was discovered[98] in which the V^{3+} ion very nearly filled the a sites and in fact $Ca_3V_2Si_3O_{12}$ and the analogous germanate have been synthesized by others and also by us (see Table 3).

It still appears, however, that in the *garnets*, site preferences depend mostly on relative ionic sizes with the largest ions tending to occupy the dodecahedral or 8-coordination sites. Usually, but not always the smallest ions prefer the tetrahedral sites. There is no doubt that the Cr^{3+} ion in both the perovskite-like and garnet compounds is smaller than the Fe^{3+} ion. In fact, according to crystal field theory it should be[50,51]. Still the Cr^{3+} ion prefers cubic or octahedral symmetry; in the garnets it appears to go exclusively into the a sites even when other ions present are larger, for example, when substituted for Fe^{3+} or Ga^{3+} ions in YFe or YGa garnet, respectively. Much more Cr^{3+} replaces the Ga^{3+} than it does the Fe^{3+} ion indicating how sensitive this replacement is to the relative ionic sizes of the Fe^{3+} and Ga^{3+} in the tetrahedral coordination[66].

As pointed out earlier, the behavior of Ga^{3+} vs Al^{3+} ion when substituted for Fe^{3+} ion is still not understood on the ionic size basis. Also it is not entirely clear why so large an ion as Co^{2+}, while preferring the octahedral sites also goes into tetrahedral sites in substantial amount. [However, Co^{2+} does have a pseudospherical ground state $(4A_2)$ in tetrahedral coordination; this may yet have some bearing on the matter.]

In a 1964 paper[95], REINEN has made certain claims regarding the site preference of the Co^{3+} ion. In particular he states: "Die von GELLER vertretene Ansicht, daß das Co^{2+}-Ion in Granaten die oktaedrische Koordination der tetraedrischen vorzieht, ist sicherlich nicht korrekt". The reference REINEN gives is to the present reference[4]. REINEN goes on to point out "... daß wie in Spinellen das Co^{2+}-Ion auch in Granaten eine starke Tendenz zu tetraedrischer Koordination besitzt." Further he says that the presence of the small Ge^{4+} ions however, blocks the tetrahedral sites and therefore weakens this tendency. I shall show that all the evidence, including even that of REINEN, supports the original conclusion that in the garnets, the Co^{2+} ions prefer octahedral sites even though some Co^{2+} ions may go into tetrahedral sites.

The situation in the case of the spinels is not at all straightforward. In $CoAl_2O_4$ the Co^{2+} ions are in tetrahedral sites; on this basis alone

one might say that Co^{2+} ions appear to prefer tetrahedral sites, else $CoAl_2O_4$ would be an inverse spinel. Contrary to REINEN's arguments, however, very little, if any, germanium seems to exchange with Co in Co_2GeO_4, even though this should be easier in the spinel than in the garnet structure. So this already moves toward refutation of REINEN's thinking even on the spinels. But the really important point is that $CoFe_2O_4$ *is* an *inverse* spinel. Magnetic measurements have shown that all the Co^{2+} ions are in octahedral sites*. There is no germanium doing any blocking in $CoFe_2O_4$; the Fe^{3+} ions could be in either site. In fact, $MnFe_2O_4$ tends to be a normal spinel so it would seem that Co^{2+} does not actually show much desire for tetrahedral sites in $CoFe_2O_4$. But the situation with the garnets is much clearer: REINEN's remarks notwithstanding, the Co^{2+} ions *prefer* the octahedral coordination even though they will go into tetrahedral sites.

Now one of REINEN's strongest arguments is his synthesis of $Ca_3Zr_2Ge_2CoO_{12}$ showing that he was able to force one cobalt per formula unit into tetrahedral sites. On the other hand, he says that the distribution in $\{Y_2Ca\}[Co_2](Ge_3)O_{12}$ is as here indicated, that is, all octahedral sites are *filled* with Co^{2+} ions.

In the earlier part of his paper, REINEN says that even in $Ca_3ZrCoGe_3O_{12}$, *much* cobalt is in tetrahedral sites with an amount of Ge^{4+} equal to it in octahedral sites. Then why does not just a little bit of Co exchange with Ge in the case of $\{Y_2Ca\}[Co_2](Ge_3)O_{12}$? Further, even though he found that $Y_2Co_3Ge_3O_{12}$ was blue when fired in N_2, he agreed with us that the distribution is as we suggested it is—that is, $\{Y_2Co\}[Co_2](Ge_3)O_{12}$. Thus logically, this implies only that even if one could make garnets in which the d sites must be *filled* with Co^{2+} ions, all one could say is that the Co^{2+} ions do not have a preference between a and d sites. Of course, no such garnet has been made.

Actually, it is not even possible to make the garnet $\{Ca_3\}[Zr_2](CoGe_2)O_{12}$ (claimed by REINEN) by solid-state reaction. We have investigated the following system: $\{Ca_3\}CoZr_yGe_{3-y}O_{12}$ to see how much Co^{2+} ion will be forced into the tetrahedral sites. We assume that little or no Ge^{4+} will be in octahedral sites and will show later why this is valid. Thus we may write the distribution formula

[98] R. H. MOENCH and R. MEYROWITZ, Goldmanite, a vanadium garnet from Laguna, New Mexico. Amer. Mineral. 49 (1964) 644–655.

* *Added in proof.* A paper (EC-1) presented at the recent International Congress on Magnetism by G. A. SAWATSKY, F. VAN DER WOUDE and A. H. MORRISH indicates that the distribution of Co^{2+} ion in $CoFe_2O_4$ is sensitive to heat treatment. Nevertheless, at most, about 20 % of the Co^{2+} ions enter tetrahedral sites.