20.4-5 Cu_2GeS_3 : A MONOCLINIC MEMBER OF THE SPHALERITE GROUP.

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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 ($F\bar{4}3m$-ZnS) via tetragonal ($I\bar{4}2m$-Cu_2FeSnS_4, $I\bar{4}2d$-$CuFeS_2$ and $I\bar{4}$-Cu_2ZnSnS_4) to orthorhombic ($Imm2$-Cu_2SiS_3 and Cu_2GeS_3). In fact we have found Cu_2GeS_3 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 reflexions in reciprocal space. The groups of reflexions appearing for a particular symmetry reduction are especially sensitive to the deviations from the higher symmetry. Thus consideration of the h+k+l=4n+2 reflexions of the sphalerite structure which distinguish it from the $Fd\bar{3}m$ diamond structure indicated that the atoms are in the ionized state. In an analogous way, the superstructure reflexions which appear when the symmetry is reduced from Imm2 to Cc allow the unambiguous choice of site for the germanium atoms.

20.4-6 DETERMINATION OF DEFECT STRUCTURE IN γ-MnO_2. by N. Yamada, M. Ohmasa, Institute of Materials science, University of Tsukuba, Japan

Recently we found that single crystals of pyrolusite(ß-MnO_2) 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 ß-MnO_2. This unknown phase was identified to be γ-MnO_2 judging from the characteristics of the diffraction patterns. However, two kinds of intensity distribution of the streaks were recognized. One of them indicates maxima at positions close to the reciprocal lattice points of ramsdellite (a=0.4533, b=0.927, c=0.2866nm, Pbnm), and the other at positions close to those of ß-MnO_2 (a=0.4400, c=0.2866nm, $P4_2/mnm$). De Wolff(P.M. de Wolff, Acta Cryst., 1959, 12, 341-345) have studied the structure of γ-MnO_2 with powder sample, and showed that the structure consists of randomly alternating layers of ramsdellite and ß-MnO_2. Since his method is applicable only to the diffuse streaks close to ramsdellite and not to that similar to ß-MnO_2, we have studied a new method to analyze both intensity distributions. Four specimens of natural pyrolusite coexisting with γ-MnO_2 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 ß-MnO_2 shown 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

$$I = \sum_{m=-N+1}^{N-1} (N - |m|)\ \mathrm{tr}\,\mathbb{V}\mathbb{F}\mathbb{P}^m \exp(-2\pi i m\zeta)$$

in case the thickness of the layers are equal, where N is the number of the layers in the crystal, V a matrix formed with Vs the layer form factors of s-kind, F a matrix of fs the probability of finding Vs at q-th position, P a matrix of Pst the probability of finding Vt after Vs, ζ the coordinate of the reciprocal lattice along a^*, and tr the trace of the matrix. Twelve independent layers composed of single chains and a double chain of MnO_8 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 P matrix. The first is composed of single chains of MnO_8 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 p matrix were determined to controle the volume ratio of the ideal structures. A result of evaluation is shown with a broken line in Fig. 1. The ratios of the single chains and the double chains in the four specimens were determined to be 1:1, 4:1, 5:6 and 8:3 respectively.

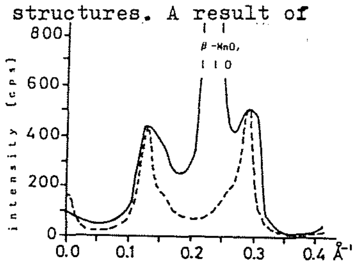

Fig. 1 A profile of a streaks along a^* of β-MnO_2