TABLE VI. Analogous average distances and ranges in β-Ga_2O_3 and in yttrium-iron garnet.

Metal-oxygen distances	β-Ga_2O_3 Averages	β-Ga_2O_3 Range	YIG[a] Averages	YIG[a] 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. Gillco, 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 Schawlow[2] on Cr^{3+}-ion-doped β-Ga_2O_3, in which it is found that the Cr^{3+} 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_I^{3+} and Ga_{II}^{3+} ions.

3. Importance of β-Ga_2O_3 Structure Relative to Substitution of Ga^{3+} and Al^{3+} for Fe^{3+} Ions in Yttrium-Iron Garnet

The Ga^{3+} and Fe^{3+} ions have very similar crystal chemistry. Both ions have spherical electronic configuration and are of very nearly the same size, the Ga^{3+} ion being somewhat smaller than Fe^{3+} ion in most structures. The relative radii derived from the perovskitelike compounds[8] put the Ga^{3+} ion $CN(6)$ radius at 0.015 A less than that of the Fe^{3+} 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, $\{Y_3\}[Ga_2](Ga_3)O_{12}$ has not yet been refined, that of yttrium-iron garnet has[25]; it is of interest to compare some analogous distances in this garnet structure with those of β-Ga_2O_3. 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-Ga_2O_3 is the same as the octahedral Fe—O distance in yttrium-iron garnet. On the other hand, the average Ga_I–O distance in β-Ga_2O_3 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 GaO_4 tetrahedron in β-Ga_2O_3 is shorter than the average O–O distance in the FeO_4 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 previously[5] that when the Ga^{3+} ion is substituted for the Fe^{3+} ion in the garnets, it shows a great preference for the tetrahedral $[CN(4)]$ site. Also there is indication that when Fe^{3+} is substituted for the Ga^{3+} 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 $Y_3Al_2Al_3O_{12}$[27] the analogous Al–O ratio is 0.91, in β-Ga_2O_3 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 Al^{3+} ion is much smaller than the Ga^{3+} 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 Fe_2O_3 phase isostructural with β-Ga_2O_3 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

[23] S. Geller, R. M. Bozorth, M. A. Gilleo, and C. E. Miller, J. Phys. Chem. Solids **12**, 111 (1960).
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[25] S. Geller and M. A. Gilleo, J. Phys. Chem. Solids **3**, 30 (1957); **9**, 235 (1959).
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[27] E. Prince, Acta Cryst. **10**, 787 (1957).
[28] M. A. Gilleo, Phys. Rev. **109**, 777 (1958).
[29] M. A. Gilleo, J. Phys. Chem. Solids (to be published).