On the relationship between the β-W and garnet structures.

By S. Geller, *Bell Telephone Laboratories, Inc., Murray Hill, New Jersey, U.S.A,*

If one looks at the powder photograph of a compound, with the β-W type structure, say Nb_3Sn (Geller, Matthias & Goldstein, 1955), one is struck by its similarity to the powder photograph of a garnet. In fact, it is easily seen that the β-W structure may be derived from that of the garnet.

A typical garnet, grossularite, (see Menzer, 1928; Abrahams & Geller, 1958), with ideal formula $Ca_3Al_2Si_3O_{12}$, belongs to space group O_h^{10}–$Ia3d$ with Ca^{2+} ions in $24c$, Al^{3+} ions in $16a$, Si^{4+} ions in $24d$ and O^{2-} ions in $96h$. Consider this garnet stripped of the oxygen ions (Fig. 1). If we allow the c and d positions to become crystallographically equivalent, each octant of the unit cell becomes a β-W type unit of structure. This unit of structure for formula A_3B belongs to space group O_h^3–$Pm3n$ with A atoms in $6c$ and B atoms in $2a$.
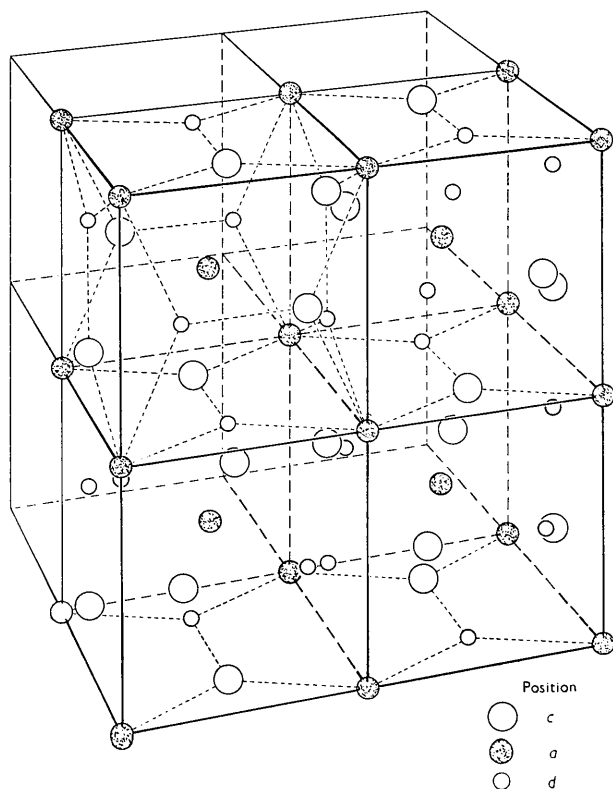

Fig. 1. The metal ions of the garnet structure. Only those in the four front octants are shown. Note that the arrangement of metal ions in each octant is similar to that of the metal atoms in the β-W structure. In the β-W structure, the c and d atoms are identical.

	Position
○	c
◉	a
○	d

There are at present no crystals with garnet structure which have atoms of the same species in the c and d positions. It is unlikely that such a crystal could be found because the d sites, tetrahedrally surrounded by h ions

are allowed least space for an ion, whereas the c cites dodecahedrally surrounded by h ions allow the most space for a metal ion. There are, however, ions which will occupy the dodecahedral and octahedral sites in the garnets but not the tetrahedral ones, and other ions which occupy the octahedral or tetrahedral sites but probably not the dodecahedral ones.

Thus the relationship of the β-W type A_3B structure to that of the garnet is a specialized one. The relationship, however, makes one wonder if there are not intermetallic compounds with formula $A_3B_2C_3$* having a structure related to that of the garnet. It is probable that the relationship would not be as close as that of the cubic $MgCu_2$ type phase (Friauf, 1927) to a normal spinel type, because there is an apparent constancy of the radii in the A–B interactions in the β-W type structure (Geller, 1956), a tendency which could lead to distortion of an $A_3B_2C_3$ 'garnet-like' structure if the A and C atoms were of different size. If they were of very nearly the same size, there might be a tendency, in favorable cases, to form a disordered β-W type structure.

It is now well known that the spinel and garnet structures are favorable to ferrimagnetism. It is interesting to note that the $MgCu_2$ structure has been shown to be favorable to superconductivity (Matthias & Corenzwit, 1957; Zhuravlev, Mingazin & Zhdanov, 1958; Zhuravlev, 1958; Matthias, Suhl & Corenzwit, 1958) and also to ferro- or ferrimagnetism (Matthias *et al.*, 1958; Nesbitt & Wernick, 1959). The β-W structure has been shown to be favorable to superconductivity, but thus far no compounds with this structure have been reported to be ferro- or ferrimagnetic. The relationship between the β-W and garnet structures may imply that under the right circumstances one might obtain ternary intermetallic compounds (or binaries of formula A_5C_3) with structures related to that of the garnet which are either superconducting or have a spontaneous magnetization at some temperature.

In the case of superconducting compounds, Matthias and co-workers have shown in a number of papers (see e.g. Matthias *et al.*, 1956) that the electron/atom ratio is of primary importance in determining the superconducting transition temperature of a compound. It has also been established that the optimum electron/atom ratio varies with the crystal structure type. Nevertheless, it may be worth investigating the possibilities of obtaining ternary compounds related to the garnet structure by choosing atoms A and C in $A_3B_2C_3$ such that they yield the same electron/atom ratio as the atom which they are replacing in the analogous β-W type compound. Undoubtedly atomic size will play an important role in structure formation and probably both atomic size and weight in the superconductivity property. Therefore, at the outset, atoms A and C should be chosen from the same period as the atom which they are replacing in the β-W type structure. For example, for Nb, take Mo and Zr or Sr and Ru or Rb and Rh. Thus analogous to the com-

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* Or A_5C_3 as a special case.

pound Nb_3Sn which has the highest known superconducting transition temperature (Matthias et al., 1954) one might try to make $Mo_3Sn_2Zr_3$ or $Sr_3Sn_2Ru_3$ or $Rb_3Sn_2Rh_3$.

The author wishes to thank H. J. Seubert for drawing Fig. 1.

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# The crystal structure of xanthophyllite.

By Y. TAKÉUCHI and R. SADANAGA, Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo, Tokyo, Japan

In spite of the numerous reports on the polymorphism in micas, little is known of the detailed structures of the individual members of this group of minerals. Since it is believed that the differences in configurations of the mica sheet are responsible for the generation of various polymorphs, the accurate analyses are desirable to elucidate the mutual relationship of the structures. The purpose of the present paper is, as a part of our research program of silicate sheet structures, to present the results of our study of xanthophyllite, the member of the simplest structure in the brittle mica group. The structure analysis of this mineral is of special advantage for the investigation of the general nature of structural change in the micas due to isomorphous replacement, because potassium atoms in the ordinary micas are fully replaced by smaller calcium atoms in the species under consideration.

The crystals used for the present X-ray analysis were from Chichibu mine, Japan. They are well developed and of pale green color. A chemical analysis made by H. Minato, gave the chemical formula as

$$Ca_{1\cdot 10}Mg_{2\cdot 18}Al_{0\cdot 72}(Al_{2\cdot 95}Si_{1\cdot 05})O_{10}(OH)_2 .$$
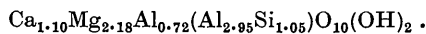
The cell dimensions were determined using precession photographs (Cu K, $\lambda = 1\cdot 5418$ Å) and they are listed in Table 1 together with those of other brittle micas. The

lattice constants of xanthophyllite give the axial ratio, $a:b:c = 0\cdot 577:1:1\cdot 082$. There are two formula units in the cell, giving the calculated density of $3\cdot 11$ g.cm.$^{-3}$ which compares well with the measured value of $3\cdot 06$ g.cm.$^{-3}$. By the missing rule of spectra and the test of piezo effect the most probable space group is shown to be $C2/m$. These data agree with those of the materials from other localities (Sanero, 1940; Forman, 1951) and suggest the single-layer mica structure. In the X-ray photographs, however, diffuse streaks are observed along the reciprocal lattice rows with $k \neq 3n$ in addition to sharp Laue–Bragg reflections, indicating the presence of mozaic blocks in which mistakes of layer stackings occur.

Intensity data were obtained by the multiple-film technique using Cu K radiation and absorption corrections for platy crystal habits (Takéuchi, 1958) were applied because it was not possible to obtain the specimens with ideal cross sections. Since, as shown in the above chemical formula, xanthophyllite contains Ca instead of K as in micas, it is expected that, if mica sheets are present in the structure, they are considerably deformed from hexagonal symmetry in such a way as to make cationic niches between the sheets shrunk. An approximate structure was derived by assuming such a deformed mica sheet and it was found to be correct in the electron-density projections

Table 1. Crystal data for xanthophyllite, margarite and seybertite

	a (Å)	b (Å)	c (Å)	β	$d_{(001)}$	Space group	Cell content		
Xanthophyllite (Chichibu)	5·19	9·00	9·74	100·1°	9·59 Å	$C2/m$	2 Ca	Mg_2 Al	$(Al_3Si) O_{10}(OH)_2$
Margarite* (Chester, Mass.)	5·13	8·89	19·40	99·5°	9·56 × 2	$C2/c$	4 Ca	Al_2	$(Al_2Si_2)O_{10}(OH)_2$
Seybertite† (Amity, N.Y. USNM 125425)	5·19	8·99	28·76		9·59 × 3	$P3_112$ or $P3_212$	6 Ca (Mg, Al, Fe)$_3$		$(Al,Si)_4O_{10}(OH)_2$

Accuracy: $\pm 0\cdot 01$ Å for lattice constants and $\pm 0\cdot 2°$ for β angles.

* Lattice constants for margarite from the same locality have also been given by Mauguin (1930).

† Orthohexagonal cell is given for comparison with others. Chemical formula of seybertite has not been exactly established but is close to that of xanthophyllite.