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Crystal Structure of Umangite, Cu_3Se_2

In the study of the phase relations of the copper-selenium system, single crystals of the composition Cu_3Se_2 have been synthesized. This compound, known as mineral umangite, is the only phase in the Cu-Se system for which the structure has not been elucidated. The structure determination has been carried out with the synthetic material.

A mixture of copper and selenium in the ratio 2.9 to 2.0 was enclosed in an evacuated silica tube and kept at 500°C for 2 days. The product was ground to fine powder, resealed in a new evacuated silica tube, kept first at 500°C for a week and then at 80°C for a month. After the run, the final product was covered with small crystals of Cu_3Se_2. The inner part of the product was, however, found to be an assemblage of crystals of two other phases, $Cu_{1.8}Se$ and CuSe.

The precession and Weissenberg methods were used to study the synthetic Cu_3Se_2 single crystals. The symmetry is tetragonal, with diffraction aspect P-2_1-, giving the possible space groups $P\bar{4}2_1m$ and $P42_12$. The cell dimensions obtained by the x-ray diffraction powder method are: $a = 6.406 \pm 0.002$ Å and $c = 4.279 \pm 0.002$ Å. With a cell content of Cu_6Se_4, the density is calculated as 6.590—in good agreement with the measured values 6.44 to 6.49 for the artificial compound (*1*).

The crystallographic data given by Berry and Thompson (*2*) are as follows: $a = 6.402$ Å and $c = 4.276$ Å, with space group $P4/mmm$. In order to elucidate the conflict between the diffraction aspects of the synthetic and natural materials, single crystals of umangite, Sierra de Umango, Argentina (*3*), were studied. The diffraction aspect of the natural specimens is P-2_1- as in the case of the synthetic crystals.

The intensities were measured visually on the Weissenberg films for the synthetic crystals. They were corrected for Lorentz and polarization factors. No absorption correction was made. Interpretations of the Patterson projections on (001) and (100) gave a structure uniquely based on the space group $P\bar{4}2_1m$. The atomic parameters obtained by the two-dimensional difference Fourier method are as follows: 2 Cu(I) in equipoint a at 0,0,0; 4 Cu(II) in equipoint e at x, $\frac{1}{2} - x$, z, with $x = 0.147$ and $z = 0.750$; 4 Se in e at x, $\frac{1}{2} - x$, z, with $x = 0.275$ and $z = 0.250$. The R-factors are 0.12 and 0.13 for ($hk0$) and ($h0l$), respectively.

The structure is projected on (001) and on (100) in Fig. 1, A and B, respectively. In this structure, as in typically intermetallic compounds, Cu atoms are as closely bonded with one another as with Se atoms. On the basis of the distribution of these bonds, the structure is considered to consist of sheets extending parallel to (001). All the Cu—Cu bonds are included inside the sheets, and their bond distances of 2.63 or 2.66 Å are slightly longer than the atomic distance found in metal copper 2.56 Å. Each Cu(I) is surrounded by four Se at 2.49 Å and four Cu(II) at 2.63 Å; and each Cu(II) by four Se at 2.43 and 2.37 Å, and by two Cu(I) at 2.63 Å and by one Cu(II) at 2.66 Å. Each Se is surrounded by two Cu(I) at 2.49 Å and by four Cu(II) at 2.43 and 2.37 Å.

Preliminary experiments on the electric properties of this synthetic Cu_3Se_2 indicate that the conductivity decreases with increasing temperature. The mechanism of conduction is, therefore, metallic.

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3. We thank Professor L. G. Berry of Queen's University for this specimen and for information on his studies of umangite. We also thank R. Kiriyama, Osaka University, for discussion and encouragement.

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Infrared Spectra from Fine Particulate Surfaces

Abstract. *Characteristic spectral information can be obtained from a surface composed of fine particles either if the spectrum is observed at sufficiently high signal-to-noise ratio or if the particles are well compacted.*

Recent publications (*1*) concerning spectral reflectance or emittance by particulate surfaces have indicated that the surface tends to appear black when the particle size is small compared with the wavelength. Thus it is generally concluded that little or no characteristic spectral information can be gained by remote sensing of lunar or planetary surfaces if the surfaces are composed of fine particles. We now show both theoretically and experimentally that most of the spectral information is not really lost under these circumstances if one observes the spectrum at sufficiently high signal-to-noise ratio or if the surface is well compacted.

We consider first the case of a semi-infinite medium having a smooth surface and composed of uniformly distributed particles of diameter and spacing much less than a wavelength. Under these conditions the reflection by the medium of a beam of radiation is predominantly a coherent surface effect caused by the discontinuity at the surface of the average values of the optical

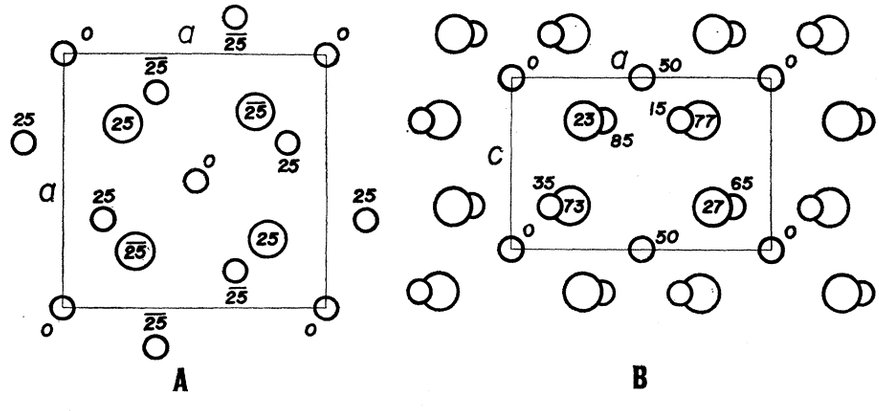

Fig. 1. (A and B) The structure of Cu_3Se_2 projected on (001) and (100), respectively. Large circles represent Se atoms and small circles Cu atoms. Numbers give z-parameters in A, and x-parameters in B.