Garnet structure refinements

For almost thirty years after the publication of MENZER's papers[1,2], no garnet structure refinement was made. However, the recognized potential importance of the iron garnets led us to carry out the structure refinement of yttrium iron garnet[9] as soon as a single crystal, grown by NIELSEN and DEARBORN[10], became available. Since then, at least two other refinements of the yttrium iron garnet structure have been made[11,12]. Some early work was done on powders by x-ray diffraction[3] and neutron diffraction[13] techniques by the French investigators.

MENZER's original paper[2] gave the mathematical details of the equipoint positions of the space group $Ia3d$ to which the garnet structure belongs. The cations are all in special positions with no positional degrees of freedom, while the oxygen atoms are in the general positions (see Table 1). It is possible to refine the oxygen parameters by choosing to measure those intensities to which only oxygen atoms contribute; these are hkl with two indices odd and the third divisible by 4 and $hk0$ with h, $(k) = 8n$ and (h), $k = 2m$ (n, m odd). There are others, e.g. $hk2$: 12, 4, 2 and 14, 6, 2; $hk4$: 12, 6, 4. There is also a large number of structure amplitudes which have

Table 1. *Description of garnet structure*

Point symmetry	222	$\bar{3}$	$\bar{4}$	$\bar{1}$
Space group position	$24c$	$16a$	$24d$	$96h$
Typical ideal formula	$\{Ca_3\}$	$[Al_2]$	(Si_3)	O_{12}
Coordination to oxygen	8	6	4	
Type polyhedron	Dodecahedron (distorted cube)	octahedron	tetrahedron	

[9] S. GELLER and M. A. GILLEO, Crystal structure and ferrimagnetism of yttrium iron garnet, $Y_3Fe_2(FeO_4)_3$. J. Physics Chem. Solids 3 (1957) 30—36. See also S. GELLER and M. A. GILLEO, The effect of dispersion corrections on the refinement of the yttrium-iron garnet structure. J. Physics Chem. Solids 9 (1959) 235—237.

[10] J. W. NIELSEN and E. F. DEARBORN, The growth of single crystals of magnetic garnets. J. Physics Chem. Solids 5 (1958) 202—207.

[11] A. BATT and B. POST, A procedure for parameter refinement in simple structures. Acta Crystallogr. 15 (1962) 1268—1270.

[12] F. EULER and J. A. BRUCE, Oxygen coordinates of compounds with garnet structure. Acta Crystallogr. 19 (1965) 971—978.

[13] F. BERTAUT, F. FORRAT, A. HERPIN et P. MÉRIEL, Étude par diffraction de neutrons die grenat ferrimagnétique $Y_3Fe_5O_{12}$. Compt. Rend. Acad. Sci. [Paris] 243 (1956) 898—901.

total cation contributions of the form $\pm 8(f_c^T - f_d^T) \sin\frac{1}{4}\pi h$, where f_c^T, f_d^T are the room temperature scattering factors of atoms in the c and d sites, respectively. The reflections involved have h, k, odd, $l = 2n$, n odd (h, k, l permutable).

I have mentioned the intensities which should be most sensitive to the oxygen parameters, as an aid to those who might wish to determine only the oxygen positions of garnets. I have already shown[14] that it is necessary to use a more nearly complete set of data if one wishes to obtain thermal parameters of all the ions involved.

Good drawings of the garnet structure may be found in References[2,15,16]. The greatest appreciation of the structure can be obtained from a three-dimensional model now purchasable from at least two different sources. A word description of the structure is given in Table 1.

Because of the importance to the magnetic properties and the crystal chemistry of the different coordination polyhedra in the garnet, Fig. 1 gives the surroundings of an oxygen ion in grossularite, the figure being taken from the Abrahams-Geller paper[17].

Silicate garnets

Since the first refinement of a garnet structure, that of yttrium iron garnet[9], there have been several others. Five refinements have been made of silicate garnets: a grossularite from Chihuahua, Mexico by ABRAHAMS and GELLER[17], synthetic pyropes by ZEMANN and ZEMANN[18], and by GIBBS and SMITH[15], a natural pyrope by EULER and BRUCE[12] and a grossularite from Xalostoc, Mexico by PRANDL[16]. The last is the most recent one reported; it was based on both x-ray and neutron data.

The results obtained by PRANDL[16] indicate that if there are any differences in positional parameters resulting from the neutron vs the

[14] S. GELLER, Parameter interaction in least squares structure refinement. Acta Crystallogr. 14 (1961) 1026—1035.

[15] G. V. GIBBS and J. V. SMITH, Refinement of the crystal structure of synthetic pyrope. Amer. Mineral. 50 (1965) 2023—2039.

[16] W. PRANDL, Verfeinerung der Kristallstruktur des Grossulars mit Neutronen- und Röntgenstrahlbeugung. Z. Kristallogr. 123 (1966) 81—116.

[17] S. C. ABRAHAMS and S. GELLER, Refinement of the structutre of a grossularite garnet. Acta Crystallogr. 11 (1958) 437—441.

[18] A. ZEMANN und J. ZEMANN, Verfeinerung der Kristallstruktur von synthetischem Pyrop, $Mg_3Al_2(SiO_4)_3$. Acta Crystallogr. 14 (1961) 835—837.