

native to the area. In that case it would be a relic, isolated from the main area of distribution of *L. littorea*, possibly by the worsening of the climate about 2500 years ago. In Spitzbergen this species existed during the climatic optimum, but now it is no longer found there (see 3). In Greenland, however, *L. littorea* is not known from the warm period; in its place other species of *Littorina* are found (see 4).

This makes it likely that *L. littorea* was introduced to North America by man. The fact that the Norse settlers came from Greenland, where the species is not found at present, does not contradict this. The limiting factor for the species in Greenland is probably the winter conditions, and ships arriving in the spring and summer from Norway or Iceland with living *Littorina* specimens on board might easily have carried them to North America the same summer.

There are historical records of Icelandic ships used in the trips from Greenland to North America, and it should also be noted that the shorelines at the Norse settlements in Greenland were submerged after A.D. 1000, so that subfossil specimens of *L. littorea* are not likely to be found at the present shores of Greenland.

The fact that this species presumably was introduced to New England from Nova Scotia by man, and the strong possibility that the fossil specimens were introduced from Europe by man also, indicate that it might be a "guide fossil" for naval exploration and settlements along the eastern coast of North America.

The reason that it was not introduced also into New England by the Norsemen was probably that they mainly visited the northern localities on Newfoundland and Nova Scotia.

It is likely that New England also was visited by the Norse settlers, but probably only by small parties on brief reconnaissance tours. The larger groups of settlers probably did not penetrate that far south. The largest group recorded, which went to North America, consisted of three ships with 160 persons and cattle. It stayed for 3 years.

Most of the Norse settlements were probably of the same type as that found by Ingstad at Lance aux Meadows. This consisted of rather large houses, and evidence is found of iron production from bog iron ore. Studies now under way will show whether these settlements were permanent ones, or whether they were visited intermittently for collecting timber and firewood, and to make charcoal and produce iron, all for the main settlements in Greenland (5).

NILS SPJELDNAES

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5. We are deeply indebted to Helge Ingstad for permission to publish some preliminary results from his expeditions. The material from these expeditions is now under study by various specialists.

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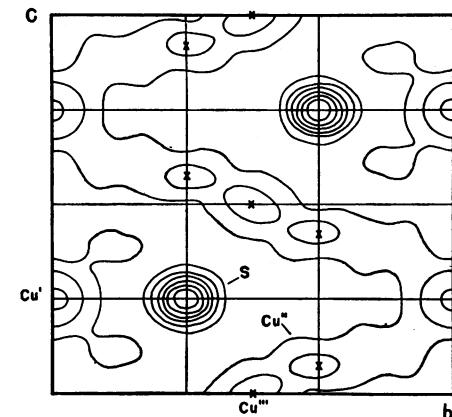


Fig. 1. Electron density section  $\rho(0xy)$  through the orthohexagonal cell for high chalcocite.

already discarded. Ueda (4) also found that no simple arrangement of copper atoms provided agreement of computed and observed intensities, and he concluded that the copper atoms were in complete disorder, a conclusion already noted by M. J. Buerger (5). The disorder was apparent also from the investigations of Jensen (6), who studied the diffusion of Cu in chalcocite; he observed that the diffusion rate increased rapidly in low chalcocite as the temperature approached the transformation temperature, and was much higher throughout the high-chalcocite range. Furthermore, the activation energy for diffusion was about 0.15 ev, an extremely low value compared to the 1 to 2 ev usually found for metal-atom diffusion in close-packed compounds.

The difficulty in finding a structure for high chalcocite has been due to its probably disordered structure, so that the four copper atoms per cell could not be placed merely on a four-fold or two, two-fold equipoints. To find the distribution of disordered copper atoms would require unorthodox methods.

For the present structure investigation we required accurate x-ray diffraction intensities. To allow for absorption we wanted to have a spherical sample and attempted to grind a sphere from the chalcocite obtained from Bristol, Connecticut. We succeeded in obtaining an ellipsoid, but developed a method of allowing exactly for its absorption. The sample was oriented with a precession camera. When oriented, it was maintained at 125°C with a heating attachment, and the full set of three-dimensional reflections were recorded on an integrating cassette on the precession camera. The intensities of these reflections, corrected for Lorentz, polarization, and transmission factors, permit-

## Distribution of Atoms in High Chalcocite, $\text{Cu}_2\text{S}$

**Abstract.** In spite of its simple composition, the structure of chalcocite,  $\text{Cu}_2\text{S}$ , has long defied analysis. In high chalcocite the sulfur atoms are in hexagonal close-packing, while three varieties of copper atoms, with four-fold, three-fold, and two-fold coordinations respectively, are in disorder in the interstices.

The investigation by Buerger (1) of the phase diagram of  $\text{Cu}_2\text{S}$ - $\text{CuS}$  established the general relations between low chalcocite and high chalcocite. The two phases are related by a rapid transformation at about 105°C which appeared to be of the order-disorder variety. In a later investigation (2) of the unit cells and space groups of low and high chalcocite the suspected substructure relationship was confirmed.

The high symmetry of high chalcocite

( $P6_3/mmc$ ) and its small hexagonal cell ( $a = 3.89 \text{ \AA}$ ,  $c = 6.88 \text{ \AA}$ , with 2  $\text{Cu}_2\text{S}$  per cell) made it appear a simple matter to find its structure. Many years ago two attempts were made in this laboratory to do this, but neither succeeded in finding, by straightforward methods, an arrangement of atoms which explained the intensities. Belov and Butuzov (3) presented a structure, but this was certainly wrong since it was one of the ones we had

ted computation of a three-dimensional Patterson function,  $P(uvw)$ .

We prepared the vector maps to be expected for all permissible equipoint combinations for four copper and two sulfur atoms in  $P6_3/mmc$  and other space groups permitted by the diffraction symbol. None matched the actual Patterson function of high chalcocite, which confirmed that routine distribution of atoms over the equipoints would not lead to a solution.

The Patterson function did, however, have a set of major peaks which could be explained by a set of atoms in close packing. We had supposed that the S atoms would be in close packing with the Cu atoms in disorder in their interstices. We therefore computed structure-factor signs based upon the supposition that these peaks were due to S atoms, and computed a trial electron density,  $\rho(xyz)$  based upon these signs. This led to a map on whose interpretation and improvement we spent a great deal of time.

The key to its interpretation was finally provided by implication maps  $I_e(x y \frac{1}{2})$  and  $I_s(x y 0)$ , based upon the Harker sections  $P(x y \frac{1}{2})$  and  $P(x y 0)$ , respectively. The projection  $\rho(x y)$  of the electron density had to be consistent with these implication maps, and this permitted us to retain only those possible Cu positions which so fitted the implication. The model we accepted had S in  $2 c$  at  $\frac{1}{3} \frac{2}{3} \frac{1}{2}$  and the copper split into three parts: Cu' in  $2 b$  at  $0 0 \frac{1}{2}$ , Cu'' in  $4 f$  at  $\frac{1}{3} \frac{2}{3} 0.578$ , and Cu''' in  $6 g$  at  $0 \frac{1}{2} 0$ .

We refined the resulting structure by least-squares methods, first using isotropic temperature factors; this produced a fair agreement between observed and calculated intensities, but we could not reduce the disagreement factor  $R$  below 31 percent for isotropic temperature factors (7). A serious difficulty was the strong interaction between the amount of Cu in each of the three sites, and the temperature factors. Section  $\rho(0 y z)$  through the Fourier synthesis of our structure, referred to an orthohexagonal cell, is shown in Fig. 1. This section contains all the atoms described.

All structure-factor signs converged during the final adjustments of the disordered copper-atom weights. Electron-density syntheses based on these signs showed that appreciable smears of electron density extended between the three types of Cu sites. The Cu atoms are evidently mobile, and it was clear that, even when anisotropic temperature fac-

tors were used, placement of discrete atoms in these sites could merely represent an approximation to the true copper distribution. It remained, therefore, to demonstrate conclusively the correctness of the structure by further improvement of the agreement between the observed and calculated structure factors.

To take into account adequately the continuous nature of the copper distribution, the unit cell was partitioned into volume elements which were represented by a grid whose unit cell is given by the sublattice

$$\begin{aligned} \mathbf{x}_1 &= \frac{1}{30} (\mathbf{a}_1 + \mathbf{a}_2) \\ \mathbf{x}_2 &= \frac{1}{30} (-\mathbf{a}_1 + \mathbf{a}_2) \\ \mathbf{x}_3 &= \frac{1}{30} \mathbf{c} \end{aligned}$$

The scattering power of a volume element  $\Delta V$  located at  $x_1 x_2 x_3$  is the fraction of an electron which the Fourier synthesis shows to be contained in that volume element. This is  $w = \rho(xyz)\Delta V$ . The amplitude scattered by reflection  $hkl$  is therefore

$$F_{hkl} = \sum_{x_1 x_2 x_3} \sum_{x_1 x_2 x_3} w_{x_1 x_2 x_3} \cos 2\pi (hx_1 + kx_2 + lx_3).$$

Of the 688 volume elements contained in the asymmetric unit, 350 contained nonzero electron density. Structure-factor calculations based on this distribution of electrons were followed by difference syntheses. Slight reapportionment of the electron-density distribution was made on the basis of these maps. The final electron-density distribution yielded a disagreement factor of 21.5 percent for all data, and a value of 18.0 percent when the unobserved reflections were excluded.

This confirms the correctness of the structure of high chalcocite which we had derived (7). While the distribution of Cu atoms is best judged from the map in Fig. 1, it can be said that the four copper atoms are distributed over the sites of  $2 b$ ,  $4 f$ , and  $6 g$  in approximately the ratio 1.24:1.63:1.13. These Cu atoms are respectively in three-fold, four-fold, and two-fold coordination. It is apparent that in the high-temperature form of chalcocite the sulfur atoms comprise a substantially fixed structure, with sulfur atoms in hexagonal close packing, while the copper atoms are mobile through the interstices of this structure. The mobility is possible because the copper atoms can assume tetrahedral, trigonal, and linear coordination. In the low-temperature form,

the thermal energy is not sufficient to maintain mobility and the structure is doubtless characterized by sulfur atoms in hexagonal close-packed array with copper atoms in at least two of the three coordinations observed in the high-temperature form. The alternation of copper in different coordinations accounts for the large superstructure cell observed for the high-temperature form (3). We have a set of three-dimensional diffraction intensities for low chalcocite, and have computed its Patterson function and the Patterson of the substructure. The latter maps indicate that the tetrahedral and trigonal sites are occupied in low chalcocite. Work on the structure of low chalcocite is continuing (7; 8).

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8. Supported by the National Science Foundation. Computations were performed on the I.B.M. 7090 computer at the M.I.T. Computation Center.

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#### Melatonin, a Pineal Substance: Effect on the Rat Ovary

**Abstract.** Daily injection of microgram amounts of melatonin in rats decreased the incidence of estrus and reduced ovarian weight. Circulating melatonin was selectively taken up and retained by the ovary and pineal gland; this effect was reduced by exposure of rats to constant light. A single injection of melatonin lowered the incidence of estrus among rats exposed to constant light.

Many observations have linked the mammalian pineal gland to gonad function. Human males with tumors which destroy the pineal gland have a high incidence of precocious puberty (1). Pinealectomy has resulted in an increase in ovarian weight (2), while pineal extracts decreased ovarian weight and