

was discovered<sup>98</sup> 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<sup>50,51</sup>. 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<sup>66</sup>.

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<sup>95</sup>, 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<sup>93</sup>. 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

<sup>98</sup> R. H. MOENCH and R. MEYROWITZ, Goldmanite, a vanadium garnet from Laguna, New Mexico. Amer. Mineral. 49 (1964) 644-655.

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

\* 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.