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## LETTER TO THE EDITOR

**Low temperature structural studies on PrAlO<sub>3</sub>****Sandra M Moussa<sup>1</sup>, Brendan J Kennedy<sup>1</sup>, Brett A Hunter<sup>2</sup>,  
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**Abstract**

The structures of PrAlO<sub>3</sub> have been studied from room temperature to 10 K, using a combination of high resolution neutron and synchrotron powder diffraction data. At room temperature, PrAlO<sub>3</sub> has a rhombohedral structure in space group  $R\bar{3}c$  which transforms to an orthorhombic structure in *Imma* on lowering the temperature to about 205 K, and to a monoclinic,  $C2/m$ , structure at about 150 K. The structure becomes more nearly tetragonal as the sample is further cooled, but the high resolution diffraction confirms that the symmetry remains monoclinic in space group  $C2/m$  down to the lowest measured temperature.

**1. Introduction**

Transitions between the different structural variants of ABX<sub>3</sub> type perovskites are often central to their technological applications [1] and are of interest in earth sciences [2]. Despite numerous studies of ABX<sub>3</sub> perovskites, accurately describing the structures in many apparently simple systems remains a challenge and the structural sequences that accompany changes in either temperature or pressure are not well understood.

It has been shown in several studies [3–5] that PrAlO<sub>3</sub> at room temperature has a rhombohedral structure (space group  $R\bar{3}c$ ), in which the AlO<sub>6</sub> octahedra are rotated about the [111]-axis. At ~1770 K PrAlO<sub>3</sub> undergoes a continuous transition to the cubic structure of the ideal perovskite [5]. In this regard, the behaviour of PrAlO<sub>3</sub> is similar to that of other rhombohedral rare-earth aluminates, and in particular it is intermediate between that of LaAlO<sub>3</sub> (transition at 820 K) and NdAlO<sub>3</sub> (transition projected to occur at about 2200 K) [5]. But PrAlO<sub>3</sub>, unlike LaAlO<sub>3</sub> and NdAlO<sub>3</sub>, undergoes two further phase transitions below room

temperature [6–8], a first-order transition near 205 K and a second-order transition near 150 K. These additional transitions are thought to be driven by electronic effects involving the  $\text{Pr}^{3+}$  ions, possibly cooperative Jahn–Teller effects [8]. In an early single crystal x-ray diffraction study, Burbank [4] confirmed the room temperature structure as rhombohedral in space group  $R\bar{3}c$ , and described the lower temperature structures as being metrically orthorhombic but truly monoclinic in space group  $C2/m$ , and metrically monoclinic in the triclinic space group  $P\bar{1}$ <sup>5</sup>. As has been noted elsewhere [8], his choice of the monoclinic rather than an orthorhombic space group for the intermediate, metrically orthorhombic phase was dictated by the appearance of a single weak reflection, attributed to displacement of the  $\text{Pr}^{3+}$  ions out of the symmetry plane. Given the continuous nature of the transition at 150 K, his choice of a triclinic space group for the lower temperature structure follows from that of the monoclinic space group for the intermediate phase. Based on Raman, optical fluorescence and electron paramagnetic resonance measurements on  $\text{Gd}^{3+}$  impurities, Harley *et al* [7] claimed that  $\text{PrAlO}_3$  undergoes another transformation, to tetragonal, on cooling below 100 K. This claim has been disputed in a neutron diffraction study [8], though no high-resolution diffraction studies of the tetragonal phase have hitherto been reported.

We report in this letter the results from new high-resolution x-ray and neutron powder diffraction measurements on  $\text{PrAlO}_3$  at temperatures from 10 K to room temperature, undertaken in an attempt to resolve the uncertainties discussed above. The different perovskite variants which might occur differ mainly in the distortion arising from the coupled tilting of the corner-linked  $\text{BX}_6$  octahedra [9–11]. Such tilting can be recognized in the powder diffraction patterns by splitting of the main perovskite peaks and/or the appearance of weak superlattice peaks arising from the concomitant enlargement of the unit cell. The intensity of superlattice peaks depends mainly on scattering from the anions which, for x-rays, is weak relative to that from the heavier cations. Consequently, neutron diffraction methods play an important role in determining the nature of the  $\text{BX}_6$  tilting. However, x-ray methods provide better resolution on the main peaks and are expected to be more sensitive to any small displacements (such as suggested by Burbank [4] for the intermediate phase) of the heavy cations.

## 2. Experimental details

The polycrystalline sample of  $\text{PrAlO}_3$  was prepared using conventional solid state methods. High-resolution variable-temperature synchrotron x-ray diffraction patterns were collected at a wavelength 0.7004 Å at X7A at the National Synchrotron Light Source, at Brookhaven National Laboratory, USA, making use of a linear position-sensitive detector with a spatial resolution of less than 50 μm [12]. The sample was housed in a 0.3 mm diameter capillary that was mounted in a closed-cycle helium cryostat.

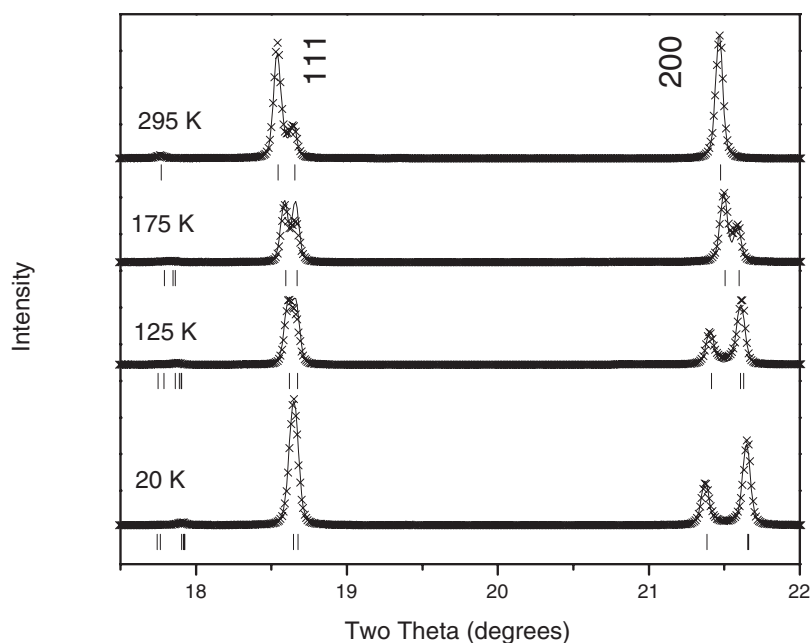
The neutron powder diffraction patterns were recorded using neutrons of wavelength 1.4925 Å in the range  $10^\circ < 2\theta < 155^\circ$  with a step size of  $0.05^\circ$  on the High Resolution Powder Diffractometer (HRPD) [13] installed on the High Flux Australian Reactor operated by the Australian Nuclear Science and Technology Organisation.

The structural refinements were undertaken using the Rietveld program Rietica [14]. In the neutron diffraction studies the background was defined by a third-order polynomial in  $2\theta$  and was refined simultaneously with the other profile parameters. For the synchrotron diffraction work a 50 point interpolated background was employed. A Pseudo–Voigt function of variable shape was chosen to describe the diffraction peak shape.

<sup>5</sup> Burbank [4] used unconventional space groups settings to describe the structures. The conventional equivalents are used here.

### 3. Results and discussion

Parts of the powder x-ray and neutron diffraction patterns from  $\text{PrAlO}_3$  recorded at several temperatures are shown in figures 1 and 2. The main peaks have been indexed as for the cubic perovskite. Symmetry was deduced by examination for peak splitting and appearance of superlattice reflections.

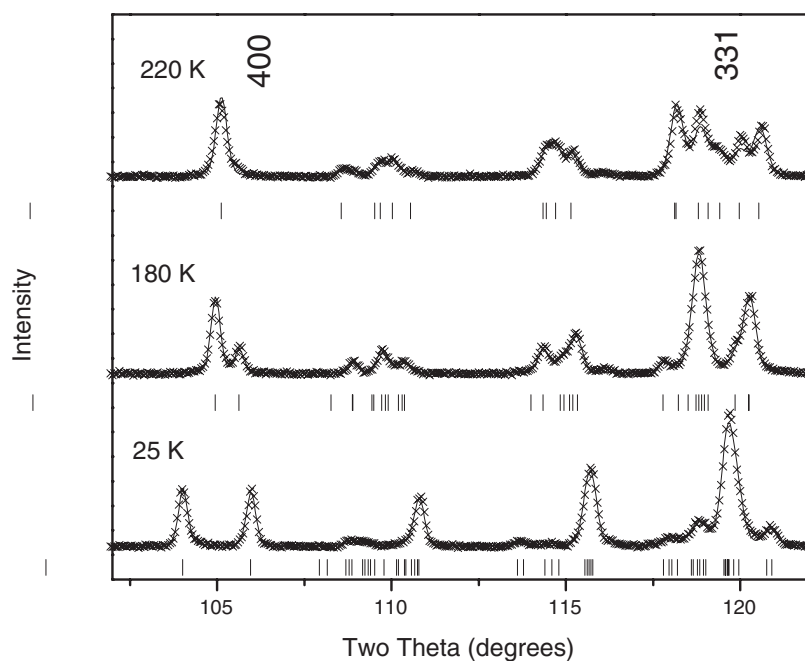


**Figure 1.** A segment from the synchrotron diffraction patterns for  $\text{PrAlO}_3$ , highlighting the pseudo-tetragonal character of the structure at 20 K. In each pattern the crosses represent the observed data and the solid line is the result of the Rietveld fit. The short vertical bars mark the positions of the Bragg reflections allowed in the appropriate space group. The reflection indices refer to the cubic aristotype.

In the patterns recorded at room temperature the  $hhh$  peaks showed splitting but not the  $h00$  peaks (figure 1). Superlattice reflections due to  $R$ -point distortions (out-of-phase tilting), but none attributable to  $M$ -point distortions (in-phase tilting) could be seen. This is consistent with the accepted rhombohedral structure, in space group  $R\bar{3}c$ , that has an  $a^-a^-a^-$  tilt system [10,11].

Upon cooling the sample below 200 K certain reflections first broaden then finally split. Again only superlattice reflections due to  $R$ -point distortions are observed and from the splitting pattern an orthorhombic structure in space group  $Imma$  ( $a^0b^-b^-$ ) appears reasonable. But for the appearance of one weak, possibly spurious reflection violating the glide plane conditions, Burbank [4] would have accepted this orthorhombic space group for the metrically orthorhombic intermediate phase.

The x-ray diffraction pattern recorded at 125 K shows further peak splitting, indicative of lower (than orthorhombic) symmetry. This peak splitting could be accounted for by assuming monoclinic symmetry—there was no suggestion of the triclinic inferred by Burbank [4]. The pattern still shows only  $R$ -point reflections, indicating that only out-of-phase tilts occur. The



**Figure 2.** Portions of the neutron diffraction patterns for  $\text{PrAlO}_3$ . The format is the same as in figure 1. That the structure does not become tetragonal at low temperatures is evident from inspection of the structure of the aristotype 331—in tetragonal this would be simply a doublet. The faint reflection at about  $116^\circ$ , which can be detected in all three patterns, is attributed to a trace impurity phase.

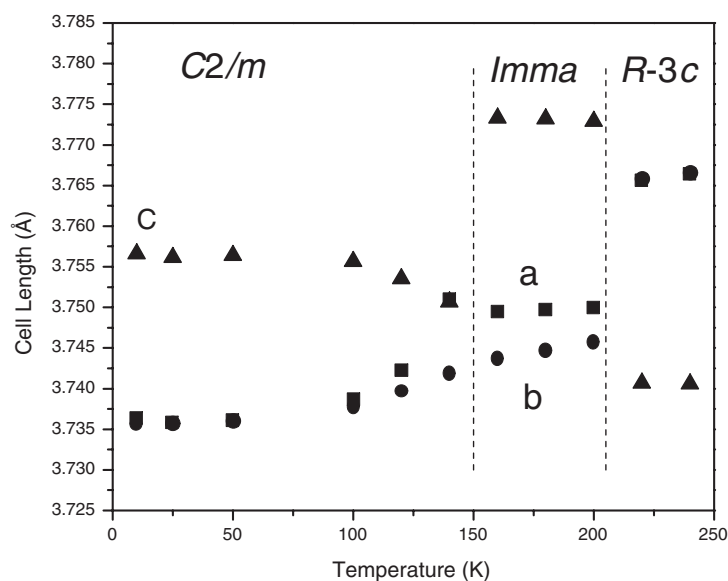
pattern can be fitted quite successfully in the monoclinic space group  $C2/m$  ( $a^0b^-c^-$ ). Cooling of the sample below 100 K results in an apparent simplification of the diffraction pattern. At 20 K the synchrotron diffraction pattern shows the 111 reflection near  $18^\circ$  as a single peak, whereas the 200 reflection near  $21^\circ$  is an apparent doublet (figure 1). Such a splitting is suggestive of a tetragonal distortion, that is, there is splitting of the  $h00$  peaks but not of the  $hhh$  peaks. However, examination of the reflections at higher angles, in the neutron pattern (figure 2), reveals a more complex splitting pattern demonstrating the symmetry remains monoclinic and the space group is still  $C2/m$ .

The powder neutron diffraction patterns provided essentially the same information as the x-ray patterns, albeit with lower resolution. Of particular importance for the assignment of the space groups is the fact that no reflections due to  $M$ -point distortions were observed.

From the diffraction pattern analysis, then, we confirm space group  $R\bar{3}c$  for  $\text{PrAlO}_3$  at room temperature, and suggest space groups  $Imma$  and  $C2/m$  for the structures between 205 and 150 K, and below 150 K respectively. In this way we have assigned Burbank's metrically orthorhombic structure to an orthorhombic space group and his metrically monoclinic structure to a monoclinic space group. According to the group theoretical analysis by Howard and Stokes [11], this assignment implies a necessarily discontinuous transition from  $R\bar{3}c$  to  $Imma$  (at 205 K) and a possibly continuous transition from  $Imma$  to  $C2/m$  at 150 K. There is convincing evidence that the 205 K transition is discontinuous whereas the 150 K is continuous, observations entirely consistent with the assignments we have made. The only problem with these space group assignments is the observation by Burbank [4], in the intermediate phase,

of a single weak reflection violating the  $Im\bar{m}a$  glide plane condition. It is not possible to resolve this additional  $03\bar{1}$  reflection in a powder diffraction study due to pseudo-symmetry and consequent overlap in the pattern. We found the model in  $Im\bar{m}a$  provided a comparable fit to that in  $I2/m$  ( $C2/m$ ), proposed by Burbank. Models in both  $Im\bar{m}a$  and  $I2/m$  allow displacement of the Pr ion from its ideal position in the parent perovskite, but the refinement in  $I2/m$  did not reproduce the off-axis displacement reported by Burbank. It seems possible that the crystal selected by Burbank [4] contained a small amount of a second domain giving rise to the reflection he observed.

Based on the above observations the structures have been refined using the Rietveld method as follows:  $T \geq 220$  K in  $R\bar{3}c$ ;  $200 \geq T \geq 150$  K in  $Im\bar{m}a$  and  $T \leq 140$  K in  $C2/m$ . Figure 3 illustrates the temperature variation in the perovskite unit cell parameters. While the 150 K phase transition is continuous, the variation in the lattice parameters just below this transition is rapid. In particular the  $C2/m$   $a$ -parameter increases markedly as the transition approaches. The first-order transition near 205 K involves a rather smaller change in the magnitude of the lattice parameters, as also observed by Birgeneau *et al* [8]. In fact, a plot of the temperature variation of the parameters of the perovskite subcell closely resembles the lattice parameter plot given by Birgeneau *et al* in figure 3 of [8], showing that our results are in very good agreement with theirs.

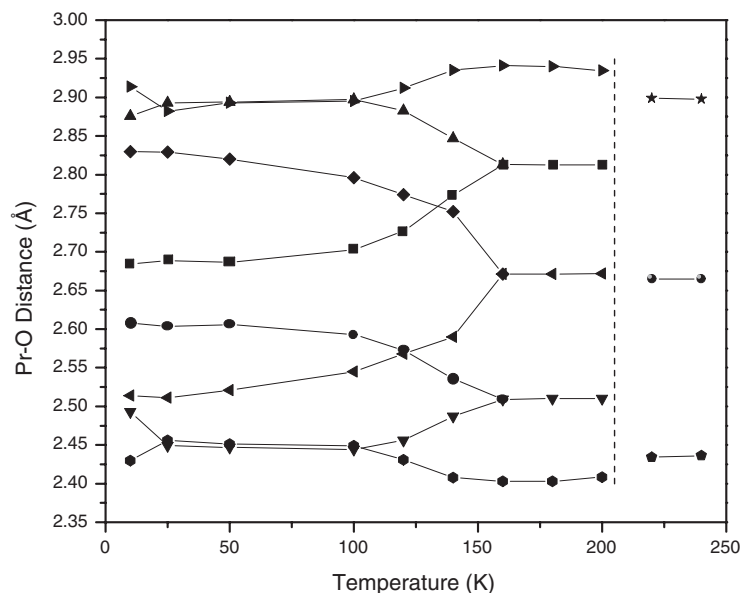


**Figure 3.** Temperature variation of the (reduced) lattice parameters for  $\text{PrAlO}_3$  obtained from analysis of the powder neutron diffraction data. For  $T \geq 220$  K the structures were refined in  $R\bar{3}c$  and the symbols represent  $a/\sqrt{2}$  and  $c/\sqrt{12}$ ; for  $200 \geq T \geq 150$  K the structures were refined in  $Im\bar{m}a$  and the symbols represent  $a/\sqrt{2}$ ,  $b/2$  and  $c/\sqrt{2}$ ; and  $T \leq 140$  K in  $C2/m$  the symbols represent  $a/2$ ,  $b/2$  and  $c/\sqrt{2}$ . The angle  $\beta$  in the monoclinic structure is approximately  $134.6^\circ$ .

Examination of the synchrotron profiles suggested the presence of two phases in the patterns collected above 150 K, and that the patterns were best fitted assuming a mixture of the  $R\bar{3}c$  and  $Im\bar{m}a$  phases. Such a mixture is not surprising given that the transition between these structures is first order. The neutron data could be adequately fitted using a single-phase model.

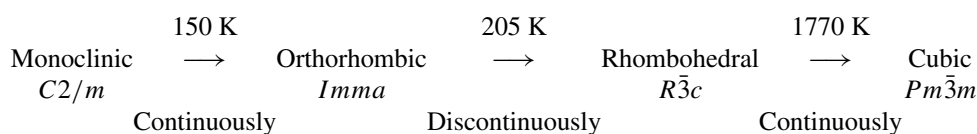
As expected the neutron diffraction measurements provide an accurate description of the structures. At all temperatures the  $\text{AlO}_6$  octahedra show very little distortion, and indeed in the low-temperature monoclinic phase the  $\text{AlO}_6$  octahedra can be considered as having a small tetragonal distortion with, at 10 K, the Al–O1 and Al–O2 distances being approximately equal (1.8961(2) and 1.8955(9) Å) and only marginally larger than the Al–O3 distance (1.8916(10) Å). This arrangement is essentially constant within the monoclinic phase and transforms to an arrangement wherein the six Al–O distances are approximately equal in the orthorhombic phase, although as the transition to the rhombohedral phase is approached the distances diverge again. The largest bond distance change occurring at the 150 K transition is only 0.003 Å or 0.15%.

The variations in the Pr–O distances are more dramatic, figure 4. Bond distance changes of up to 5% are observed at the  $\text{Imma} \rightarrow \text{C}2/m$  transition, and somewhat smaller changes are seen at the  $\text{R}\bar{3}c \rightarrow \text{Imma}$  transition. The  $\text{PrO}_{12}$  unit can be considered as a distorted cuboctahedron. In the rhombohedral phase the 12 oxygen atoms surrounding the Pr separate into three groups of four, the four furthest O atoms having only a small contribution to the bonding as gauged by bond valence considerations. On cooling to the orthorhombic structure the movement of the Pr atoms causes the four second-nearest O atoms to split, one now being the closest Pr–O atom near 2.40 Å and one the furthest near 2.93 Å. The remaining eight O atoms remain in two groups of four. Further cooling into the monoclinic structure results in considerable distortion of the  $\text{PrO}_{12}$  cuboctahedron. Both the closest and furthest groups of four O atoms split into two pairs and ultimately, to a reasonable approximation, the Pr again has three groups of four O atoms. These large changes in the Pr–O distances are consistent with a transition driven by a Jahn–Teller effect.



**Figure 4.** Temperature variation of the various Pr–O bond distances obtained following Rietveld analysis of the powder neutron diffraction data. Note the dramatic changes in bonding at the first-order transition, associated with off-centre displacement of the Pr ion, and further rapid changes in coordination below the continuous transition at about 150 K (see text).

In summary we have shown that the three phases examined here involve only out-of-phase tilts. The assignment of these three phases to space groups  $R\bar{3}c$ ,  $Imma$  and  $C2/m$  is consistent with the group theoretical analysis, which shows the  $R\bar{3}c \rightarrow Imma$  transition must be discontinuous whereas the  $Imma \rightarrow C2/m$  transition can be continuous. The complete sequence of structures in  $PrAlO_3$  can now be summarized in the schematic



Given the dramatic changes in both the lattice parameters and the Pr–O distances at the  $C2/m \rightarrow Imma$  transition a study of this transition using finer temperature intervals, similar to that reported recently for  $SrZrO_3$  [15], would be beneficial.

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