radiation in all the so called "window" regions. Part of this may be instrumental and, of course, some of it is due to the long atmospheric path, which affects the window regions considerably though it has little effect on the strong absorption regions.

It is interesting to note that the black radiation at about -40° C was observed for the arctic regions from Explorer VII (4; 5).

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Confirmation of the Crystal Structure of Tetrahedrite, Cu_{1.2}Sb₄S₁₃

Abstract. The crystal structure of tetrahedrite, proposed in 1934 by Pauling and Neuman, has been confirmed. Least-squares refinement reduced the initial disagreement factor from 27.9 to 4.9 percent. Antimony displays three short orthogonal bonds to sulfur atoms. Two types of copper are tetrahedrally and triangularly coordinated by sulfur, respectively.

Tetrahedrite is a common mineral of a family of sulfosalts with general composition $X_{12}Y_4S_{13}$. A complete series of solid solutions exists between Y = Sb(tetrahedrite) and Y = As (tennantite). The metal atom X is mainly Cu, but usually Zn, Fe, Ag, Hg, Pb, Ni, or Co are present in amounts up to 20 percent.

The general nature of the tetrahedrite structure was determined by Machatschki (1). A more detailed determination of the structure was later given by Pauling and Neuman (2). The atomic arrangement which was pro-

posed was a curious derivative structure based on the sphalerite (ZnS) arrangement. The Pauling and Neuman investigation, however, was made at a time when many of the modern methods of structure determination had yet to be developed. The arrangement was guessed from a large number of possibilities which were permitted by the probable space group of tetrahedrite. The structure was based on only 18 measured intensities of which seven were not detectable. Furthermore, the seven unobservable intensities accounted for two-thirds of the superstructure reflections which were studied. It is the superstructure reflections which are primarily influenced by the departures from an ideal sphalerite-like arrangement. Accordingly, it was felt that the Pauling and Neuman structure might possibly prove to be incorrect, or at any rate, require major parameter adjustments upon refinement.

The material selected for a reinvestigation of the structure was naturally occurring tetrahedrite from Horhausen, Westerwald, Germany. The composition of this material is unusual in that Y is almost entirely Sb, and X is primarily Cu (3). Preliminary x-ray examination confirmed I43m as the probable space group. The lattice constant, obtained by a precision back-reflection Weissenberg technique, was found to be $10.3908 \pm .0006$ Å. A suitable specimen was ground into a spherical shape for the collection of diffracted intensities. An equi-inclination diffractometer, equipped with a proportional counter, was used. Of 154 independent reflections contained within the $CuK\alpha$ sphere, 136 were accessible with the instrument used. Only 2 of these reflections were undetectable. The observed intensities were reduced to a set of structure factors by application of suitable corrections for absorption and for Lorentz and polarization factors.

The disagreement index,

$R = \Sigma ||F_{\text{obs}}| - |F_{\text{cal}}|| / \Sigma |F_{\text{obs}}|,$

for the arrangement proposed by Pauling and Neuman proved to be 27.9 percent. This value was low enough to suggest that the structure was correct. Several cycles of least-squares refinement reduced R to 9.0 percent when isotropic temperature factors were used to represent the thermal motion of the atoms, and to 4.9 percent when anisotropic temperature factors and anomalous scattering corrections were em-



Fig. 1. Arrangement of polyhedrons formed by metal atoms coordinated about the sulfur atoms in tetrahedrite. The Sb locations are represented by small circles; all other vertexes of the polyhedrons represent Cu sites.

ployed (4). The low value obtained for the disagreement index confirms the correctness of the Pauling and Neuman structure. The improved values obtained for the atomic coordinates, however, permit a more detailed interpretation of the structure.

An asymmetric unit of the structure contains five atoms. Antimony is located in the set of equivalent positions 8 c with coordinates xxx, and so forth, with $x = 0.2682 \pm 0.0002$. There are two types of Cu atoms: Cu(1) is in 12 d with symmetry-fixed coordinates $\frac{1}{2}0$, and so forth; Cu(2) is in 12 e, x00, and so on; $x = 0.212(7) \pm 0.0008$. There are also two types of S atoms: S(1) is in 24 g, xxz, and so forth, with $x = 0.115(3) \pm 0.0007$, $z = 0.360(3) \pm 0.0009$; S(2) is in 2 a, 000.

The structure, and its relationship to sphalerite, is most readily visualized by considering the arrangement of the polyhedrons formed by the metal atoms about sulfur. The S(2) is coordinated by 6 Cu(2) which together form a regular octahedron. The S(1) is coordinated by 1 Sb, 1 Cu(2), and 2 Cu(1). These metal atoms form a distorted tetrahedron; the bond angles range from 117°15' to 101°1' as opposed to the bond angles of 109°28' which would exist for a regular tetrahedron. The manner in which these polyhedrons are linked is shown in Fig. 1. One quarter of a cell is shown. The Sb locations have been indicated by small circles; all other vertexes of the polyhedrons represent Cu locations. Each vertex of a S(2)-Cu(2) octahedron is shared by two tetrahedrons. The remaining vertexes of the tetrahedrons are linked in a sphalerite-like fashion to a second set of tetrahedrons. The second set of tetrahedrons, in turn, share vertexes with other octahedrons. Inspection of Fig. 1 shows that the structure differs from a sphalerite arrangement in that (i) three of the four sulfur atoms which would be given by an equipoint with coordinates $\frac{1}{8}$ $\frac{1}{8}$ are absent, while the fourth has been displaced to 000, and (ii) Sb is substituted for those Cu atoms which lie closest to the octahedral arrangement.

While consideration of the metal polyhedrons facilitates visualization of the structure, the reasons for this curious arrangement become more apparent when the coordination of sulfur about the metal atoms is considered. The Cu(1) is coordinated by four S(1) at distances of 2.343 Å. The bond angles for this tetrahedron are all 110°47', which represents only a slight distortion from a regular tetrahedron. The Cu(2) is coordinated by two S(1) at 2.292 Å and one S(2) at 2.210 Å. This group of four atoms lies in a symmetry plane and is therefore planar. This coordination has been found in other copper sulfides such as CuS (5), Cu₂S (6), and CuAgS (7). Triangular coordination for a B-subgroup metal is very unusual and, for inorganic compounds, appears to be unique to copper sulfides. Three S(1)atoms are coordinated to Sb at distances of 2.436 Å. The bond angles, S(1) to Sb to S(1), are 90°32'. This polyhedron represents a trigonal pyramid with Sb at its apex.

The metal polyhedrons are linked in a complex fashion. Six CuS₃ triangles share a corner at 000, and form a sixbladed "spinner." Since the triangles lie in the (110) symmetry planes of the cell, the corners of three different triangles are in close proximity. The base of a SbS₃ pyramid links these three corners. In addition to the vertex of the SbS₃ pyramid, each corner of a triangle is further shared by vertexes from two different CuS₄ tetrahedrons. Each corner of a tetrahedron links four different spinners in this fashion.

The coordination of S about Sb gives the key to the reason for the formation of the structure. The structures of several other sulfosalts containing Sb have been determined. The coordination of S about Sb in these structures is similar to that found in the present study, except that the bond distances are not equal. The Sb atom in these structures displays a minimum distance of 2.4 Å 30 AUGUST 1963

to only one closest neighboring S. The three short bond distances and the orthogonal disposition of these bonds in tetrahedrite suggests a very strong bond involving the p^{3} electrons of Sb. The failure of a fourth S atom to coordinate with Sb accounts for the S atoms which are missing from a completed sphalerite-like arrangement. The nature of the Sb to S bond also explains why the tetrahedrite structure is not merely a derivative structure of sphalerite in which the different metal atoms substitute in an ordered fashion (for example, chalcopyrite, $CuFeS_2$). It is misleading to describe the structure of tetrahedrite in terms of Sb atom substitution for a tetrahedrally coordinated Cu. The SbS₃ group is really a different sort of coordination polyhedron (8).

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Photochemical Generation of the Hydrated Electron

Abstract. A transient species with properties similar to the hydrated electron produced previously by electron irradiation has been observed by flash photolysis of aqueous solutions of inorganic salts and aromatic compounds including amino acids.

Hart and Boag (1) have identified with the hydrated electron an optical absorption produced by irradiating deaerated water and aqueous solutions with electron pulses of 1.8 Mev. A species with similar properties has been obtained by ultraviolet-light flash photolysis of compounds showing "electrontransfer" spectra. The irradiations were performed in a 26-cm long fused-silica cell on solutions evacuated to 1×10^{-5} mm-Hg. The light source was of 40 µsec



Fig. 1. Transient spectra from the flash photolysis of air-free 0.0005M potassium iodide at pH 7. The band at 390 m μ is due to the diiodide ion; the shorter-lived red absorption bands are due to the hydrated electron.

duration from a 700 joule capacitor discharge. The spectra were taken with a 10-µsec xenon spectroflash lamp on a Hilger E 498 (medium) quartzprism spectrograph and Kodak I-N plates.

Figure 1 shows transient spectra from aqueous 0.0005M KI. The band at 390 m μ is due to diiodide ion (I₂⁻), which was investigated by Grossweiner and Matheson (2, 3). The shorter-lived bands at 625, 700, and 790 m_{μ} have a spectrum and lifetime that agree with the hydrated-electron absorption reported by Hart and Boag (1). These shorter-lived bands are not observed for air-saturated KI solutions, although the \mathbf{I}_{2}^{-} absorption is enhanced in that case. On the assumption that each I_2^- present immediately after the flash corresponds to one hydrated electron, and by using the reported value of the I2 molar absorbance (3), the hydrated-electron molar absorbance is estimated to be 15,000 \pm 30 percent at 695 m μ . Strong hydrated-electron spectra were observed by flash photolysis of air-free, aqueous solutions of 0.05M Na₈PO₄, 0.1M Na₂CO₃, and 0.07M Ca(OH)₂. Associated radical products were not detected in these cases. A very weak absorption was found for air-free, doubly-distilled water, presumably due to residual salts.

The same hydrated-electron spectrum was obtained from air-free, aqueous solutions of aromatic compounds buffered at pH 11.8 with Na₃PO₄. Figure 2 shows transient spectra from 0.05M p-cresol irradiated through a filter of 0.20M Na₃PO₄, so that light absorption by the buffer was negligible. The narrow bands at 388 and 405 m_{μ} identify the phenoxyl radicals, as reported from the flash photolysis of phenol, phenolate ion, and their de-