A, whereas those to O_I^{2-} are the shortest ones: $Ga_I-O_I = 1.80$ A and $Ga_{II}-O_I = 1.95$ A (2). The Ga_I-O_{II} distance 1.83 A is equal to the average Ga_I-O distance, but the $Ga_{II}-O_{II}$ distance, 1.95 A, is 0.05 A 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-Al_2O_3[19,20]; none have as yet been reported.

Nevertheless, the aforementioned criterion defined by Pauling[18] 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-Ga_2O_3 structure (Figs. 1 and 2) appears to be quite different from that of α-Ga_2O_3 which has the α-corundum structure. The latter has the oxygen ions in approximately hexagonal close-packed array with all the Ga^{3+} ions octahedrally coordinated to O^{2-} ions. Also in the α phase, octahedra share edges and faces
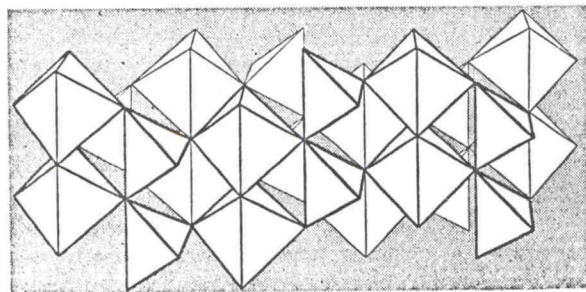

FIG. 1. Perspective view of the arrangement of the oxygen octahedra and tetrahedra in β-Ga_2O_3.

[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 $a = 11.83\pm0.02$, $b = 2.92\pm0.01$, $c = 5.64\pm0.01$ A, and $\beta = 104.0\pm $ $.5°$. The powder data, however, are not completely correct, the most outstanding discrepancy being that of d_{001} which should be 5.47 A as against the reported 5.25 A. Also it is possible that some observable lines have been omitted; one of these is the $[40\bar{1}]$ reflection.
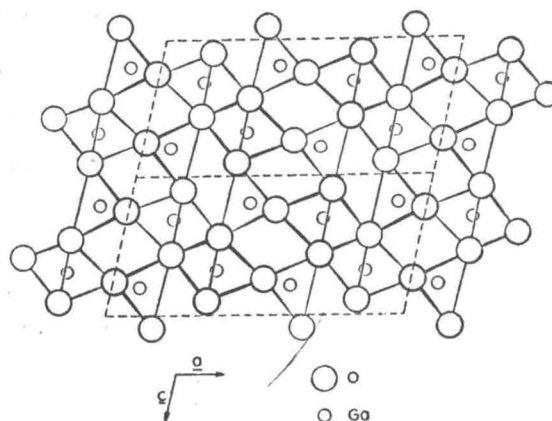
FIG. 2. Plan view of the β-Ga_2O_3 structure. Lines connecting atoms indicate the manner in which the octahedra and tetrahedra are constructed from and joined by the oxygen atoms in the three consecutive symmetry planes. Only the upper faces of the polyhedra are depicted. For increased clarity, this figure should be studied simultaneously with Fig. 1.

which brings the metal ions very near each other. Accurate atomic positional parameters for α-Ga_2O_3 have not been determined. However, in Fe_2O_3,[1] the closest approach of two Fe^{3+} ions through a shared octahedral face is 2.88 A and through a shared edge 2.96 A.[21] In β-Ga_2O_3 no faces are shared between polyhedra and the shortest $Ga^{3+}-Ga^{3+}$ distance is 3.04 A.

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 shown[10] that although the α-Ga_2O_3 forms at lower temperatures than does β-Ga_2O_3, 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-Ga_2O_3) just the reverse of the gallia. Yet it appears that although seen rarely in comparison with the α phase, the θ-Al_2O_3 is the thermodynamically stable phase at room temperature[19] and that although α-Al_2O_3 is thermodynamically metastable at room temperature the $\alpha \rightarrow \theta$ transition of Al_2O_3 is "infinitely" sluggish at such temperature.

As one might expect, the lower average coordination in the β-Ga_2O_3 is accompanied by a lower density; the volumes per Ga_2O_3 in the α and β phases are 47.8 and 52.8 A^3, respectively.

[21] Recent accurate work on Ti_2O_3 and V_2O_3 by Nordmark[22] has led to the Me–Me distances: 2.55 and 2.64 A, respectively, across the shared face and 2.99 and 2.88 A, respectively, across the shared edge. In any case, the closest approach of Ga^{3+} ions in β-Ga_2O_3 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.