## COMPARISON OF THE CRYSTAL STRUCTURES OF BINNITE, $Cu_{12}As_4S_{13}$, AND TETRAHEDRITE, $Cu_{12}Sb_4S_{13}$

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Tetrahedrite and binnite are isostructural and have a curious superstructure based on a distorted sphalerite-like arrangement of atoms. The structure was proposed by Pauling and Neuman in 1934 on the basis of a limited number of reflections. The two structures have been refined to confirm this arrangement, to compare the nature of the distortions in the As and Sb phases, and to compare the results of refinement of photographically recorded data with those obtained by counter techniques.

Tetrahedrite has been refined to $R=3.9\%$ using counter data. The structure contains two sorts of Cu atoms. A first type is coordinated by four S atoms at 2.342 Å which form a nearly regular tetrahedron. A second type of Cu is in triangular coordination, being bonded only to one S atom at 2.234 Å and two at 2.272 Å. This group is planar and the Cu atom has a highly anisotropic thermal motion. The Sb atom is bonded to three S at 2.446 Å which form bond angles of 95°8′ and is also in van der Waals contact with six second-nearest S neighbors. The absolute configuration of the structure was established.

Binnite has been refined to $R=7.2\%$ using photographic data. Corresponding bond lengths in the coordination polyhedra are 2.337 Å for the tetrahedrally coordinated Cu, 2.204 and 2.258 Å for the triangularly coordinated Cu, and 2.246 Å and 98°22′ for the bond length and bond angle in the $AsS_3$ pyramid. The As atom is not in van der Waals contact with its second-nearest S neighbors. Some Sb had substituted for As in the binnite studied. The occupancy of this site was also refined, and a value in excellent agreement with a chemical analysis was obtained.

The nature of the distortion of the $CuS_4$ tetrahedron differs in the two structures. This may be explained in terms of a slightly different mode of S packing. It is found that the results of the two refinements were quite comparable. With the photographic data, however, a larger fraction of the diffracted intensities are unobservable, and the standard deviations of the parameters of the structure, the bond lengths, and the bond angles are roughly 50% higher.

## THE CRYSTAL STRUCTURE OF COPPER(II) SULFATE TRIHYDRATE

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Crystals of $CuSO_4 \cdot 3H_2O$ (bonattite) are monoclinic, space group *Cc*, with $a=5.59$, $b=13.03$, $c=7.34$ Å, $\beta=97.1°$, $Z=4$, $D_x=2.68$ g. cm$^{-3}$. Three dimensional data were collected on a Buerger precession camera with Mo-$K\alpha$ radiation. The structure was solved from a three dimensional Patterson synthesis and refined by least squares techniques to $R=0.069$ for 936 $F_{hkl}$ with $\sin\theta/\lambda<0.8$ Å$^{-1}$. The coordination polyhedra around the $Cu^{2+}$ ions do not share any edges or corners with each other; they are connected by hydrogen bonds and via linking sulfate groups. The square planar coordination around the copper ion consists of three water oxygen atoms and one sulfate oxygen atom at an average distance of 1.96 Å. Two more sulfate oxygen atoms at 2.39 and 2.45 Å complete the distorted octahedral coordination. The average S-O bond length in the sulfate tetrahedron is 1.472 Å. Each water oxygen atom forms two hydrogen bonds. One of the sulfate oxygen atoms accepts two hydrogen bonds: it is the only oxygen atom in the structure which does not belong to the octahedral coordination around the copper ion. The average hydrogen bond length is 2.74 Å. The study was aided by a grant from the Office of Saline Water.