

TABLE VI. Analogous average distances and ranges in β -Ga₂O₃ and in yttrium-iron garnet.

Metal-oxygen distances	β -Ga ₂ O ₃		YIG ^a	
	Averages	Range	Averages	Range
Octahedral	2.00 A	1.95-2.08 A	2.00 A	All equal
Tetrahedral	1.83	1.80-1.85	1.88	All equal
O-O distances				
In octahedron	2.84	2.67-2.90	2.84	2.68-2.99 A
In tetrahedron	3.02	2.93-3.13	3.06	2.87-3.16

^a S. Geller and M. A. Gillico, *J. Phys. Chem. Solids* **3**, 30 (1957); **9**, 235 (1959).

2. Possibility of Disorder

That the structure is ordered appears to be established by the paramagnetic-resonance work by Peter and Schawlow² on Cr³⁺-ion-doped β -Ga₂O₃, in which it is found that the Cr³⁺ ions prefer only one set of octahedral sites. It is likely that these ions replace the Ga_{II}³⁺ ions in octahedrally coordinated sites: There is not enough space for foreign ions in the remaining octahedrally coordinated holes. Thus it is improbable that there is the type of disorder which would allow drastic change in the environment of any of the Ga_I³⁺ and Ga_{II}³⁺ ions.

3. Importance of β -Ga₂O₃ Structure Relative to Substitution of Ga³⁺ and Al³⁺ for Fe³⁺ Ions in Yttrium-Iron Garnet

The Ga³⁺ and Fe³⁺ ions have very similar crystal chemistry. Both ions have spherical electronic configuration and are of very nearly the same size, the Ga³⁺ ion being somewhat smaller than Fe³⁺ ion in most structures. The relative radii derived from the perovskitelike compounds⁸ put the Ga³⁺ ion CN(6) radius at 0.015 A less than that of the Fe³⁺ ion. This does not mean that average metal-oxygen distances will be exactly the same in different structures. For example, the relative ionic radii derived from the perovskitelike compounds are applicable to the garnets,^{5,23,24} but the CN(6) metal-oxygen distances in the garnets are uniformly somewhat larger than the sums of these radii.

Although the structure of yttrium-gallium garnet, {Y₃}[Ga₂](Ga₃)O₁₂ has not yet been refined, that of yttrium-iron garnet has²⁵; it is of interest to compare some analogous distances in this garnet structure with those of β -Ga₂O₃. The averages and ranges of these analogous distances are compared in Table VI. It is seen that the average Ga_{II}-O distance in β -Ga₂O₃ is the same as the octahedral Fe-O distance in yttrium-iron garnet. On the other hand, the average Ga_I-O

²³ S. Geller, R. M. Bozorth, M. A. Gilileo, and C. E. Miller, *J. Phys. Chem. Solids* **12**, 111 (1960).

²⁴ S. Geller and D. W. Mitchell, *Acta Cryst.* **12**, 936 (1959).

²⁵ S. Geller and M. A. Gilileo, *J. Phys. Chem. Solids* **3**, 30 (1957); **9**, 235 (1959).

distance in β -Ga₂O₃ is substantially smaller than the tetrahedral Fe-O distance in the garnet. The average O-O distances of the octahedra in the two structures are equal but the average O-O distance in the GaO₄ tetrahedron in β -Ga₂O₃ is shorter than the average O-O distance in the FeO₄ tetrahedron of the garnet. Now from the least-squares calculations, the aforementioned differences are not significant. However, on a crystal chemical basis, there is reason to believe that the differences are meaningful.

We have shown previously⁶ that when the Ga³⁺ ion is substituted for the Fe³⁺ ion in the garnets, it shows a great preference for the tetrahedral [CN(4)] site. Also there is indication that when Fe³⁺ is substituted for the Ga³⁺ ion in yttrium-gallium garnet, it greatly prefers the octahedral [CN(6)] site.²⁶ We have also mentioned elsewhere that the ratios of effective size of ions in different coordinations may differ and probably depend largely on the nuclear charge and external electronic configuration of the atom.^{23,24} The ratios of tetrahedral to octahedral Fe-O distances in yttrium-iron garnet is 0.94; in Y₃Al₂Al₃O₁₂²⁷ the analogous Al-O ratio is 0.91, in β -Ga₂O₃ the ratio of tetrahedral to octahedral average Ga-O distances is 0.91, in fact very similar to that of the Al-O distances in the aluminum garnet.

Now despite the fact that the Al³⁺ ion is much smaller than the Ga³⁺ ion, the quantitative site preference in the substituted iron garnets of the latter is very close to that of the former^{5,9}; this is in agreement with the above considerations.

4. Magnetic Aspects

If an Fe₂O₃ phase isostructural with β -Ga₂O₃ were found, it should be antiferromagnetic, because the Ga_I-O-Ga_{II} angles of about 123° (Table V) are (and presumably the Fe_I-O-Fe_{II} angles would be) favorable to superexchange interaction^{9,25,28,29} and the network of octahedra and tetrahedra involving these favorable angles continues throughout the structure.²⁹ Counting the possible significant magnetic interactions we find

²⁶ S. Geschwind, *Phys. Rev. Letters* **3**, 207 (1959).

²⁷ E. Prince, *Acta Cryst.* **10**, 787 (1957).

²⁸ M. A. Gilileo, *Phys. Rev.* **109**, 777 (1958).

²⁹ M. A. Gilileo, *J. Phys. Chem. Solids* (to be published).