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# Short Communications

*Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

## The space group of LaAlO3 below 720 °K, and the compounds NdAlO3 and PrAlO3, probably isomorphous at room temperature.

By B. DERIGHETTI, J. E. DRUMHELLER, F. LAVES, K. A. MÜLLER and F. WALDNER, *Physik-Institut der Universität Zürich, Institut für Kristallographie und Petrographie der ETH Zürich, and IBM Zürich, Research Laboratory Rüschlikon, Switzerland*

Geller & Bala (1956) investigated $LaAlO_3$ by X-rays and found a symmetry change at 720 °K (independently confirming results of Gränicher & Müller, 1957). Whereas $LaAlO_3$ has the ideal perovskite structure (*i.e.* cubic with one formula unit per cell) above this temperature, a rhombohedral deformation takes place at 720 °K continuously increasing with decreasing temperature. In addition, extra reflexions observed at room temperature indicated a doubling of the rhombohedral $c$ axis. Geller & Bala proposed as most probable the space group $R\bar{3}m$ ($D^5_{3d}$) with La in $(c) - 3m \pm (0, 0, z)$, Al in $(a) - \bar{3}m$ $(0, 0, 0)$ and $(b) - \bar{3}m$ $(0, 0, \frac{1}{2})$, and O in $(h) - m \pm (x\bar{x}z; x, 2x, z; 2\bar{x}, \bar{x}, z)$ if hexagonal axes are chosen. On the other hand, consistent with their published X-ray data the space group $R\bar{3}c$ ($D^6_{3d}$) with La in $(a) - 32 \pm (0, 0, \frac{1}{4})$, Al in $(b) - \bar{3}$ $(0, 0, 0; 0, 0, \frac{1}{2})$ and O in $(e) - 2 \pm (x, 0, \frac{1}{4}; 0, x, \frac{1}{4}; \bar{x}, \bar{x}, \frac{1}{4})$ would also be possible. In $R\bar{3}m$ three parameters would be needed to characterize the structure; however, only one would be needed in $R\bar{3}c$, and the Al positions would be equivalent.

The nuclear quadrupole resonance measurements of $^{139}La$ and $^{27}Al$ (Müller, Brun, Derighetti, Drumheller & Waldner, 1964) and the electron paramagnetic measurements of crystals doped with $Gd^{3+}$, $Cr^{3+}$ (Kiro, Low & Zusman, 1963) and $Fe^{3+}$ (Müller *et al.*, 1964) give information on the point symmetry of the La and Al positions and indicate that the space group $R\bar{3}m$ is improbable. From the data on $^{139}La$ and $Gd^{3+}$ one sees one La site, its surroundings being axially deformed. The data on $^{27}Al$ and $Cr^{3+}$ show also only *one* Al site with axially deformed surroundings. The electron paramagnetic resonance spectrum of $Fe^{3+}$ consists of two sets of lines showing two sets of cubic axes rotated along the rhombohedral $c$ axis, whereas the distances to the nearest neighbours seem to be equal for both sets. The rotation angle $\pm \alpha$ is measured to be $6 \cdot 0° \pm 0 \cdot 2°$ at $298° \pm 3$ °K.

Thus, a structure with equivalent La sites and equivalent Al sites would be more consistent with the measurements mentioned above. Only two space groups, $R3c$ and $R\bar{3}c$, would conform with the X-ray data *and* the resonance data. Further, the observed two sets in the $Fe^{3+}$ spectrum could be attributed to the two types of equivalent Al positions which would have in both space groups rotated near-octahedral surroundings related by glide planes. As there are no data yet known to necessitate the assumption of $R3c$ we propose $R\bar{3}c$ as the most probable space group for $LaAlO_3$.

The oxygen parameter $x \neq \frac{1}{2}$ is still unknown but should be strongly temperature dependent. A calculation from the angle $\alpha$ of the $Fe^{3+}$ spectrum would give $x = 0 \cdot 53$ at room temperature in hexagonal coordinates, if one neglects possible structure deformations by the impurity ion.

From a crystal-chemistry point of view it is interesting to note that the more $x$ deviates from $\frac{1}{2}$ the more the La coordination number deviates from 12 (in the ideal perovskite structure) to 9. As the compounds $NdAlO_3$ and $PrAlO_3$ are reported to be isomorphous with $LaAlO_3$ (Geller & Bala, 1956) it is probable that they too have the space group $R\bar{3}c$.

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