

distance given by ZEMANN and ZEMANN is 1.62 Å; my calculations gave 1.63 ± 0.02 Å, so that from these determinations, it is not possible to say unequivocally that the Si—O distances in the two garnets are significantly different.

GIBBS and SMITH¹⁵ have also carried out a careful and detailed study on a synthetic pyrope. They did a least-squares refinement on the data of ZEMANN and ZEMANN to ascertain that the synthetic pyrope prepared by COES¹⁹ had essentially the same detailed structure as the crystal they used, prepared by BOYD. The data for the Gibbs-Smith refinement were obtained from a polyhedral crystal of 0.32 mm and 0.41 mm minimum and maximum dimensions, respectively. Intensities of 374 independent reflections were measured with a scintillation-counter equi-inclination Weissenberg diffractometer using monochromatized MoK α radiation. Corrections for absorption and polarization of the beam by the monochromator were found to be negligible and therefore, were not needed. The oxygen positional parameters obtained from the refinement are -0.0328 , 0.0501 , 0.1533 (all ± 0.0006) (as compared with the values: 0.034 , 0.050 , 0.154 obtained by ZEMANN and ZEMANN).

The Si—O and Al—O distances obtained by GIBBS and SMITH are 1.635 Å and 1.886 Å, respectively. EULER and BRUCE found a value of 1.64 ± 0.02 and 1.90 ± 0.02 Å for these distances in a natural pyrope with formula $\{Mg_{1.6}Fe_{1.2}Ca_{0.2}\}[Al_2](Si_3)O_{12}$. Thus one is tempted to conclude (at present, more on intuition than on the basis of the calculated error limits) that in these silicate garnets, the Si—O distances are less affected by a change in the size of the divalent cation than are the Al—O distances. But if we compare PRANDL's result with that of GIBBS and SMITH on the Si—O distances in grossularite vs pyrope, 1.651 ± 0.005 vs 1.635 ± 0.006 Å, respectively, we see that there does appear to be some effect on the Si—O distance, which could be larger than the 0.005 Å proposed by GIBBS and SMITH¹⁵.

ZEMANN and ZEMANN¹⁸ had noticed anisotropy of the electron density about the Mg²⁺ ions and attributed this tentatively to statistical disorder of the arrangement of these ions about the special positions. However, these ions are in rather low symmetry positions, 222, and the results of GIBBS and SMITH show that the anisotropy of thermal vibrations of the Mg²⁺ ions accounts for the electron-density anisotropy observed by ZEMANN and ZEMANN.

¹⁹ L. COES, High pressure minerals. *J. Amer. Ceram. Soc.* **38** (1955) 298.

In a paper²⁰ on the crystal chemistry of the garnets, ZEMANN discusses the question of the distortion of the coordination polyhedra. ZEMANN shows that if regular octahedra and tetrahedra are assumed with reasonable distances, 1.90 or 1.95 Å for Al—O and 1.62 Å for Si—O, a very short O—O distance of 2.44 Å is obtained for an unshared edge of the distorted cube, i.e. about 0.31 Å shorter than its minimum probable value of 2.75 Å. I should point out, however, that it seems possible that a garnet could be made in which at least the octahedron could be very nearly regular. In synthetic pyrope, the six O—O distances in the plane perpendicular to the threefold axis are longer than the six others by 0.08 Å, while in grossularite the exact reverse is true (see Table 1 of ZEMANN's paper).

Rare-earth and yttrium garnets

Structural refinements based on single-crystal data have been made on a substantial number of rare-earth and yttrium aluminum, gallium and iron garnets. Most of these have been reported recently by EULER and BRUCE¹². As indicated earlier, the first was made on yttrium iron garnet by GELLER and GILLO⁹; BATT and POST¹¹ reported a refinement in 1962 and EULER and BRUCE¹² also worked on yttrium iron garnet. The structure of gadolinium iron garnet was refined by WEIDENBORNER²¹ and EULER and BRUCE¹² refined the structures of Lu, Yb, Y and Gd aluminum, Lu, Yb and Y gallium and Lu, Yb, Y, Dy and Sm iron garnets.

Our work and that of WEIDENBORNER were based on visually estimated intensities on Weissenberg photographs; the work of EULER and BRUCE and of BATT and POST was based on counter data. The last was based essentially on ten observational equations for refining the three positional parameters of the oxygen ion. That is, intensity ratios of reflections, with equal $h^2 + k^2 + l^2$, to which only oxygen ions contributed, were used, on the assumption that the oxygen thermal motions in the garnet are truly isotropic. This was hardly to be expected and as results of PRANDL¹⁶ and of GIBBS and SMITH¹⁵ show, they are anisotropic in the grossularite and in the synthetic pyrope. Further, although the discrepancy factor for the ten ratios is 7.7%, three of the ten have discrepancies of over 18%.

²⁰ J. ZEMANN, Zur Kristallchemie der Granate. *Beitr. Mineralogie und Petrographie* **8** (1962) 180–188.

²¹ J. WEIDENBORNER, Least squares refinement of the structure of gadolinium-iron garnet, $Gd_3Fe_2Fe_3O_{12}$. *Acta Crystallogr.* **14** (1961) 1051–1056.