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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.

Reference

Vousden, P. (1951). *Acta Cryst.* **4**, 545.

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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 $MnO_{1{\cdot}95}{\cdot}0{\cdot}25H_2O$, 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,

$$a_0 = 9{\cdot}88 \pm 0{\cdot}03,\ c_0 = 2{\cdot}845 \pm 0{\cdot}005\ \text{Å}\,,$$

were based on the thallous chloride simple cubic unit cell with $a_0 = 3{\cdot}834$ Å (Wyckoff, 1948). These values differ slightly from our own unpublished data for cryptomelane, namely

$$a_0 = 9{\cdot}83,\ c_0 = 2{\cdot}862\ \text{Å}\,.$$

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

$$a_0 = 9{\cdot}81 \pm 0{\cdot}03,\ c_0 = 2{\cdot}86 \pm 0{\cdot}01\ \text{Å}\,,$$

the oxide again having a cryptomelane structure.

We thus consider that there is a significant difference