20.4-5  

**Cu₂GeS₃**: A MONOCLINIC MEMBER OF THE SPHALERITE GROUP.


Parthé (Cristallochimie des structures tétraédriques, Gordon and Breach, Paris 1972) has discussed the tetrahedral sulphides that have a sphalerite (cubic ZnS) structure. They occur in space groups from cubic (Fd̅₃m-ZnS) via tetragonal (I₄̅m-Cu₂FeSnS₄, I₄̅d-CuFeS₂ and I₄-Cu₂ZnSnS₄) to orthorhombic (Immm-Cu₂Si₂S₅ and Cu₂GeS₃). In fact we have found Cu₂GeS₃ to have lower symmetry (Cc) with a larger monoclinic cell (a=6.435, b=11.299, c=6.417Å, β=108.4°) having four formula units.

We have determined its structure and by use of the Bärnighausen tree (MATCH, 1980, 9, 139-175) have developed the group-subgroup relations between the different structures.

Lowering of the symmetry from a given space group to one of its subgroups will give rise to a so-called superstructure with its accompanying extra reflections in reciprocal space. The groups of reflections appearing for a particular symmetry reduction are especially sensitive to the higher from the symmetry. Thus consideration of the h+k+1=4n+2 reflexions of the sphalite structure indicated that the atoms are in the ionized state. In an analogous way, the superstructure reflections which appear when the symmetry is reduced from Immm to Cc allow the unambiguous choice of site for the germanium atoms.

20.4-6  

DETERMINATION OF DEFECT STRUCTURE IN r-MnO₂. by H. Yamada, M. Ohmasa, Institute of Materials science, University of Tsukuba, Japan

Recently we found that single crystals of pyroloxalite(U-MnO₂) from various localities distinct diffuse streaks along one of tetragonal a's on X-ray diffraction patterns and that an unknown phase giving the streaks coexists with the host U-MnO₂. This unknown phase was identified to be r-MnO₂ judging from the characteristics of the diffraction patterns. Since the structure consists of randomly alternating layers of ramsdellite and U-MnO₂, De Wolff (P.M. de Wolff, Acta Cryst., 1959, 12, 341-345) have studied the structure of r-MnO₂ with powder sample, and showed that the structure consists of randomly alternating layers of ramsdellite and U-MnO₂. Since his method is applicable only to the diffuse streaks close to ramsdellite and not to that similar to U-MnO₂, we have studied a new method to analyse both intensity distributions. Four specimens of natural pyroloxalite coexisting with f-MnO₂ were available for the present investigations. We employed the strong synchrotron radiation beam as X-ray source and a vertical four-circle diffractometer for measurements of the diffuse streaks. A profile of a streaks along a of U-MnO₂ showed with a solid line in Fig. 1. Since the diffuse streaks indicates characteristics of the diffraction from one dimensionally disordered crystals, we applied the matrix method reported by Kakinoki & Komura (J. Kakinoki & Y. Komura, Acta Cryst., 1965, 19, 137-147). The intensity of crystals with one dimensional disorder is expressed as

\[ I(,l,m,n) \propto \sum_{k} P(k) V \sum_{n} F(k,n) \times \delta(\alpha - a_{k,n}) \]

in case the thickness of the layers are equal, where N is the number of the layers in the crystal, \( Y \) a matrix formed with \( V \) the layer form factors of a-kind, \( P \) a matrix of \( \delta(a - a_{k,n}) \) the probability of finding \( a \) at q-th position, \( F \) a matrix of \( \sum_{n} V \sum_{n} F(k,n) \) the coordinate of the reciprocal lattice along \( \alpha \), and \( V \) the trace of the matrix. Twelve independent layers composed of single chains and a double chain of MnO₆ octahedra were derived in the present case to describe disordered structure. Three ideal structures with no disorder were introduced to reduce enormous number of combinations of the layers in \( F \). The first is composed of single chains of MnO₆ octahedra, the second is composed of double chains, and the third alternation of a single chain and a double chain. The combination of the layers in \( F \) matrix were determined to control the volume ratio of the ideal structures.

![Fig. 1 profile of a streaks along a of U-MnO₂](image_url)

Fig. 1. Profile of a streaks along a of U-MnO₂.