{Ca$_3$}[Zr$_{1+x}$Co$_{1-x}$](Co$_x$Ge$_{3-x}$)O$_{12}$. The garnet REINEN claims to have made has $x = 1.00$ and has a lattice constant of 12.62 Å. Our specimen with an attempted $x = 1.00$ is *not* single phase; the garnet present has $a = 12.619 \pm 0.002$ Å. We have made several other specimens.

$$x = 0.00 \qquad a = 12.528 \text{ Å}$$
$$0.20 \qquad 12.557$$
$$0.40 \qquad 12.588$$
$$0.60 \qquad 12.619.$$

Note that with $x = 0.60$, that is for {Ca$_3$}[Zr$_{1.6}$Co$_{0.4}$](Co$_{2.6}$Ge$_{2.4}$)O$_{12}$ the lattice constant is the *same* as for the garnet phase present in the specimen attempted with $x = 1.00$ and also equal to the value obtained by REINEN. Further, even the specimen with $x = 0.60$ is not quite single phase. However, maximum x in this system is very near 0.60. So that even in this system, Co^{2+} does *not* show a *preference* for tetrahedral sites. That is, it does not seem possible to force more than 60% of the Co^{2+} into these sites.

REINEN also bases some of his claim on the observation that in the {Ca$_3$}Me^{4+}Co^{2+}Ge$_3$O$_{12}$ garnets, *many* Ge^{4+} ions are in octahedral sites while many Co^{2+} ions are in tetrahedral sites. (This is required if Co^{2+} ions are to be in tetrahedral sites, else the crystals would be of a complex vacancy type.) Now in our 1960 paper[43] we did not, of course, rule out the possibility that some of the Co^{2+} ions did go into tetrahedral sites in the garnets discussed in that paper, but we said that they were few and I still think so.

In a paper, overlooked by REINEN, it was shown by PAPPALARDO, WOOD and LINARES[99] that the tetrahedrally coordinated Co^{2+} ion has *much* stronger absorption than the octahedral Co^{2+} ion. In fact that paper points out the discussions that those authors had with me. Our differences were resolved by just the point mentioned[99]: it is possible by optical spectroscopy to observe *very* small amounts of tetrahedral Co^{2+} ion, but even large amounts of octahedral Co^{2+} ion in the presence of very small amounts of tetrahedral Co^{2+} ion are not observable by this technique. The oscillator strengths of tetrahedral Co^{2+} appear to be between about two and three orders of magnitude larger than those of octahedral Co^{2+}. This appears to be the case for

[99] R. PAPPALARDO, D. L. WOOD and R. C. LINARES, JR., Optical absorption study of Co-doped oxide systems. II. J. Chem. Physics 35 (1961) 2041–2055.

Ni^{2+} also[100] and possibly accounts for REINEN's conclusions about Ni^{2+} ion in the garnets. In this case also, there is evidence[55,100] that very few Ni^{2+} ions enter tetrahedral sites in the garnets (see below). In the paper by PAPPALARDO, WOOD and LINARES[100], they show that Ni^{2+} doped yttrium gallium garnets contain *only* octahedrally coordinated Ni^{2+} ions.

With regard to REINEN's results concerning the effect of temperature on distribution, if the tetrahedral site occupancy by Co^{2+} ions is low, a small absolute change will result in a high-percentage change in the tetrahedral sites. It is this percentage change that is seen in REINEN's Fig. 12. Thus, REINEN's results on Ca$_3$ZrCoGe$_3$O$_{12}$ imply only a small amount of Co^{2+} ion in tetrahedral sites. We have also fired our specimen of {Ca$_3$}ZrCoGe$_3$O$_{12}$ at three different temperatures: 1320 °C (in air), 1190 and 1125 °C in N$_2$. Contrary to REINEN's findings, the lattice constant was unchanged by these heat treatments. Also we saw no reddish gray color; the specimen fired at 1125 °C has a light blue-gray color.

I may also point out that in a paramagnetic resonance study of Co^{2+} ion in yttrium gallium garnet by CHAMBERLAIN and COOPER[101], no spectrum was observed having the S_4 symmetry for the tetrahedral sites; only a spectrum with the C_{3i} symmetry of the a sites was observed. This does not mean that there were no Co^{2+} ions in the tetrahedral sites of their YGa garnet specimen, just as the observation that the optical spectrum comes only from the tetrahedral Co^{2+} ions does not mean that there are only tetrahedral Co^{2+} ions in YGa garnet.

In the magnetic studies of the {Y$_3$}Co$_x$Fe$_{5-2x}$Si$_x$O$_{12}$ and {Y$_3$}Co$_x$Fe$_{5-2x}$Ge$_x$O$_{12}$ systems[97], we arrived at a good accounting for the observed results through application of the model[7] mentioned earlier and results obtained[55] on other divalent ion substituted yttrium iron garnets. In the first system, that is, the one in which the Co^{2+} ion was compensated by Si^{4+}, samples with $0.10 \leq x \leq 1.00$ were prepared, while for the system with Ge^{4+} ion compensation, specimens with $0.20 \leq x \leq 2.50$ were prepared. Our conclusion was: when $0.20 \leq x \leq 2.20$, 20% of the Co^{2+} ions were in tetrahedral sites. This demonstrates further the preference of Co^{2+} ions for the octahedral

[100] R. PAPPALARDO, D. L. WOOD and R. C. LINARES, JR., Optical absorption spectra of Ni-doped oxide systems. I. J. Chem. Physics 35 (1961) 1460–1478.
[101] J. R. CHAMBERLAIN and R. W. COOPER, Paramagnetic resonance in yttrium gallium garnet: Co^{2+} and Mn^{2+}. Proc. Physic. Soc. [London] 87 (1966) 967–970.