

# Crystal Defects in Manganese (II) Oxide and their Influence on Antiferromagnetic Behaviour

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Antiferromagnetic domain walls in synthetic MnO crystals are found by electron microscopy to exist at temperatures up to  $\sim 25^\circ\text{K}$  above  $T_N$ . Precipitates of  $\text{Mn}_3\text{O}_4$  and dislocations associated with them impede the motion of walls and are the main cause of their retention above  $T_N$ . On cooling to below  $T_N$ , such defects apparently can also provide the basis of a "memory" for the re-establishment of earlier domain configurations. Electron diffraction shows that the manganous oxide is non-stoichiometric and at room temperature possesses both short-range order and a superlattice (with  $a_{\text{sup}} = 2a_0$ ). The superlattice is believed to be magnetic in origin but the short-range order is manifest as structural microdomains, probably with ordering of cation vacancies. The microdomains occur as lamellae parallel to  $\{111\}$ , with an average thickness of  $30 \text{ \AA}$ .

## 1. Introduction

The importance of lattice and magnetic defects in magnetic materials is now generally recognised. There is also considerable current interest in the ways in which metal oxides accommodate deviations from stoichiometry. In this paper, direct observations of magnetic and structural inhomogeneities in manganese (II) oxide, MnO, and certain interrelations are reported.

In common with the divalent metallic oxides of Ti, Fe, Co and Ni, MnO has the sodium chloride structure. Like CoO and NiO, MnO is antiferromagnetic and below the antiferromagnetic Néel temperature  $T_n$  ( $\sim 122^\circ\text{K}$  for MnO) it undergoes a small lattice distortion. It has been established [1, 2] that in all three oxides the spin structures are similar: the electrons with uncompensated spins have their spins aligned ferromagnetically within sheets parallel to the  $\{111\}$  planes and antiparallel to those in the adjacent sheets. In CoO the distortion is tetragonal while in NiO and MnO, X-ray evidence suggests that the distortions are rhombohedral ( $\alpha > 60^\circ$ ). It should be noted, however, that neutron diffraction [3] indicates that the true symmetry of NiO when antiferromagnetic is orthorhombic and the deviation from rhombohedral is too small to be detected by X-ray methods. It is also known that the oxides contain

domains when in the antiferromagnetic state. Previous work on NiO [4] and CoO [5] using electron microscopy has reported some features of the domain structures.

Previous studies have also shown that in practice the transition to the normal state at the Néel temperature is not total. Renninger *et al* [6] deduced from neutron scattering data that small regions of antiferromagnetic order exist well above  $T_n$ . At  $\sim 10^\circ\text{K}$  above  $T_n$  the regions were calculated to have an average size of  $46 \pm 5 \text{ \AA}$ . Also relevant is the observation of Remaut *et al* [5] that the crystallographic deformation associated with the antiferromagnetic state in CoO had a long relaxation time at room temperature. No direct observations of domains above  $T_n$  were reported, however, and forbidden reflections could be due to other sources of elastic strain.

Recently there have been several studies of the crystallography of defect structures in non-stoichiometric metal oxides. Particular attention has been given to the  $\text{MeO}_3$  compounds and other systems which incorporate defects by means of shear structures. Little work has been done on transition metal oxides with the NaCl structure and virtually none on MnO. The preliminary findings of our work were reported recently [7, 8] and while this work was nearing

completion, Delavignette and Amelinckx [9] reported finding  $Mn_3O_4$  inclusions in a crystallographic relationship with the MnO host lattice and also the presence of fine structural lamellae. Our results are in accord with the findings but are more extensive and also deal with antiferromagnetic effects.

## 2. Experimental Details

Most of the samples examined were cut from a boule of synthetic MnO grown by the flame fusion method and supplied by the Nakazumi Crystals Corporation. We also report a few results on a sample of natural manganosite, MnO, which was kindly supplied by the Smithsonian Museum of Natural History (catalogue No. C 1413, from New Jersey).

Samples were prepared for electron microscopy by preshaping, followed by partial dissolution in a mixture of dilute hydrochloric and nitric acids, to produce electron-transparent areas. Samples were examined at both 100 and 650 kV (the latter being done with the microscope at the University of California, Berkeley, California). The observations of antiferromagnetic domains were made with the aid of a liquid-nitrogen cooled stage (no tilt facilities).

## 3. Experimental Results

### 3.1. General Observations on Crystal Perfection

Both the synthetic and natural "MnO" crystals showed extreme colour variations; although the majority were bright green (the "normal" colour) some parts were red. X-ray precession photographs of uniformly red parts from each source showed that the red material was not MnO at all, but  $Mn_3O_4$  – the mineral Hausmannite. This red material was discarded and our observations relate to the green crystalline material, which gave good X-ray patterns corresponding to MnO. Other X-ray photographs (Laue) taken in the course of the work reported in [7] gave no indications of misorientations  $\geq 2^\circ$  or of severe strain. Optical microscopy on thin sections of the MnO, however, showed that the synthetic material contained coarse ( $\sim 15 \mu\text{m}$  diameter) cruciform-like precipitates while the mineral MnO contained thin lathes of second phase, intimately associated with geometrically-shaped voids. Fig. 1 is a scanning electron micrograph which shows the spiked form of the precipitates in the artificial MnO quite clearly. The particles commonly possess eight main arms, and often

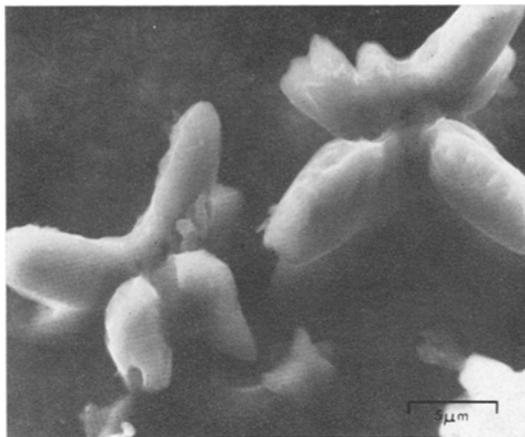
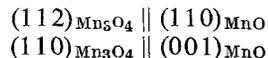


Figure 1 Scanning electron micrograph of precipitates leached out of synthetic MnO crystals by dissolution with dilute nitric acid.



Figure 2 Transmission optical micrograph of a thin section of a natural crystal of MnO containing lathe-like precipitates and voids.

some minor ones. Fig. 2 shows the appearance of natural MnO in thin section. X-ray microanalysis was incapable of clearly identifying the nature of the precipitates beyond the fact that they were an oxide of manganese. The small change in oxygen content compared with the matrix first led to the mistaken conclusion that the second phase was  $Mn_2O_3$  [8]. Further extensive work by electron diffraction, utilising the extra sample penetration afforded by the 650 kV microscope, proved that the heavily twinned precipitates are  $Mn_3O_4$  and are in epitaxial relationship with the MnO lattice:



These results are in agreement with the findings of  $Mn_3O_4$  in MnO by Delavignette and Amelinckx [9] and by Gjønnes *et al* [10]. In addition to the coarse precipitates of  $Mn_3O_4$  in synthetic MnO, electron microscopy revealed that there were some smaller ones and small voids. These small precipitates were found pinning many dislocation networks and sometimes apparently generating irregular systems of loops. It was soon discovered that glide dislocations were easily generated in MnO as a result of stresses caused by the electron beam. Slip apparently proceeds on the normal system for NaCl structure, namely  $\{110\} \langle 1\bar{1}0 \rangle$ . Fig. 3 shows extensive slip and the surface traces left by the moving dislocations should be noted. The significance of these is discussed in section 3.3.

The electron diffraction pattern from synthetic MnO (fig. 4a) showed certain anomalies: the presence of weak  $110$  reflections (which are "forbidden" for NaCl structures) and the occurrence of either semi-continuous streaking along  $\langle 110 \rangle$  directions in reciprocal space or alter-

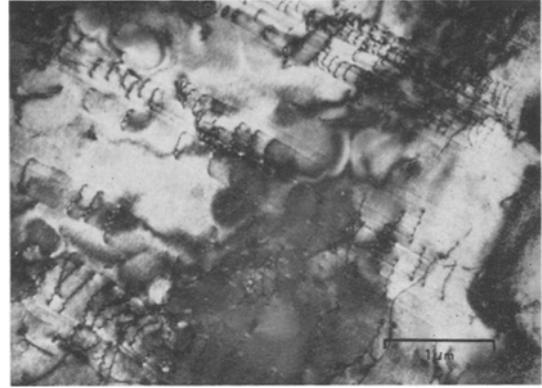


Figure 3 Slip dislocations induced by thermal stresses caused by the electron beam (650 kV.) Note the surface traces left by the moving dislocations.

natively, fine satellite spots displaced from the main spots along the  $\langle 110 \rangle$  directions. All of these features have been reported before [8, 9] but the previous explanations are not completely adequate. Streaking parallel to  $\langle 110 \rangle$ , however,

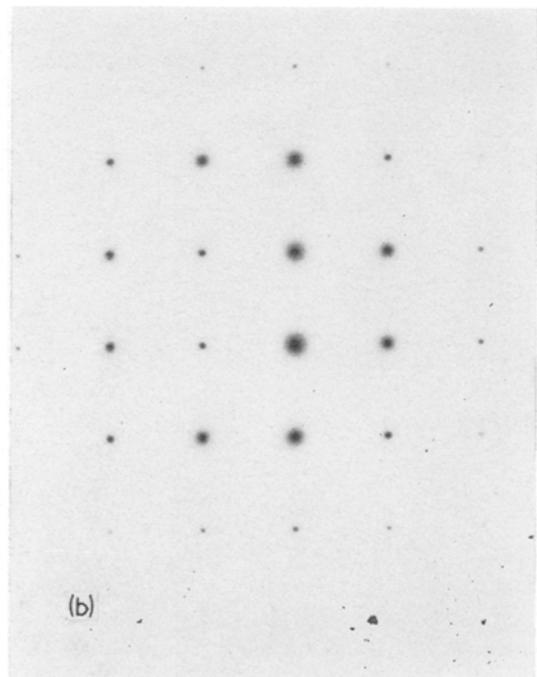
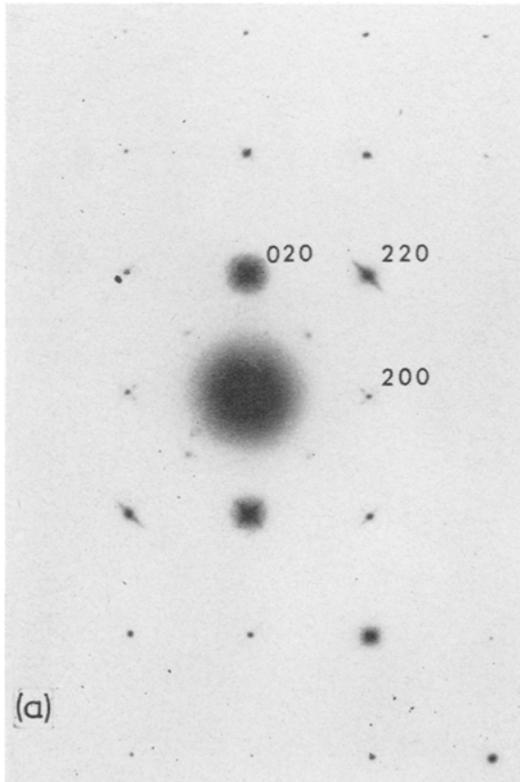


Figure 4 (a) Electron diffraction pattern (650 kV) from (001) foil of synthetic MnO. (b) Electron diffraction pattern (650 kV) from (001) foil of natural MnO.

has been correctly attributed by Delavignette and Amelinckx [9] to the presence of the  $\text{Mn}_3\text{O}_4$  precipitates.

In contrast to the complex pattern from synthetic  $\text{MnO}$ , the pattern from the more perfect regions of the natural  $\text{MnO}$  is simple and free from anomalies, as shown in fig. 4b. Although other more complex effects can be found in the mineral, fig. 4b may be taken as a relative standard for  $\text{MnO}$  crystals. The cause of anomalies in the pattern will be discussed in section 3.3.

### 3.2. Observations of Antiferromagnetic Structure near the Néel Temperature

On cooling foils to below the Néel temperature ( $122^\circ\text{K}$ ) by means of the liquid nitrogen cooled stage, domain walls appeared. It was normal to use (001) foils and the walls then usually appeared parallel to the [100] and [010] directions, suggesting that they were T-walls, parallel to the {011} planes. (S-walls are not normally seen but may sometimes be imaged weakly.) The disposition of T-walls (wedge-shaped because of

the foil geometry) show that they bound parallel-sided domains of differing spin vector, figs. 5a and b. No change in the diffraction pattern was noticed at the antiferromagnetic Néel temperature.

When a sample was repeatedly heated and then cooled again through the antiferromagnetic transition, there was seen to be a marked tendency for domain walls to appear in the same locations each time. They could also be removed from a small area by focusing the electron beam while the bulk of the foil remained in the antiferromagnetic state. On defocusing the beam, the previous configuration was usually re-established unless the migrating walls were impeded by precipitates.

In the absence of other evidence, it would be reasonable to attribute the basic reproducibility of the domain structure to the fact that it was the lowest energy configuration, influenced to some degree, no doubt, by ease of nucleation at precipitates and other structural defects. But the following observations suggest that antiferromagnetic effects can occur well above the

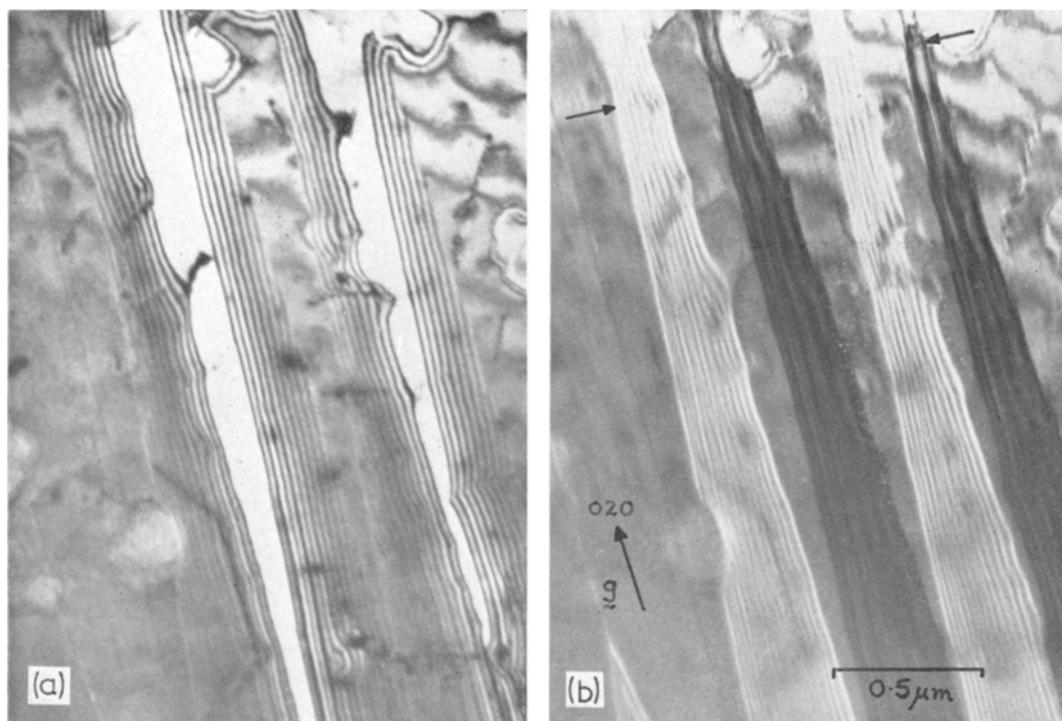


Figure 5 (a), (b) Antiferromagnetic domains in  $\text{MnO}$  cooled to below the Néel temperature. There are three parallel-sided domains between the arrows in (b), which point to domain walls inclined at  $45^\circ$  to the plane of the (001) foil, (100kV).

accepted Néel temperature and may also play an important role.

It was observed that most of the domain walls disappeared almost instantaneously at a temperature within a few degrees in excess of 122° K (the accuracy of temperature measurement with the cold stage is at best 10° K). But by the same standards, small segments of domain wall were found to persist and to vanish only after some further 20 to 25° K rise in temperature beyond the point at which the majority had disappeared. Almost invariably, the small segments of wall were associated with visible crystal defects and, by careful control of the heat input from the electron beam, they could sometimes be made to shrink slowly. The "free" end of the walls was always terminated by a dislocation which glided as the wall contracted. Figs. 6a and b show a short length of wall pulling away from a small precipitate. It should be noted that stacking faults and large twins are not found in MnO and there can be no doubt that the fringed interface is an antiferromagnetic domain wall.

### 3.3. Observations of Non-Stoichiometric Effects in MnO

The presence of addition diffraction spots in the pattern from synthetic MnO suggested two

things: (i) that there were fine structural lamellae present giving rise to the satellites (ii) that the 110 spots might result from the presence of some type of superlattice.

In the first case, although the satellites implied that the lamellae spacing had a mean value of  $\sim 40 \text{ \AA}$  in the  $\langle 110 \rangle$  directions, this did not rule out the possibility that the lamellae were aligned parallel to other than the  $\{110\}$  planes. To examine this, foils were tilted through angles so that 011 and 111 diffraction patterns could be seen. Fig. 7a shows a 110 pattern, which contains weak "forbidden" spots, as before, and strong streaking, but without resolvable intensity maxima (satellites). Fig. 7b shows another 110 pattern, selected so as to optimise the visibility of the satellites.

The streaks in these patterns extend along the  $\langle 1\bar{1}1 \rangle$  directions in reciprocal space but are completely absent in the  $\langle 1\bar{1}0 \rangle$  and  $\langle 001 \rangle$  directions. This is proof that the fine lamellae are indeed parallel, or almost parallel, with the  $\{111\}$  and not the  $\{110\}$  planes. Rigorous parallelism is almost certainly absent because the streaking makes a small but definite angle with the  $\langle 111 \rangle$  directions. This is a rather strange observation, but seems to have some correlation with the results of Renninger *et al* [6] who noted

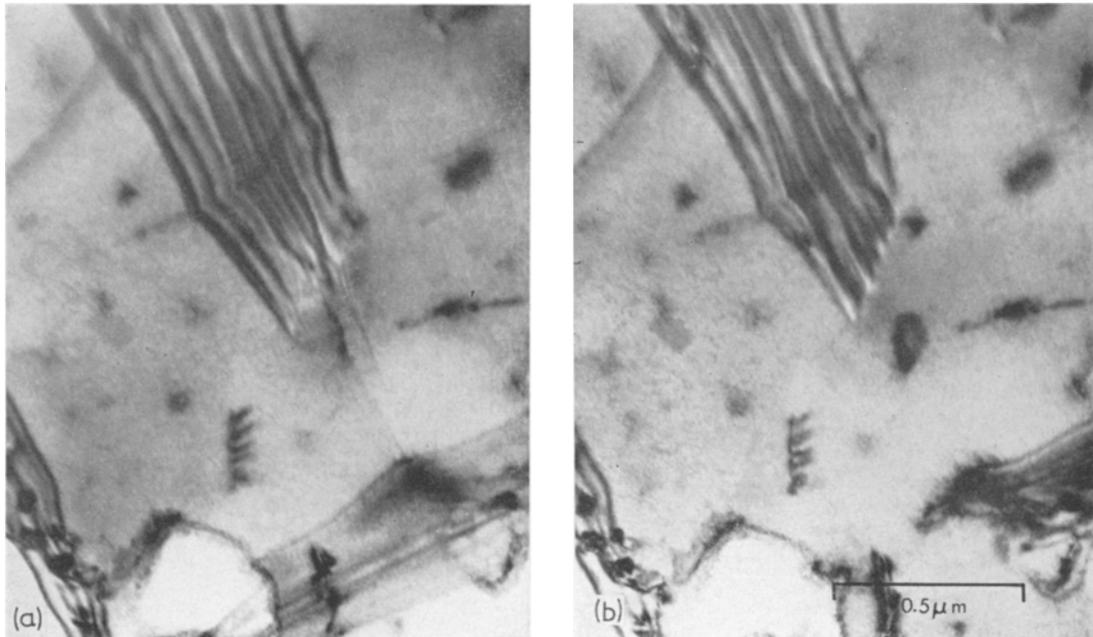


Figure 6 (a), (b) Domain walls shrinking away from pinning precipitates and an etch pit at a few degrees above  $T_N$ . Approximately 20 sec elapsed between recording the two images, (100 kV).

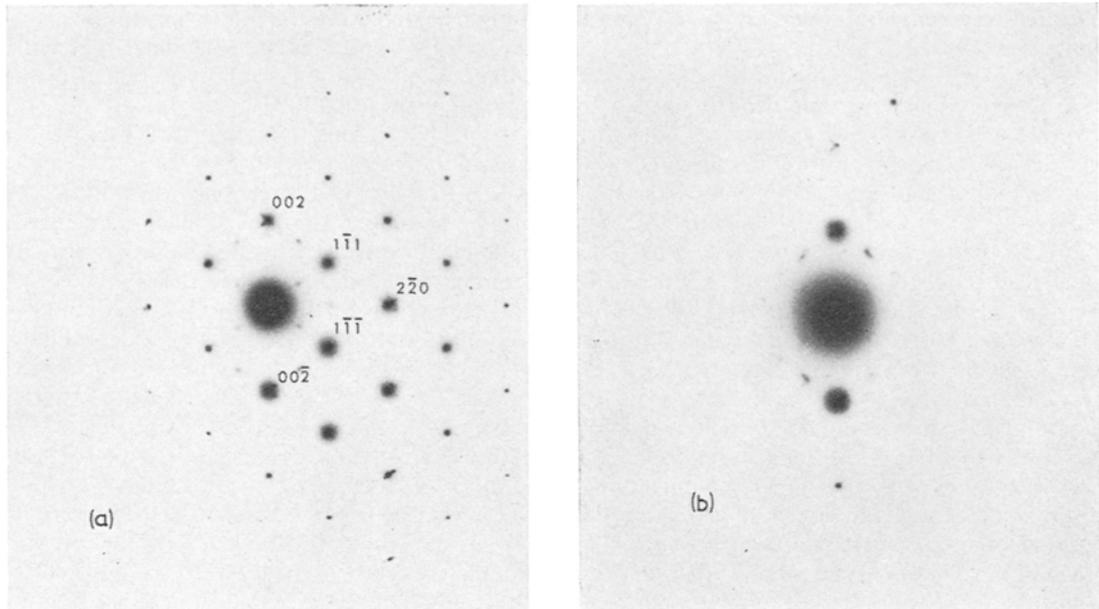


Figure 7 (a), (b) Electron diffraction patterns (650 kV) from (110) foils of synthetic MnO.

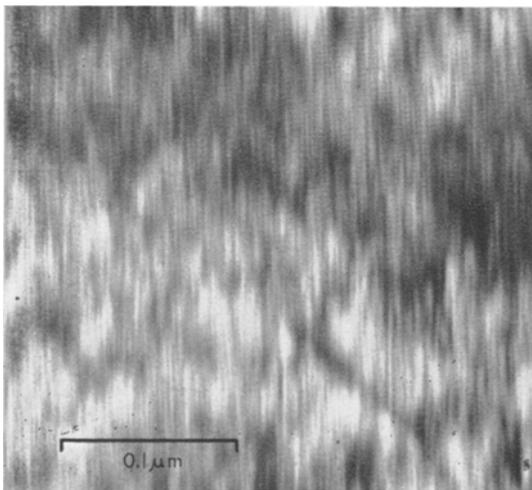


Figure 8 Fine lamellae parallel to  $\langle 110 \rangle$  caused by non-stoichiometry in synthetic MnO (650 kV).

that there was evidence for tilt of the  $\{111\}$  lattice planes associated with magnetic microdomains.

Direct resolution of the lamellae, shown in fig. 8, reveals a spread in orientations rather than a definite deviation from  $\{111\}$ . The measured spacing here, in a foil of  $\{001\}$  orientation has an average value of  $33 \text{ \AA}$ . This value is deduced by measuring between the centres of black stripes wherever the detail is well defined. It is in fair

agreement with the value deduced from the separation of the satellites along the  $110$  directions in reciprocal space (fig. 4a), namely  $37 \text{ \AA}$ . The true spacing in the  $\langle 111 \rangle$  directions deduced from this last value is  $30 \text{ \AA}$ , which in turn agrees well with that derived directly from fig. 7b, which is  $28 \text{ \AA}$ .

The  $110$  diffraction pattern in fig. 7a supplies us with further information not present in the  $001$  pattern. It can be seen at once that the so-called forbidden reflections must be produced by the presence of a superlattice. In the  $110$  pattern the innermost set of weak spots cannot be indexed unless we assume that they arise from a structure with a unit cell of side equal to twice the cell parameter for MnO. This means that the superlattice cell has eight times the volume of the normal structural MnO unit cell and is therefore identical with the magnetic unit cell. These findings, then, suggest that to some degree, long-range structural order having the same diffraction properties as the antiferromagnetic order, exists at room temperature in the imperfect synthetic sample of MnO. In contrast, there is no indication of either a superlattice or lamellae from the diffraction pattern of natural MnO (fig. 4b). The natural crystal does contain large numbers of dislocations, however, and some broad bands whose nature is not yet understood. The latter are shown in the dark field micrograph

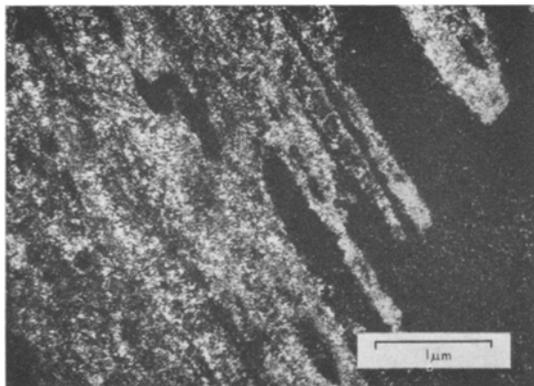


Figure 9 Dark field micrograph (650 kV) of finescale precipitation occurring in bands in natural MnO.

in fig. 9. We believe that they may be regions containing high densities of small incoherent precipitates; the only effect on the diffraction spots is a slight broadening. The mineral does exhibit at least one strange difference from synthetic MnO, for the former is attracted to steel tweezers, i.e. it is weakly ferromagnetic.

The nature of the lamellae or microdomains, as we may term them, is still far from clear. But there is evidence that points to their being correlated with non-stoichiometry. It was mentioned in section 3.1 that moving dislocations leave traces in the foil surface. The changes in surface structure may not be irreversible but they persist indefinitely without further treatment. Unlike similar phenomena in metals, which have been attributed to disruption at the metal/metal oxide interface, the effect in manganous oxide must arise from a modification of the crystal structure in the surface of the foil. Using the dark field

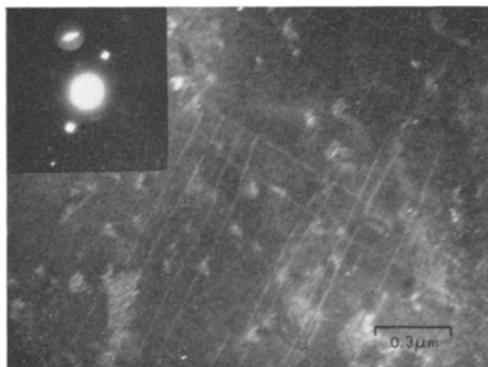


Figure 10 Dark field micrograph (650kV) of surface traces produced by gliding dislocations.

method it has been possible to relate the surface traces to the streaking in the diffraction patterns and thus to the microdomains. It was observed that there was a particularly strong  $\langle 110 \rangle$  streak through a  $2\bar{2}0$  spot in the selected area diffraction pattern from a deformed part of the foil. When this spot was used to form the dark field image, the surface slip traces were in contrast, but apart from their extremities, the slip dislocations were not in contrast (fig. 10). This suggests that the movement of dislocations through the lattice either creates new lamellae at the foil surface or else enhances the order in existing ones. Also when a strong  $330$  spot (referred to the normal MnO unit cell) was used for imaging, it was seen that the glide dislocations were again out of contrast except where their ends met the foil surfaces; the traces were also imaged, although not strongly. It seems likely from these observations that non-stoichiometry is greater at the surfaces of the foils, after some exposure, than in the interior. Both the vacuum and beam heating may play a part in this but we do not believe that the non-stoichiometric effects reported here can be wholly a result of conditions in the electron microscope. The lamellar structure evolves only slowly, if at all, and we are convinced that it exists prior to inserting the samples in the microscope.

#### 4. Discussion and Conclusions

Several of the foregoing results indicate that the matrix crystal is non-stoichiometric and it is likely that manganous oxide, like nickel oxide, will accommodate large numbers of cation vacancies. As yet there is no evidence for the existence of intermediate phases in the Mn—O system. The lamellae or microdomains we have observed are strongly diffracting objects and are undoubtedly structural in origin, rather than magnetic. It is reasonable to suppose that the cation vacancies in the  $Mn_{1-x}O$  crystal are in an ordered arrangement and that the boundaries between the microdomains are in fact, antiphase boundaries. In other words, the oxygen sub-lattice is continuous and virtually complete, but the manganese sub-lattice is faulted on a scale of  $\sim 30\text{Å}$ . The presence of precipitates of  $Mn_3O_4$ , and the surface degradation effect, which is produced by dislocation motion, lead one to anticipate that the face-centred cubic manganous oxide is part way converted to the distorted spinel structure, representing  $Mn_{0.75}O$ . The two structures are simply related: it only requires the

ordering of cation vacancies on alternate  $\{111\}$  planes and the conversion of some Mn ions to tetrahedral co-ordination to effect the change. It is thus clear that antiphase domains in  $\text{Mn}_{1-x}\text{O}$  are to be expected. The smearing of the satellite diffraction spots from some regions of the samples and the fact that they are non-rational in spacing shows that the compositional disorder fluctuates from place to place.

The evidence for a superlattice is much harder to explain with confidence. The extra reflections are generally weak and do not reveal any hidden structure when used for dark-field imaging. And from purely crystallographic and chemical considerations the existence of a superlattice is unlikely. We believe, therefore, that the superlattice is magnetic in origin and its stability accounts for the weak antiferromagnetic resonance above  $T_N$  found by Evans [7] in the same crystals. Its presence may also assist in the retention of domain walls above  $T_N$  (section 3.2) and be related to the "memory" of the foil in re-establishing domain patterns. No change in the intensity of the superlattice diffraction spots from our crystals was detected at  $T_N$ . In contrast, Remaut *et al* [5] reported the presence of similar superlattice reflections in CoO only when it was below the antiferromagnetic transition temperature.

The next question to consider is whether there is any significance to the simultaneous occurrence of antiphase domains and the superlattice in our synthetic manganous oxide and that studied by Delavignette and Amelinckx [9], while both defects are absent in the mineral sample. Renninger *et al* [6] postulated that fine scale compositional fluctuations (which we are calling antiphase domains) might well occur in MnO, but found no experimental evidence for them. Nor did these workers see any reason why such compositional effects, if they occurred, should be related to antiferromagnetic microdomains, which they did report. The evidence now seems to indicate that there may be a connection: the antiphase lamellae observed by us differ in size from Renninger *et al's* magnetic microdomains, but the size of the former, at least, will vary with stoichiometry. In their paper, Renninger *et al* speak of antiphase boundaries, but they are referring to faulting in the ideal sequence of spins in adjacent  $\{111\}$  planes. These magnetic antiphase boundaries could have coincided with faults in the ordering of the Mn sub-lattice, even although neutron scattering gave no evidence for

the latter.

Without further experimental evidence as to the nature of the defect ordering in  $\text{Mn}_{1-x}\text{O}$ , no proper explanation of the magnetic anomalies can be given. But the pinning of magnetic domain walls in non-stoichiometric MnO is in accord with other recent evidence, summarised by Roth [11]. He has also pointed out that clusters of defects can have magnetic properties greatly different from those of the host crystal. Perhaps we can extend this idea to encompass that of a new  $\text{Mn}_{1-x}\text{O}$  phase, with cation vacancies ordered in the sub-lattice, possessing a different lattice parameter, different superexchange forces and a different Néel temperature. In other words, we can anticipate that short range structural order will be accompanied by a weak magnetic order, perhaps above the established Néel temperature. It is not surprising, then, to see the conclusions of Shull *et al* [1] that in MnO (presumably non-stoichiometric) at room temperature "the magnetic moments are not randomly arranged but there exists a short-range order with neighbouring moments tending to be aligned". Further work is now desirable on manganous oxide of both stoichiometric and known non-stoichiometric composition, which is free from particles of second phase. Unfortunately, good quality MnO is currently very difficult to obtain.

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