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Neutron diffraction evidence of the 3-dimensional structure of Ba_2MnTeO_6 and misidentification of the triangular layers within the face-centred cubic lattice

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Ba_2MnTeO_6 was first characterised using X-ray diffraction and reported to show a small distortion[1] from the idealised cubic perovskite which displays face-centred cubic arrangement of Mn^{2+}. A recent report has asserted that this leads to a layered configuration of Mn^{2+} that serves as an example of a triangular lattice, i.e. a 2D structure containing discreet layers[2]. Here we show how neutron scattering gives great confidence in establishing the crystal structure being an undistorted cubic phase and how this can be mis-assigned as a triangular layered structure. This has profound implications for the understanding of the magnetic properties of the system.

Magnetically frustrated systems are readily visualised by considering antiferromagnetic coupling between magnetic centres on the points of an equilateral triangle. Such a configuration can be realised physically in a number of well-studied structures giving rise to kagome, pyrochlore, triangular, and face-centred cubic lattices[3]. The interpretation of the resultant magnetic properties relies on a precise understanding of the geometry of the crystal lattice which underpins and determines the spatial distribution of magnetic ions. Ba_2MnTeO_6 contains high-spin (d^5) Mn^{2+} embedded in an otherwise diamagnetic crystal structure and the absence of orbital angular momentum in this $L = 0$ ion makes it an excellent candidate to study the impact of lattice geometry on magnetic interactions.

The correct identification of the crystal structure of Ba_2MnTeO_6 is of central importance in interpreting the magnetic properties as the magnetic interactions are defined by the geometry of the crystal structure. The magnetic interactions in Ba_2MnTeO_6 have been interpreted[2] using the assumption that it is a model 2-dimensional triangular lattice. Such triangular lattices are of wide interest, and examples lead to a variety of novel magnetic states[4]. In this instance, the structure of Ba_2MnTeO_6 is actually an isotropic 3-dimensional structure. Here we expand our previous report[5] to explain the unambiguous evidence from high resolution neutron powder diffraction data and clarify the relationship between the 3D cubic structure and the 2D triangular lattices that have been reported.

Distortions in the perovskite structure commonly arise from displacements of the oxide anions that break the $Fm\overline{3}m$ symmetry of the cubic cation-ordered double perovskite aristotype[6]. This can lead to ambiguities in perovskite structure determination where the weak X-ray scattering from oxide anions is largely masked by the presence of dominant scatterers such as Ba^{2+} and Te^{6+} that undergo negligible displacement in response to the reduction of symmetry.

This point can be illustrated by X-ray diffraction patterns calculated from the recent report[2] of $R\overline{3}m$ Ba_2MnTeO_6 and compared with the $Fm\overline{3}m$ structure[5] as shown in Fig. 1. These data illustrate that laboratory X-ray diffraction data provide no meaningful differentiation between these two structures. The crystallographic convention is that the higher symmetry is used to describe the structure, in this case $Fm\overline{3}m$. This point is of

[1]Department of Material Science and Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, UK. [2]School of Chemical and BioPharmaceutical Sciences, Technological University Dublin, Dublin, Ireland. [3]ISIS Pulsed Neutron and Muon Source, STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot OX11 0QX, UK. [4]Johnson Matthey Battery Materials, Blount's Court, Sonning Common, Reading RG4 9NH, UK. [5]Department of Chemistry and Materials Science, Aalto University, Helsinki, Finland. 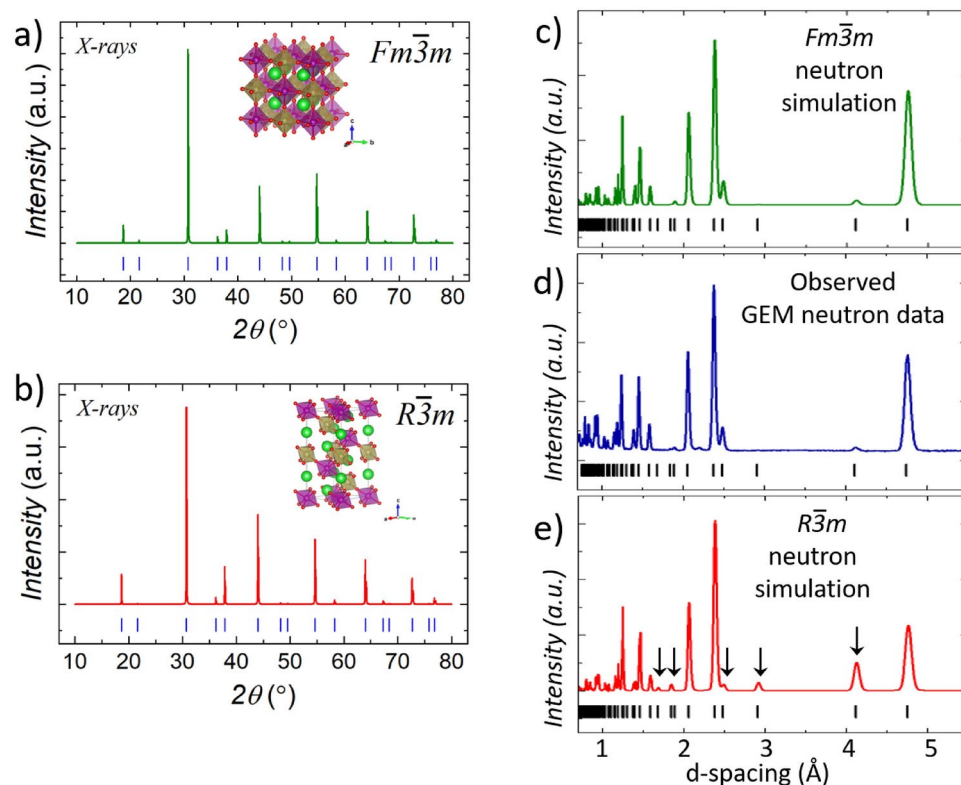[6]This comment refers to the article available online at https://doi.org/10.1038/s41598-021-84876-5. ✉email: Edmund.cussen@TUDublin.ie

Fig. 1. Calculated X-ray diffraction profiles for (**a**) Fm$\overline{3}$m and (**b**) R$\overline{3}$m structures using published parameters from Khatua et al.[2]. Repeating the calculation using the previous structure report of Wulff et al. showed no discernible difference[1]. The data for Fm$\overline{3}$m were taken from 100 K structure solution[5]. The displacement parameters. For the R$\overline{3}$m model were not reported and values for U_{iso} were taken as 0.001 Å^2 for Ba/Mn/Te and 0.002 Å^2 for O as identified in the Fm$\overline{3}$m solution. There are no large differences between these X-ray diffraction profiles. (**c**) The simulated neutron diffraction pattern from the Fm$\overline{3}$m solution shows an excellent agreement with the observed neutron diffraction profile (**d**), but shows very large intensity mismatches indicated by arrows in (**e**) compared to the simulated neutron diffraction profile from the distorted perovskite described by the R$\overline{3}$m structure.

fundamental importance in considering the properties of this material. Discussion of the magnetic properties of Ba_2MnTeO_6 in the context of layering makes no more sense that attempting to understand the mechanical and optical properties of the face centred cubic diamond as arising from triangular layers of carbon with chemical bonding between the layers.

Any ambiguities in analysis of the X-ray profile can be resolved using neutron scattering where the sensitivity to oxide is much greater[7]. High quality neutron diffraction data were collected using the GEM diffractometer[8] and Fig. 1 compares the recently reported observed neutron diffraction profile[5] to diffraction profiles calculated using either the Fm$\overline{3}$m perovskite or the proposed R$\overline{3}$m structure. Due to the negligible distortion from metric cubic symmetry of the rhombohedral structure both patterns have apparently similar distribution of permitted Bragg reflection positions. The greater sensitivity of the incident neutron wave to the oxygen atoms mean that even small displacements of oxide from the special positions of the Fm$\overline{3}$m structure have a significant impact on the diffracted neutron profile. The simulated pattern for the R$\overline{3}$m structure shows that several Bragg peaks should have considerably enhanced intensity that is evidently not present in the observed pattern. A recent neutron diffraction measurement over a more limited d-spacing range was able to fit the data equally well with either cubic or rhombohedral symmetry[9]. Thus we conclude that there is no evidence of structural distortion from cubic symmetry in Ba_2MnTeO_6 and that the Fm$\overline{3}$m space group can be assigned with utmost confidence.

Given the similarity of the X-ray diffraction profiles of the Fm$\overline{3}$m and R$\overline{3}$m structures it was unexpected to see that the structure of Ba_2MnTeO_6 was being considered as an example of a 2D triangular lattice. The arrangement of Mn and Te cations in the Fm$\overline{3}$m structure is compared to that reported as a 2D triangular lattice in Fig. 2. In the R$\overline{3}$m structure, the apparently layered 2D structure is generated by connecting each Mn cation to six neighbouring ions at a distance of 5.816 Å to form a hexagonal net composed of triangles. However, each Mn ion has another six neighbours at an almost identical distance (5.817 Å) that connect into adjacent 'layers'. In the Fm$\overline{3}$m structure these two distances become symmetry equivalent. The apparently layering within the R$\overline{3}$m structure can be achieved by selectively drawing half of the linkages between neighbouring Mn ions and omitting to draw the other half. Once the connections are drawn to link all nearest Mn–Mn pairs it is clear that the 3D structure is composed of edge-sharing equilateral triangles that is a familiar feature of the face-centred
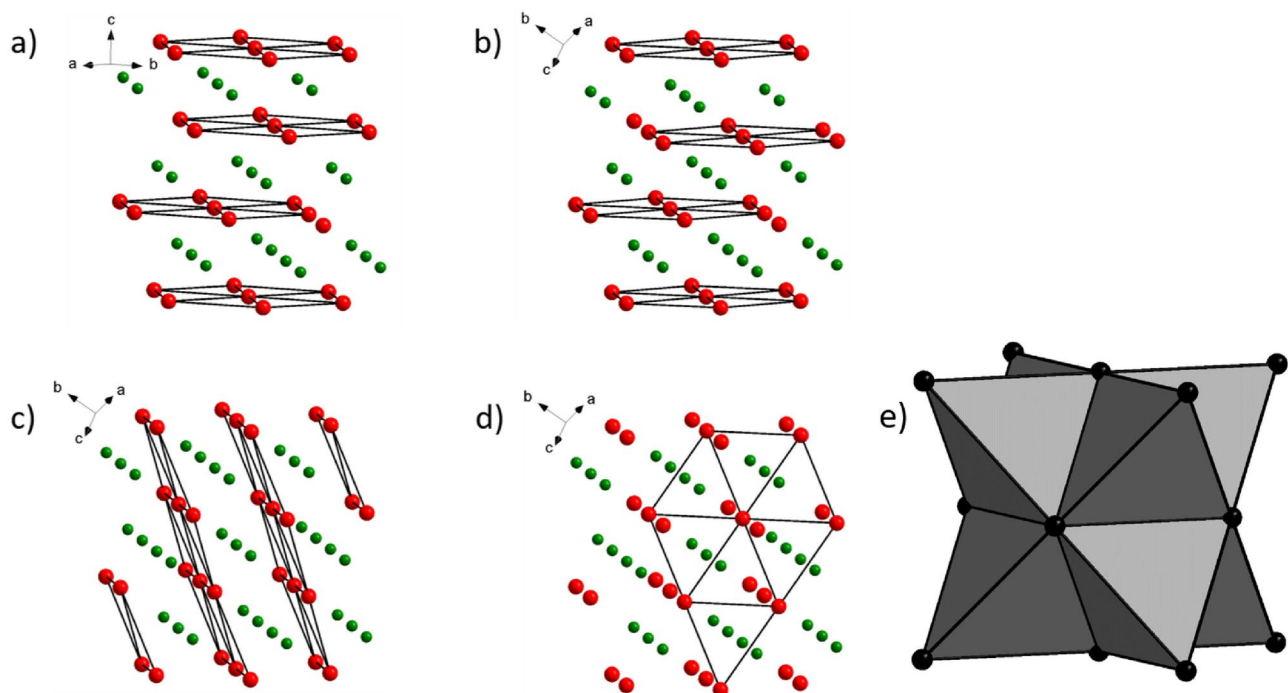
Fig. 2. The arrangement of Mn (red spheres) and Te (green spheres) in the crystal structure of Ba_2MnTeO_6 derived from (**a**) the $R\overline{3}m$ model, with lines drawn to reproduce the illustration of layers[2] of Mn cations. (**b**) The $Fm\overline{3}m$ structure derived from neutron diffraction data uses the same projection and scale as (**a**) to display and selectively links some of the Mn cations that are separated by a distance of 5.8 Å. This reproduces the suggested 2D layered structure in (**a**). Figures (**c**) and (**d**) makes connections between other layers of Mn cations that are symmetry equivalent to the linkages shows in (**b**). This shows that the apparent 2D triangular lattice is an artefact arising from viewing only a single projection, and ignoring the 3D connectivity. The 3D arrangement of edge-sharing equilaterally triangles is a well-established feature[3] of double perovskite structure as shown in (**e**).

cubic lattice. The three-dimensional connectivity arising from the cubic symmetry in Ba_2MnTeO_6 means that this material is not a model for a 2D triangular lattice.

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Author contributions

OM, CP, HM contributed to all aspects of the material synthesis, data collection and analysis. HW and GS assist-

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Declarations

Competing interests
The authors declare no competing interests.

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