$\theta_{11\bar{3}}$	d_{111} (Å)	$d_{11\bar{3}}$ (Å)	α	a (Å)
82	0.66	6°48.5′	12°56′	5.057	2.678	90°33±5′	8.843
93	0.75	6°48.5′	12°56′	5.057	2.678	90°33±5′	8.843
104	0.82	6°48′	12°56′	5.063	2.678	90°30±5′	8.845
113	0.91	6°47.5′	12°56′	5.072	2.678	90°23±5′	8.844
123	0.98	6°46′	···	5.085	···	···	···
125	1.00	6°44′	···	5.113	···	···	···
129	1.03	6°44′	···	5.113	···	90°	8.856[a]
298	2.45	···	···	5.132	···	90°	8.888[a]

[a] Cubic structure, calculated from {222} and {622} nuclear peaks.

but all of the six planes, $\{\bar{3}11\}$, $\{3\bar{1}\bar{1}\}$, $\{1\bar{3}1\}$, $\{\bar{1}3\bar{1}\}$, $\{11\bar{3}\}$, $\{\bar{1}\bar{1}3\}$ contribute to the second. These data are summarized in Table I. The interplanar spacing between Mn^{2+} ion sheets, which corresponds to d_{222}, and the deviation of the rhombohedral angle, $\delta=\alpha-90°$, shown in Fig. 2 indicate an experimental Néel temperature of about 125°K, which is quite close to the commonly accepted value, 122°K. It is evident that the spacing of the magnetic planes and the rhombohedral angle appear to change with temperature. The determination of the cell parameter is subject to a substantial error, estimated at ±0.028 Å, and is thus unsuitable for the determination of volume changes at the magnetic transition. Our cell parameters at 82°K, $a=8.843$ Å, $\alpha=90°\,33'$, are significantly different from the values given by Roth at 4°K, $a=8.873$ Å and $\alpha=90°\,26'$, and these differences are at present unreconciled. However, our results at room temperature agree well with the x-ray value, $a=8.888$ Å.[7,8]

The spin arrangement may be inferred from the scattered intensity. The diffracted intensity P in a powder line is given by

$$P=KjF^2e^{-2M}A(\theta)/\sin\theta\sin2\theta, \tag{4}$$

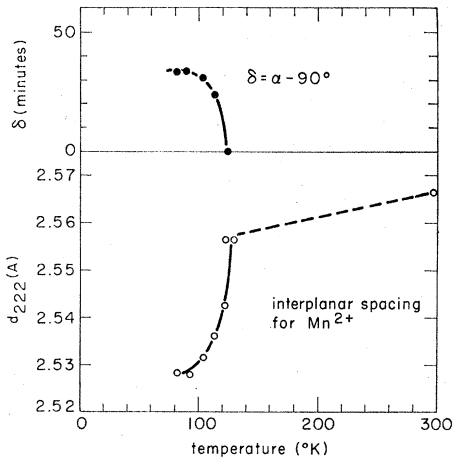

FIG. 2. Interplanar spacing and rhombohedral angle.

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[6] G. E. Bacon, *Neutron Diffraction* (Oxford University Press, London, 1962).
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[8] N. Kuriyama and F. Hosoya, J. Phys. Soc. Japan **17**, 1022 (1962).

TABLE II. Comparison of ordered spin models.

Plane	$\sin\theta$	e^{-2M}	j	f	$F^2/1024$ (barns)	P (measured)	$P_{[100]}$	$P_{[1\bar{1}0]\{111\}}$
111	0.118	0.996	2	0.865	$1.360q^2$	680	641	961
311	0.223	0.986	6	0.65	$0.771q^2$	183	312	242
222	0.238	0.984	2	···	0.90	656	656	656
222	0.235	0.984	6	···	0.90			
400	0.271	0.979	6	···	0.043	17	18	18
331	0.295	0.975	6	0.50	$0.456q^2$	108	115	124
333	0.352	0.965	2	0.378	$0.261q^2$	75	59	75
511	0.352	0.965	6	0.378	$0.261q^2$			
440[a]	0.384	0.958	12	···	0.043	···	18	18
531	0.401	0.954	12	0.285	$0.148q^2$	···	39	32
622[a]	0.449	0.942	24	···	0.90	561	563	563

[a] All planes are assumed to have the same angular position.

where K is a constant, j the multiplicity of the reflection, e^{-2M} the Debye-Waller temperature factor, $A(\theta)$ the absorption factor, and 2θ the Bragg angle. The absorption factor was found to be almost constant in this angular range and the temperature factor was calculated assuming a Debye temperature, $\theta=502$°K. The relative intensities were calculated and compared with the measured values, using the {222} nuclear peak intensity as a reference. If we assume that the spins are parallel or antiparallel to the [100] direction, the directional factor, $q^2=\frac{2}{3}$, and is independent of diffracting plane. If we assume that the spins lie along $[1\bar{1}0]$ directions in the {111} plane, the values of q^2 depend on the diffracting plane with $q^2=1$ for {111}, $q^2=17/33$ for $\{\bar{3}11\}$, $q^2=41/57$ for $\{33\bar{1}\}$, $q^2=23/27$ for {333} {511}, $q^2=19/35$ for $\{5\bar{3}1\}$. The resultant comparison is shown in Table II. It is evident that the $[1\bar{1}0]\{111\}$ model fits better than the [100] model, particularly if it is recognized that the long-range spin order is not perfect and that the measured magnetic peaks will thus not exhibit the full intensity value. A strong diffuse scattering was observed in the vicinity of the {111} magnetic peak. This arose from the residual short-range order[4] and was not included in the peak intensity.

Using the $[1\bar{1}0]\{111\}$ spin model, we may evaluate the Bragg and Williams long-range order parameter S defined by

$$S=r_a-w_b=r_b-w_a, \tag{5}$$

where: r_a=fraction of spin-up sublattices occupied by the right spin (up), w_a=fraction of spin-up sublattices occupied by the wrong spin (down), r_b=fraction of spin-down sublattices occupied by the right spin (down), w_b=fraction of spin-down sublattices occupied by the wrong spin (up). The value of the order parameter may be calculated from the ratio, $S^2=P$(measured)$/P$(calculated), and it is apparent that the value is dependent on the spin model.

The superstructure lines {111} and $\{11\bar{3}\}$ were measured as a function of temperature. The long-range order parameter was calculated from the {111} peak, using the $[1\bar{1}0]\{111\}$ model. These values are tabulated in Table III. This was supplemented by observing the

TABLE III. Long-range order parameters.

Temp. (°K)	T/T_c	111 intensity (counts)	$11\bar{3}$ intensity (counts)	S	(111) intensity / ($11\bar{3}$) intensity
82	0.66	747±23	200±12	0.84	3.74±0.34
93	0.75	686±22	189±12	0.81	3.64±0.35
104	0.82	555±20	154±10	0.73	3.62±0.36
113	0.91	470±18	122±10	0.67	3.83±0.46
123	0.98	331±16	···	0.57	···
125	1.00	15	···	0.12	···
129	1.03	0	0	0	···
77[a]	0.63	1072	308	0.83	3.48
4.2[b]	0.04	804	258	0.90	3.12

[a] Shull *et al.* (Ref. 1).
[b] Roth (Ref. 3).

ratio of the line intensities {111}/$\{11\bar{3}\}$. This ratio should have a value 3.96 for the model chosen, and Table III shows that the observed values are close to this, further substantiating the $[1\bar{1}0]\{111\}$ model. Values of S were also calculated from the data of Shull *et al.*[1] and Roth.[3] The values of S calculated from the latter data are probably somewhat low, because of the low values of the intensity ratio {111}/$\{11\bar{3}\}$, but they are included for comparison.

Figure 3 shows the variation of the long-range parameter with temperature. There is a rapid decrease

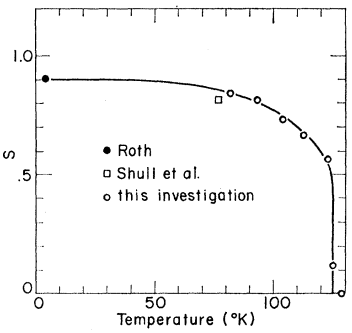

FIG. 3. Long-range order parameter as a function of temperature.

in order in the vicinity of the Néel temperature, but the order does not appear to be complete even at 4°K. The width of the superstructure lines at half-maximum was found to remain at a constant value, $2\theta=20'$, even at temperatures just 2°C below the critical temperature. Thus, it appears that the ordered domains are sizable, i.e. 1000 Å or larger, even at the very onset of order.

III. DISCUSSION OF RESULTS

The failure of S to reach a value of unity has been discussed by Roth.[3] Recent measurements[9] of neutron magnetic scattering from single crystals of MnO have shown that there is a systematic antiphase domain arrangement at temperatures just above the critical. It thus seems probable that antiphase boundaries are present below the Néel temperature, and the persistence of such boundaries will result in a residual disorder.

This spin system is analogous to the atomic order found in the alloy CuPt. The latter alloy orders by forming alternate layers of copper and platinum atoms on {111} planes, and the ordered structure is also rhombohedral with the rhombohedral angle slightly greater than 90°.

Walker[10] also observed that the rhombohedral angle varied with the degree of order and derived a relationship between these two parameters. Following Walker, we define l_{aa}= distance between two near-neighbor parallel spins, l_{ab}= distance between two near-neighbor antiparallel spins, l_1= average distance between two neighboring sites in the same {111} plane, l_2= average distance between two neighboring sites in adjacent {111} planes, $\delta=\alpha-\pi/2$, in radians. We assume that all of the spins have the orientation $[1\bar{1}0]\{111\}$, with the order indicated by the parameter S. Then, neglecting second-order terms,

$$(l_1/l_2)^2-1=(2/\sqrt{3})\delta. \tag{6}$$

In terms of the near-neighbor distance, l_{aa} and l_{ab},

$$l_1=\tfrac{1}{2}[r_a(r_a l_{aa}+w_a l_{ab})+w_a(r_a l_{ab}+w_a l_{aa}) +r_b(r_b l_{aa}+w_b l_{ab})+w_b(r_b l_{ab}+w_b l_{aa})] \tag{7}$$

with a similar expression for l_2. Introducing the long-range order parameter, S,

$$l_1=\tfrac{1}{2}[(l_{aa}+l_{ab})+S^2(l_{aa}-l_{ab})], \tag{8a}$$

$$l_2=\tfrac{1}{2}[(l_{aa}+l_{ab})-S^2(l_{aa}-l_{ab})], \tag{8b}$$

and

$$S^2=(2/\sqrt{3})M^2\delta/[1+(4/\sqrt{3})\delta], \tag{9}$$

where

$$M=\tfrac{1}{2}[(l_{aa}+l_{ab})/(l_{aa}-l_{ab})]^{1/2}. \tag{10}$$

Using the data obtained at 82°K, $M=8.4$. If we assume that the characteristic distances l_{aa} and l_{ab} do not vary greatly with temperature, and neglecting the normal expansion behavior, which results in much smaller dimensional changes, the order parameter may be calculated from Eq. (9). This relationship becomes $S^2=70.9\delta$. Values of the order parameter calculated in this way are compared with those obtained from peak intensities in Table IV, and the agreement is quite close. The relative interspin distances may be calculated from Eq. (10), and this results in the quantity, $(l_{aa}-l_{ab})/l_{aa}=0.0081$. The antiparallel coupling is thus about 0.8 percent smaller than the parallel coupling, and this result is indicative of the strong antiferromagnetic exchange between manganese ions.

TABLE IV. Long-range order parameters.

T (°K)	T/T_c	δ (min)	S Calculated from δ	S From peak intensities
82	0.66	34	0.84	0.84
93	0.75	33	0.82	0.81
104	0.82	29	0.77	0.73
113	0.91	23	0.69	0.67

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[9] Alan Renninger, S. C. Moss, and B. L. Averbach, Phys. Rev. Letters (to be published).

[10] C. B. Walker, J. Appl. Phys. 23, 118 (1952).