

sites in the garnets. In these garnets, more Fe^{3+} ion could be in the octahedral sites but apparently this does not occur.

The amounts of Ge^{4+} in octahedral sites in the $\{\text{Y}_3\}\text{Co}_x\text{Fe}_{5-2x}\text{Ge}_2\text{O}_{12}$ system are quite small: according to our estimates⁹⁷, there is 0.1 atom per formula unit in octahedral sites when $x = 1.00$ and 0.1 when $x = 2.20$.

I wish to make it very clear that I do not argue that Co^{2+} ion prefers octahedral coordination in all crystals, but it surely does in the garnets. It also prefers it in its own monoxide, CoO ; after all it could have chosen the zinc blende structure as one form of ZnO does. There is also no question about Co^{2+} ions entering tetrahedral sites in some garnets; as we have said elsewhere⁹⁷, it is the only divalent ion known to enter these sites in substantial amount. It may be that, logically, one could accept the statement that Co^{2+} ion shows a strong affinity for tetrahedral sites in the garnets if such statement were not coupled with the one that Co^{2+} does not prefer the octahedral sites in the garnets. In other words, relative to other divalent ions the Co^{2+} ion has by far a greater affinity for tetrahedral sites in the garnets; however, in the garnets it has a much higher affinity for octahedral sites than it does for tetrahedral sites.

If the Ni^{2+} ions do go into tetrahedral sites in the garnets, very little do so indeed. This is indicated not only by the work of PAPPALARDO *et al.*¹⁰⁰ but also by some additional work that we have done. We have investigated the system $\{\text{Ca}_3\}[\text{Zr}_{1+x}\text{Ni}_{1-x}](\text{Ni}_x\text{Ge}_{3-x})\text{O}_{12}$ analogous to the one for Co^{2+} ion described above. A specimen with $x = 0.10$ is not single phase. Even a new specimen with $x = 0.00$ is somewhat suspect, but it has the same lattice constant, 12.50 Å, as reported in our 1960 paper⁴³. The garnet phase in the $x = 0.10$ specimen has precisely the same lattice constant. However, this is the case only if no GeO_2 is lost. When GeO_2 is lost, lattice constants do change, as one would expect. Contrary to results reported by REINEN, firings at different temperatures do not have any effect on the lattice constant of the specimens in this system provided that no GeO_2 is lost. Further, no marked change in color occurs when the firing is carried out in N_2 atmosphere—even when GeO_2 is lost. This, also, is contrary to REINEN's reported results which indicate a yellow-green color associated with the lower temperature firing.

We believe that the reason for REINEN's observation of a change in lattice constant in $\{\text{Ca}_3\}\text{ZrNiGe}_3\text{O}_{12}$ is not a simple redistribution of ions. It results from a loss of GeO_2 at the higher temperatures.

In fact, when our specimen with $x = 0.00$ lost 3% by weight of the original GeO_2 , the lattice constant of the garnet present was 12.515 Å; REINEN's 12.52 Å for his specimen fired at the higher temperature agrees with this value.

Thus, in view of the results of PAPPALARDO *et al.*¹⁰⁰ implying no tetrahedral Ni^{2+} and of our results, it may well be that the tetrahedral Ni^{2+} ion observed by REINEN is in an extraneous phase present with the garnet. On the other hand, a loss of GeO_2 would require Ni^{2+} ion in the tetrahedral sites if the specimen were single phase; however, our specimen which had this loss was definitely not single phase, and I therefore doubt that REINEN's was.

Distribution of ions in the $\{\text{Y}_3\}\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ system

My prime task in this paper was to survey the crystal chemistry of the garnets. So much work has now been done on the garnets, that several volumes could be written on them alone. A recent paper of mine¹⁰² gives a review of our work on the static magnetic behavior of the substituted garnets, and I shall not repeat that here. But I do wish to point out that the model⁷ proposed by me and my colleagues for this magnetic behavior, provides a basis for obtaining valuable information (and also for making predictions) on the crystal chemistry of the garnets. Aside from unifying the results of magnetic measurements on the substituted yttrium iron garnets when the site preferences are essentially known, it has helped us to understand the low-temperature behavior of the substituted gadolinium iron garnets⁷⁵ and the garnets in which other paramagnetic ions are substituted for the Fe^{3+} ion⁵⁵. It has especially given us an understanding of the very complex $\{\text{Y}_3\}\text{Co}_x\text{Fe}_{5-2x}\text{Ge}_x\text{O}_{12}$ and the analogous $\{\text{Y}_3\}\text{Co}_x\text{Fe}_{5-2x}\text{Si}_x\text{O}_{12}$ systems⁹⁷. It has also enabled us to determine the ionic distribution in the systems $\text{Y}_3\text{Fe}_{5-x}\text{Al}_x\text{O}_{12}$ ⁷, $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$ ²⁷ and $\{\text{Y}_{3-x}\text{Ca}_x\}\text{Fe}_{5-x}\text{Ti}_x\text{O}_{12}$ ⁸².

As an example, we show the distributions obtained for the aluminum and gallium substituted YFe garnet systems in Fig. 6. The method for accomplishing this has been described elsewhere^{7,27}. Shown also are the points obtained in a nuclear resonance study¹⁰³ of the gallium

¹⁰² S. GELLER, Magnetic behavior of substituted ferrimagnetic garnets. *J. Appl. Physics* **37** (1966) 1408–1415.

¹⁰³ R. L. STREEVER and G. A. URIANO, Nuclear resonance study of gallium-substituted yttrium iron garnet. *Physic. Rev.* **139** (1965) A305–A313.