

which enter the garnet structure and their site preferences are given. Numerous examples of garnets and garnet systems that have been investigated are listed. Some are reported here for the first time.

The ionic site preference in the garnets is discussed; it appears that relative ionic size is of primary importance, but for certain ions like  $\text{Cr}^{3+}$  and  $\text{Mn}^{3+}$ , the electronic configuration also plays an important role. Considerable discussion is given to the  $\text{Co}^{2+}$  ion for which the evidence maintains that the  $\text{Co}^{2+}$  ion prefers, by far, the octahedral sites to the tetrahedral. Garnets have been prepared with  $\text{Co}^{3+}$  ion in the tetrahedral and in the octahedral sites. The determination of the distribution of ions in the system  $\text{Y}_3\text{Fe}_{5-x}\text{Ga}_x\text{O}_{12}$  by different techniques is reviewed.

### Introduction

Time has shown that the mineral world itself contains not only important materials but also clues to others which do not occur naturally. Sometimes these clues are quite subtle; in the garnet case, considerable time elapsed before they were recognized. While for many years the garnet structure, originally solved by MENZER<sup>1,2</sup>, has been important to the mineralogist, it has been important to the physicist for only a little over ten years. Its greatest importance to the physicist is in the existence of the ferrimagnetic garnets<sup>3,4</sup>, and the garnet structure first elucidated by MENZER played no small role in their discovery. The Néel theory<sup>5</sup> of ferrimagnetism must also be given tribute because it points to those crystal structures in which ferrimagnetism might exist.

The technological importance of the naturally occurring garnets has been limited to that of mild abrasives. An example is the garnet paper, obtained in a hardware store, used to smooth wood. Even this use is limited, because there are better abrasives for this application. Some silicate garnets are semi-precious and are used in jewelry. But the ferrimagnetic garnets have important technological uses in modern electronic devices. More recently neodymium doped yttrium aluminum and gallium garnets have been found to be good laser

<sup>1</sup> G. MENZER, Die Kristallstruktur von Granat. Centralbl. Min. [A] 1925. 344–345; Z. Kristallogr. 63 (1926) 157–158.

<sup>2</sup> G. MENZER, Die Kristallstruktur der Granate. Z. Kristallogr. 69 (1928) 300–396.

<sup>3</sup> F. BERTAUT et F. FORRAT, Structure des ferrites ferrimagnétiques des terres rare. Compt. Rend. Acad. Sci. [Paris] 243 (1956) 382–384.

<sup>4</sup> S. GELLER and M. A. GILLES, Structure and ferrimagnetism of yttrium and rare earth iron garnets. Acta Crystallogr. 10 (1957) 239.

<sup>5</sup> L. NÉEL, Propriétés magnétiques des ferrites; ferrimagnétisme et anti-ferromagnétisme, Annales Physique [Paris] 3 (1948) 137–198.

materials<sup>6</sup>. Thus the synthetic garnets have become a rich field for both scientific and technological exploration. The scientific literature of recent years abounds with papers on various studies of the garnets.

My own work in this field dates from the discovery of the ferrimagnetic garnets by GILLES and me<sup>4</sup> in the Bell Telephone Laboratories. (As indicated earlier, the discovery had also been made independently and in a different manner from ours by BERTAUT and FORRAT<sup>3</sup> at Grenoble.) Since the discovery, I have been directly interested in the static magnetic behavior and in the crystal chemistry of the garnets. As a result of intensive work in these fields with the collaboration of several colleagues, we have developed a model<sup>7</sup> which accounts well for the magnetic behavior of the substituted ferrimagnetic garnets. This model enables one to make certain predictions concerning the behavior of as yet unmade garnets and to determine ion distributions in substituted yttrium iron garnets from a knowledge of the 0°K moments.

This paper will give mainly a survey of the crystal chemistry of the garnets including a discussion of the garnet structure refinements that have been reported and of the site preferences of various ions in the garnets. References to the magnetic behavior of the garnets will be made mainly as elucidation to the site preference determinations. In a few instances some heretofore unreported work will be included.

I do not intend this to be an *exhaustive* review in which I set myself the task of discussing every paper of any relevance whatever to the subject. But I hope that I shall not have missed any which cause me to omit a point of importance. I should point out that only once before have I written a paper<sup>8</sup> which included a review of the overall crystal chemistry of the garnets; that paper was written about eight years ago.

<sup>6</sup> J. E. GEUSIC, H. M. MARCOS and L. G. VAN UITERT, Laser oscillations in Nd-doped yttrium aluminum, yttrium gallium and gadolinium garnets. Appl. Physics Letters 4 (1964) 182–184. See also T. H. MAIMAN, Laser applications. Physics Today 20 (1967) 24–28.

<sup>7</sup> S. GELLER, H. J. WILLIAMS, G. P. ESPINOSA and R. C. SHERWOOD, Importance of intrasublattice magnetic interactions and of substitutional ion type in the behavior of substituted yttrium iron garnets. Bell System Tech. Jour. 43 (1964) 565–623.

<sup>8</sup> S. GELLER, Magnetic interactions and distribution of ions in the garnets. J. Appl. Physics Suppl. 31 (1960) 30S–37S.