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Remarks on Vousden's structure of ferroelectric sodium niobate.

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In a recent paper Vousden (1951) discusses the crystal structure of ferroelectric $NaNbO_3$, to which he has assigned the space group $P22_12$. There are several points in this paper which require discussion, but we wish to remark on only one of these: the space group assignment.

In the opening sentence of his concluding section (§ 9), Vousden states "this structure determination raises a serious problem in the theory of ferroelectricity because the space group of $NaNbO_3$ is non-polar". This challenging sentence is sufficient to cause one to survey the evidence for his structure with more than usual care.

Vousden has apparently indexed his X-ray diffraction maxima from complete rotation diagrams. Experience in our own laboratory in single-crystal studies of $KNbO_3$ and AlF_3 has indicated that it is extremely dangerous to attempt to index X-ray maxima from these structures, with their very high pseudo-symmetry, with anything less than Weissenberg diagrams. When the Weissenberg technique is applied, it has appeared that the room-temperature symmetries of the two structures mentioned are not those previously assigned. It seems clear that Vousden has failed to eliminate effects of twinning, and that his otherwise astonishing results are due to a false space group assignment.

Until much stronger contradictory evidence appears than Vousden presents, one can feel safe in regarding evidence of ferroelectric activity in a crystal as proof that not more than one rotation axis is present in the structure (and not so many mirror planes that a center of symmetry will result). If a contrary result actually could be proved, one would be faced with the necessity for revision not only of the theory of ferroelectricity, but of that of piezo- and pyroelectricity as well.

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Electron diffraction evidence for the existence and fine structure of a cryptomelane modification of manganese dioxide prepared in the absence of potassium.

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In the course of an investigation of the properties of artifically prepared manganese dioxides, we have studied the less well defined products which Moore, Ellis & Selwood (1950), on evidence from magnetic susceptibility measurements, have termed 'disperse oxides'. The products from a preparative method due to Glemser (1939), using $MnSO_4$ and $(NH_4)_2S_2O_8$, proved to be particularly interesting. 'Analar' reagents were used without further purification.

The precipitated oxide, by analysis, had a formula of $MnO_{1\cdot95}\cdot0\cdot25H_2O$, and gave an X-ray powder pattern consisting of six diffuse rings having spacings of 4·03, 2·42, 2·12, 1·63, 1·39 and 1·06 Å.

The material was examined in a Metropolitan-Vickers E.M 3 electron microscope, by direct microscopy, and by diffraction, suitable specimens being prepared either by dispersing the oxide in air and allowing it to settle on collodion films on copper grids, or by evaporating a drop of an aqueous suspension placed on a collodion film. It appeared from the electron-microscope examination that a considerable amount of the preparation consisted of straw-shaped particles about 1 μ in length and of cross section of the order of one-fiftieth of this. Very similar evidence of this habit for a normal cryptomelane containing potassium has been given by McMurdie & Golovato (1948).

Electron diffraction gave the powder pattern reproduced in Fig. 1. There is no doubt from our own X-ray work on manganese dioxides that this material has the same structure as cryptomelane, although potassium can only be present in minute traces. Except in the work of Dubois (1936) it has generally been considered that potassium or sodium are essential constituents of this oxide.

The diffraction patterns were internally calibrated using thallous chloride as standard, the composite specimens being prepared either by the evaporation of the chloride *in vacuo* on to the supported oxide specimens, or by deposition from an aqueous solution. The dimensions of the body-centred tetragonal unit cell of the manganese dioxide,

$$a_0 = 9\cdot88\pm0\cdot03,\ c_0 = 2\cdot845\pm0\cdot005\ \text{Å}\,,$$

were based on the thallous chloride simple cubic unit cell with $a_0 = 3\cdot834$ Å (Wyckoff, 1948). These values differ slightly from our own unpublished data for cryptomelane, namely

$$a_0 = 9\cdot83,\ c_0 = 2\cdot862\ \text{Å}\,.$$

These latter figures, however, agree very closely with electron-diffraction data, obtained in a similar manner to that described above, from a second preparation of a disperse oxide by the reaction between potassium permanganate and manganous sulphate, for which

$$a_0 = 9\cdot81\pm0\cdot03,\ c_0 = 2\cdot86\pm0\cdot01\ \text{Å}\,,$$

the oxide again having a cryptomelane structure.

We thus consider that there is a significant difference

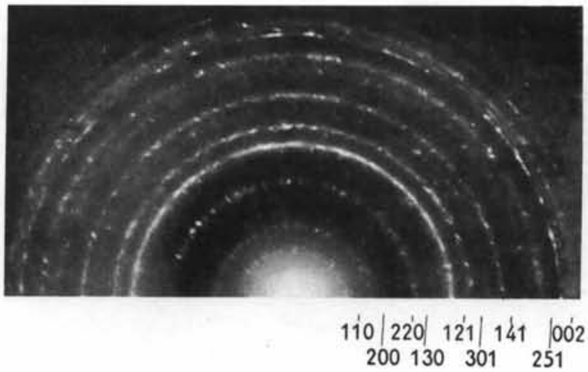

Fig. 1. Electron diffraction pattern from manganese dioxide. The cryptomelane lines are indexed.

in the unit cell for the oxide prepared in the presence and absence of potassium ions and it is tentatively suggested that the ammonium ion may replace the potassium in the cryptomelane lattice.

The diffraction spots constituting the rings of Fig. 1, and similar patterns from the second preparation, show the very interesting crystal-shape effects previously described by Rees & Spink (1950) and by Burgers (1951) for the case of ZnO. From the indexed figure it is seen that in the case of planes parallel to the *c* axis, the diffraction spots cut the rings at right angles; with the (002) plane the spots lie along the ring and for other planes at varying angles to the *c* axis the diffraction spots are at oblique angles to the diffraction rings. This is explained if we assume that the minute crystals pack with the short *c* axis in line with the long axis of the straw-shaped aggregates as revealed in the electron micrographs. The *c* axis is thus parallel to the surface of the collodion film and perpendicular to the beam, and the reciprocal lattice points may be considered approximately as domains in the form of discs perpendicular to the c^* axis.

A point of further interest arising from our electron-diffraction examination of artificial manganese dioxides is that, as prepared, surface layers of MnO and Mn_3O_4 or γMn_2O_3 are usually present. This may contribute significantly to the apparent oxygen defficiency as revealed by chemical analysis. A detailed paper on the work is in preparation.

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The crystal structure of hydrazinium bromide, N_2H_5Br.

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As a part of our study on the structure of hydrazine salts ($N_2H_6SO_4$ (Nitta, Sakurai & Tomiie, 1951) and N_2H_5Cl (Sakurai & Tomiie, to appear shortly), the crystal structure of hydrazinium bromide has been determined. Crystals of hydrazinium bromide are very fine needles parallel to the monoclinic *b* axis, of which those about 0·08 mm. in diameter were selected for X-ray work. The procedures taken in the analysis were the same as in the case of hydrazinium chloride.

There are eight formula units in the unit cell of the dimensions

$$a = 12{\cdot}85,\ b = 4{\cdot}54,\ c = 11{\cdot}94\ \text{Å},\ \beta = 110^\circ\ 16',$$

and the probable space group is C^6_{2h}–$C2/c$. The parameters of the atoms were determined by the Patterson maps projected on (010), electron-density projections on (010) and (001), and by the method of trial and error. They are given in Table 1.

Table 1. *Atomic co-ordinates*

	x	*y*	*z*
Br	$-0{\cdot}103_7$	0·097	$0{\cdot}080_2$
N_I	$0{\cdot}149_2$	0·390	$0{\cdot}135_0$
N_{II}	$0{\cdot}141_0$	0·620	$0{\cdot}216_5$

Table 2. *Interatomic distances*

$N_I \cdots N_{II}$	1·45 Å	$N_I \cdots N_I$	3·48 Å
$N_{II}H \cdots N_I$	2·93	$N_{II} \cdots N_{II}$	3·73
$N_I \cdots Br$	3·42, 3·56, 3·70	$Br \cdots Br$	3·87, 4·00
$N_{II} \cdots Br$	3·29, 3·36, 3·37		

The interatomic distances are listed in Table 2. The accuracy of these values is not as high as in the chloride. Each $N_2H_5^+$ group has eight closest neighbours, six bromine and two nitrogen atoms, and their arrangement about one $N_2H_5^+$ group closely resembles that in hydrazinium chloride. The N–N distance within the $N_2H_5^+$ ion has the same value, 1·45 Å, as found in the chloride. From a consideration of the $N \cdots Br$ distances, it can be concluded that N_I and N_{II} represent the $-NH_2$ group and the $-NH_3^+$ group respectively. Both $N_{II} \cdots Br$ and $Br \cdots Br$ distances are nearly equal to the corresponding values derived from the ionic radii of Br^- (1·95 Å) and NH_4^+ (1·41 Å, corrected for coordination number four).

Cations are linked together by $N^+H \cdots N$ hydrogen bonds in the same manner as in the chloride, and these hydrogen bonds form infinite spiral chains along the *b* axis. Owing to the presence of a centre of symmetry in this structure, however, there are two kinds of chains with opposite senses in the bromide, in contrast to the existence of one kind of chains along the polar *c* axis in the chloride.

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