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Letter to the Editor

An Inconsistency in a Classical Paper on the Structure of Ramsdellite

Lachlan A. H. MacLean† and Frank L. Tye

Energy Technology Centre, Middlesex University, Bounds Green Road, London N11 2NQ, UK

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In 1949 Byström[1] published a paper on the crystal structure of the rare manganese dioxide polymorph ramsdellite. For the first time the space group and position of atoms in the unit cell were determined and the structure's simple relationship to that of pyrolusite discovered.

Today this paper remains central to recent successful attempts[2–4] to model the random non-periodic layer structures which battery-active manganese dioxides exhibit. Such models have revived initial attempts to determine the relationship of ramsdellite to γ-MnO_2 from their differing but apparently related X-ray diffraction patterns. De Wolff[5] was the first to develop a quantitative mathematical theory which closely followed a proposal given earlier by Byström and Byström.[6]

The ramsdellite structure also occurs in fields other than that of manganese dioxide, notably that of solid electrolyte ion-conducting materials.[7–9] Reference to the citation index over the last 45 years shows that citations to this classical paper continue at an undiminished level.

Owing to the importance of Byström's work the authors consider it worthwhile drawing attention to an inconsistency between the parameters as listed in the paper and the derived interatomic distances.

Originally the inconsistency was noticed in the following way. If the length of a distorted octahedron in the *c*-direction, *r*, is 2.866 Å as shown in Fig. 1 (which is the magnitude of the *c* unit-cell dimension), and the distance defining the shared edge for chains of such an octahedron, *s*, is 2.58 Å (line 5, p. 167) as also marked in Fig. 1, then by Pythagoras' theorem the distance from opposite corners to the central Mn atom must be greater or equal to 3.86 Å (Fig. 2). Using the Mn–O distances listed, however (p. 165, penultimate line), which are those marked 1 and 2 in Fig. 1, this distance is only equal to 1.86 + 1.92 = 3.78 Å.

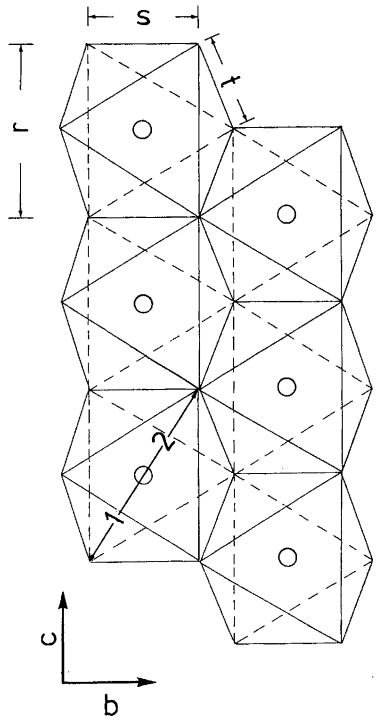

Fig. 1. Projection of a double string of distorted occupied octahedra from the ramsdellite structure in the *bc*-plane. Circles mark Mn atoms and vertices correspond to the position of oxygen atoms. *r*, *s* and *t* correspond to O–O distances within an octahedron. *r* is the O–O distance in the *c*-direction, *s* is the shared edge in a single string of octahedra and *t* is the shared edge between two single chains. 1 and 2 mark Mn–O distances.

The above inconsistency prompted us to recompute the interatomic distances of ramsdellite using the original parameters. The following discrepancies with the values stated in Byström's paper were found. The first concerns the O–O distance *s* defining a shared edge linking octa-

† To whom correspondence should be addressed.

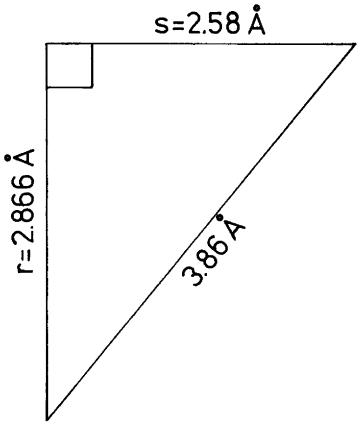

Fig. 2. Demonstration of the inconsistency in Byström's paper. Distances are marked as stated in the paper. The sum of the Mn–O distances 1 and 2 (i.e. 1.86+1.92=3.78 Å) must be greater or equal to $(r^2+s^2)^{1/2}=3.86$ Å by Pythagoras' theorem.

hedra in the *c*-direction, which is stated in the paper as 2.58 Å: however, using the parameters listed (p. 165) it has the value 2.47 Å. This means that the distance stated above as 3.86 Å is now 3.78 Å and thus removes the inconsistency. The manganese atom therefore appears to be situated in the middle of the rectangular plane formed by four of the six oxygens of a distorted octahedron, a point which was not previously noted. This also means that the shortest O–O distance is 2.47 Å rather than 2.48 Å (line 7, p. 166). The value of 2.58 Å does not correspond to any other interatomic distance in the structure.

A second slight discrepancy concerns the shared edge linking octahedra between the double chains running in the *c*-direction (distance *t* in Fig. 1). This distance is claimed to be 2.48 Å in the paper (line 7, p. 167), whereas again using the parameters listed a value of 2.47 Å is also found.

All other calculated interatomic distances were found to agree with those stated in the paper.

The authors also wish to point out that in the paper it is stated that 'The shortest Mn–Mn distance is 2.91 Å.' (bottom line, p. 165), which would be true if only one unit cell is considered, whereas the Mn–Mn distance between unit cells in the *c*-direction must be equal to 2.866 Å (the magnitude of the *c* unit-cell vector).

In summary, an inconsistency between the parameters as stated in the paper and the derived interatomic distances has been uncovered which leads to a revision of the interatomic distances as given in Table 1.

Table 1. Revised interatomic distances in ramsdellite.

Octahedral shared edge distance as marked in Fig. 1	Ref. 1/Å	Revised distance/Å
s	2.58	2.47
t	2.48	2.47

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