

A, whereas those to O_I²⁻ are the shortest ones: Ga_I-O_I=1.80 Å and Ga_{II}-O_I=1.95 Å(2). The Ga_I-O_{II} distance 1.83 Å is equal to the average Ga_I-O distance, but the Ga_{II}-O_{II} distance, 1.95 Å, is 0.05 Å shorter than the average Ga_{II}-O distance. Thus the sum of the bond numbers of the bonds to an O_{II}²⁻ ion is somewhat greater than two, but not importantly so (see footnote reference 20).

Actually, the statistical calculation tells us that: there are no significant differences in Ga_I-O distances, nor in the Ga_{II}-O_I and Ga_{II}-O_{II} distances, nor in the two Ga_{II}-O_{III} distances. The shorter Ga_{II}-O_{III} distance is only possibly significantly different from the Ga_{II}-O_I and Ga_{II}-O_{II} distances. However the long Ga_{II}-O_{III} distance is significantly larger than the shortest distances. Unfortunately, the oxygen ions contribute little to the intensities in comparison with gallium ions and it is unlikely that much greater reliability can be attained even from more accurate intensity data. Also it would appear to be quite difficult to obtain crystals of the aluminum isomorph designated as θ -Al₂O₃^{19,20}; none have as yet been reported.

Nevertheless, the aforementioned criterion defined by Pauling¹⁸ indicates that the oxygen polyhedra must be irregular and therefore that the calculated distances are perhaps better than indicated by the standard deviations.

DISCUSSION

1. Comparison with α -Corundum Structure

The β -Ga₂O₃ structure (Figs. 1 and 2) appears to be quite different from that of α -Ga₂O₃ which has the α -corundum structure. The latter has the oxygen ions in approximately hexagonal close-packed array with all the Ga³⁺ ions octahedrally coordinated to O²⁻ ions. Also in the α phase, octahedra share edges and faces

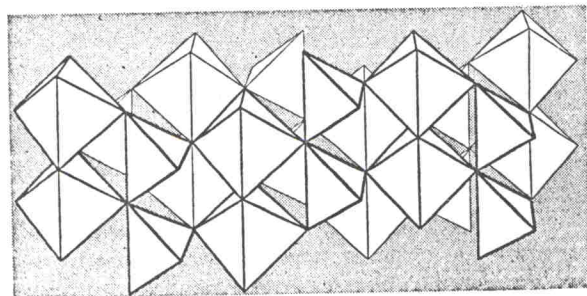


FIG. 1. Perspective view of the arrangement of the oxygen octahedra and tetrahedra in β -Ga₂O₃.

¹⁹ H. C. Stumpf, A. S. Russell, J. W. Newsome, and C. M. Tucker, *Ind. Eng. Chem.* **42**, 1398 (1950).

²⁰ The lattice constants of this phase derived by the present author from the powder data given by Stumpf *et al.*¹⁹ are $a = 11.83 \pm 0.02$, $b = 2.92 \pm 0.01$, $c = 5.64 \pm 0.01$ Å, and $\beta = 104.0 \pm 1.5^\circ$. The powder data, however, are not completely correct, the most outstanding discrepancy being that of d_{001} which should be 5.47 Å as against the reported 5.25 Å. Also it is possible that some observable lines have been omitted; one of these is the [401] reflection.

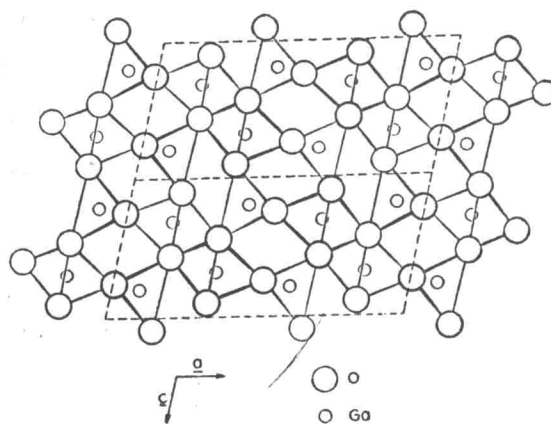


FIG. 2. Plan view of the β -Ga₂O₃ structure. Lines connecting atoms indicate the manner in which the octahedra and tetrahedra are constructed from and joined by the oxygen atoms in the three consecutive symmetry planes. Only the upper faces of the polyhedra are depicted. For increased clarity, this figure should be studied simultaneously with Fig. 1.

which brings the metal ions very near each other. Accurate atomic positional parameters for α -Ga₂O₃ have not been determined. However, in Fe₂O₃,¹ the closest approach of two Fe³⁺ ions through a shared octahedral face is 2.88 Å and through a shared edge 2.96 Å.²¹ In β -Ga₂O₃ no faces are shared between polyhedra and the shortest Ga³⁺-Ga³⁺ distance is 3.04 Å.

Now it is recognized that usually structures in which faces of polyhedra are shared are less stable than those in which edges are shared, which in turn are less stable than structures in which only corners are shared.¹⁸ Thus, one would expect the β phase to be more stable than the α phase. Foster and Stumpf have shown¹⁰ that although the α -Ga₂O₃ forms at lower temperatures than does β -Ga₂O₃, the α phase is metastable. In the case of alumina, it appears that the α phase forms at higher temperatures than the θ (isostructural with β -Ga₂O₃) just the reverse of the gallia. Yet it appears that although seen rarely in comparison with the α phase, the θ -Al₂O₃ is the thermodynamically stable phase at room temperature¹⁹ and that although α -Al₂O₃ is thermodynamically metastable at room temperature the $\alpha \rightarrow \theta$ transition of Al₂O₃ is "infinitely" sluggish at such temperature.

As one might expect, the lower average coordination in the β -Ga₂O₃ is accompanied by a lower density; the volumes per Ga₂O₃ in the α and β phases are 47.8 and 52.8 Å³, respectively.

²¹ Recent accurate work on Ti₂O₃ and V₂O₃ by Nordmark²² has led to the Me-Me distances: 2.55 and 2.64 Å, respectively, across the shared face and 2.99 and 2.88 Å, respectively, across the shared edge. In any case, the closest approach of Ga³⁺ ions in β -Ga₂O₃ is substantially greater than that of the metal ions in any of the α phases.

²² C. Nordmark, in Final Technical Report, "Studies on the crystal chemistry of titanium, vanadium and molybdenum oxides at elevated temperatures" by A. Magnéli *et al.*, University of Stockholm (October, 1959), p. 16. See also R. E. Newnham and Y. M. de Haan, American Crystallographic Association Meeting, Washington, D. C., January, 1960, Paper No. D-5.