Such material occurs as secondary nests in some bauxite deposits, and it forms in an acid environment. When the overburden is eroded from pyrite-bearing bauxite deposits, strong oxidation of this iron sulfide mineral takes place and sulfuric acid is formed. This acid dissolves most of the iron minerals and in some places even part of the alumina minerals. As the downward-percolating solution is neutralized several meters below, Al(OH)₃ gel precipitates and forms white nests within the lower part of the deposit. Bárdossy (12) found such nests 2 to 5 cm in diameter below oxidized pyritebearing bauxites in mines at Szoc and Nyirád, Hungary. They contained 10 to 60 percent amorphous Al(OH)₃ gel together with poorly crystallized gibbsite. Similar precipitations occur at the contact of the footwall limestone or dolomite at Sümeg and Cserszegtomaj, Hungary. The amorphous material forms nests in the precipitated gibbsitic layer 2 to 10 cm thick; here the neutralizing effect of the carbonate rocks is quite obvious.

There are no reported minerals which exhibit infrared spectra identical to that of carbonate-containing $Al(OH)_3$ gel. However, Duffin and Goodyear (13) have reported data for scarbröite, a crystalline aluminum hydroxy carbonate with a formula $Al_2(CO_3)_3 \cdot 12Al(OH)_3$. Nemecz and Varju (14) found scarbröite occurring in small nests at the contact of the footwall dolomite in the deposit of clavev bauxite at Pilisvörsösvar. Hungary. Serna et al. (15) have reported that the infrared spectrum of scarbröite is similar to that of carbonate-containing Al(OH)₃ gel. They suggested that the difference between carbonate-containing Al(OH)₃ gel and scarbröite is particle size along with very slight differences in ordering, and noted that scarbröite had been found associated with gibbsite, the final crystalline form in the aging of $Al(OH)_3$ gel.

G. Bárdossy Hungarian Aluminium Corporation, Budapest, Hungary

JOE L. WHITE Department of Agronomy, Purdue University, West Lafayette, Indiana

References and Notes

- P. H. Hsu, Soil Sci. Soc. Am. Proc. 30, 173 (1966); G. J. Ross and R. C. Turner, *ibid.* 35, 389 (1971); R. I. Barnhisel and C. I. Rich, *ibid.* 29, 531 (1965); P. H. Hsu, in Proceedings of the Third International Congress on Studies of Studies of Bauxite and Aluminum Öxides-Hydroxides, J. Nicolas, Ed. (International Commission for Studies of Bauxites and Aluminum Oxides-Hy-
- droxides, Nice, France, 1973), p. 613. N. K. Kwong and P. M. Huang, *Clays Clay Miner.* 23, 164 (1975); C. J. Lind and J. D. Hem, U.S. Geol. Surv. Water Supply Pap. 1827-G (1975), pp. 1–50.

- N. J. Kerkhof, J. L. White, S. L. Hem, J. Pharm. Sci. 64, 940 (1975); *ibid.* 66, 1533 (1977).
 S. L. Hem, E. J. Russo, S. M. Bahal, R. S. Levi, *ibid.* 59, 317 (1970).
 S. L. Nail, J. L. White, S. L. Hem, *ibid.* 65, 1400 (1972).
- 1192 (1976). J. L. White and S. L. Hem, *ibid*. **64**, 468 (1975). S. L. Nail, J. L. White, S. L. Hem, *ibid*., p. 7. S
- 1166.
- N. J. Kerkhof, R. K. Vanderlaan, J. L. White, S. L. Hem, *ibid.* 66, 1528 (1977).
 S. L. Nail, J. L. White, S. L. Hem, *ibid.* 65, 100 (1977). 1255 (1976).
- G. Bárdossy, A. Csanády, A. Csordás-Tóth, Clays Clay Miner. 26, 245 (1978). 10. G. Bárdossy
- G. Bárdossy, K. Jónás, A. Imre, K. Solymár, Econ. Geol. 72, 573 (1977).
 G. Bárdossy, Karstic Bauxites (Akadémiai Kiadó, Budapest, Hungary, 1977) (in Hungari-an).
- 13. M. A. Duffin and J. Goodyear, Mineral. Mag. 32. 352 (1962)
- 32, 352 (1962).
 14. E. Nemecz and G. Varju, *Acta Geol. Acad. Sci. Hung.* 11, 453 (1967).
 15. C. J. Serna, J. L. White, S. L. Hem, *J. Pharm. Sci.* 67, 324 (1978).
 16. Journal paper No. 7240 of the Purdue University Agricultural Experiment Station.

14 August 1978; revised 10 October 1978

Djurleite (Cu_{1.94}S) and Low Chalcocite (Cu₂S): **New Crystal Structure Studies**

Abstract. Additional x-ray structure studies on low chalcocite generally confirm the previously reported structure but show that either disorder is present or the true space group is not P2₁/c but Pc, four of the 96 copper atoms in the monoclinic unit cell taking on twofold (linear) coordination. The crystal structure of djurleite has been solved in space group P2 $_1/n$, the monoclinic cell having parameters a = 26.897, b = 15.745, and c = 13.565 angstroms; $\beta = 90.13^\circ$; and a content of 248 copper and 128 sulfur atoms. Of the 62 different copper atoms in the structure, 52 are in threefold, triangular coordination with sulfur, nine in tetrahedral, and one in linear coordination.

Chalcocite, a major ore mineral of copper having the essential composition Cu₂S, has long been the subject of structure study, but only in 1971 was its complex crystal structure finally revealed (1). A second phase of closely related chemical composition $Cu_{1.96}S$, which was discovered in an x-ray study of the Cu-S system by Djurle in 1958 (2), was established as the mineral species djurleite in 1962 (3). Since then, much of what was formerly considered to be chalcocite has been found to be actually djurleite; the two minerals are both very common and frequently intermixed. In the field of solid-state physics, the significance of the





0036-8075/79/0126-0356\$00.50/0 Copyright © 1979 AAAS

phase relationship of chalcocite and djurleite in the function of cadmium sulfide solar cells has been emphasized (4). Thus, the structures and crystal chemistry of these phases, which are very complex, are of considerable interest in many areas. I previously reported the structure of low chalcocite (1); I now report the determination of the crystal structure of djurleite. The essential results of the structure determination are given below.

My determination of the crystal structure of low chalcocite was based on a monoclinic unit cell containing 96 Cu₂S (1). Continued study of this complex structure has shown that although the reported structure is generally correct, either there is disorder in the structure or the true space group is Pc rather than $P2_1/c$. This ambiguity is brought about by the behavior of two of the 24 copper atoms in the asymmetric unit of the structure in $P2_1/c$, each of which splits into two types of atom, one having triangular coordination and one having linear (twofold) coordination. A very similar situation was found in the synthetic compound Bi₂Cu₃S₄Cl by Lewis and Kupčík (5). The best conventional reliability index R that could be attained (with absorption corrections) for a centrosymmetric, isotropic model for low chalcocite is 0.157; the centrosymmetric anisotropic model refined to 0.107. The latter refinement revealed extreme anisotropy for Cu(15) and Cu(19), strongly indicating a dual nature for these atoms.

SCIENCE, VOL. 203, 26 JANUARY 1979

When each is split equally into a threecoordinated and a two-coordinated moeity, an anisotropic, disordered model in $P2_1/c$ refines to give R = 0.107; an ordered model in Pc refines to R = 0.082. The former is based on 342 parameters, the latter on 648; whether the results are significantly different is not certain.

The crystallography of djurleite was described in detail by Takeda *et al.* (6). Their study of complexly twinned crystals led to the definition of an orthorhombic unit cell closely related to the pseudo-orthorhombic cell of low chalco-

cite but one-third larger. Both are based on a small hexagonal subcell containing 2 Cu_2S , corresponding to that of high chalcocite (7). Takeda *et al.* (6) expressed the strong suspicion that the true symmetry of djurleite may be monoclinic. I was able to study carefully all their singlecrystal film patterns and to reach this conclusion unequivocally (8). Nevertheless, no attempt at structure analysis could be made without first obtaining untwinned crystals.

Such crystals came to light unexpectedly in 1976 from the Ozark Lead Co. mine at Sweetwater, Missouri, and I was able to undertake the structure problem (9). The crystals are thin plates as much as 5 mm across and bright bluish-black except where they are altered to digenite. Single-crystal precession photographs showed the crystals to be of high quality with no trace of twinning, and clearly revealed monoclinic symmetry in space group $P2_1/n$. The unit cell was refined from x-ray powder data measured from Guinier-Hägg patterns and, in close agreement with the results of Potter and Evans (l0), was found to have axial lengths a = 26.897(7), b = 15.745(3), and c = 13.565(5) Å; angle $\beta = 90.13(2)^\circ$;



Fig. 2. View of the djurleite structure along the *a* axis (normal to the sulfur layers) in three sections, (A) to (C), as indicated in Fig. 1. Shaded triangles indicate CuS_3 groups; CuS_4 tetrahedra are shown as triangularly hatched figures. The single twofold CuS_2 group is shown in the lower left region of (B).

Atom	x	у	z	Atom	x	у	Z.	Atom	x	у	z
S(1)	0.0652	0.9917	0.1734	Cu (1)	0.0585	0.4995	0.0013	Cu (32)	0.1082	0.0815	0.0721
S (2)	0.0571	0.2572	0.1613	Cu (2)	0.0629	0.7546	0.0057	Cu (33)	0.1068	0.3423	0.0638
S (3)	0.0580	0.5131	0.1751	Cu (3)	0.0658	0.1287	0.2463	Cu (34)	0.1032	0.9108	0.0500
S (4)	0.0562	0.7546	0.1751	Cu (4)	0.0666	0.9891	0.4950	Cu (35)	0.1081	0.5347	0.3120
S (5)	0.0615	0.1176	0.4136	Cu (5)	0.0547	0.2432	0.5000	Cu (36)	0.1120	0.7677	0.3252
S (6)	0.0571	0.3717	0.4211	Cu (6)	0.0637	0.5088	0.4961	Cu (37)	0.1086	0.9563	0.3169
S (7)	0.0700	0.6329	0.4106	Cu (7)	0.0674	0.1130	0.7588	Cu (38)	0.1082	0.6590	0.5622
S (8)	0.0674	0.8637	0.4137	Cu (8)	0.0618	0.3601	0.7429	Cu (39)	0.1075	0.8336	0.5589
S (9)	0.0570	0.9926	0.6629	Cu (9)	0.0684	0.6153	0.7550	Cu (40)	0.1049	0.0073	0.8886
S (10)	0.0663	0.2347	0.6674	Cu (10)	0.1882	0.9989	0.9975	Cu (41)	0.1077	0.2500	0.8788
S (11)	0.0651	0.4905	0.6678	Cu (11)	0.1932	0.2538	0.9947	Cu (42)	0.1129	0.4712	0.8329
S (12)	0.0692	0.7459	0.6725	Cu (12)	0.1801	0.7454	0.9895	Cu (43)	0.1091	0.7740	0.8161
S (13)	0.0653	0.1311	0.9272	Cu (13)	0.1886	0.1258	0.2391	Cu (44)	0.1392	0.4992	0.1277
S (14)	0.0636	0.3746	0.9152	Cu (14)	0.1944	0.6213	0.2498	Cu (45)	0.1372	0.7337	0.1493
S (15)	0.0616	0.6295	0.9252	Cu (15)	0.1901	0.8707	0.2424	Cu (46)	0.1392	0.1697	0.4233
S (16)	0.0656	0.8733	0.9023	Cu (16)	0.1817	0.9986	0.4833	Cu (47)	0.1397	0.3639	0.4205
S (17)	0.1888	0.1290	0.0734	Cu (17)	0.1940	0.7508	0.4955	Cu (48)	0.1404	0.0064	0.6588
S (18)	0.1870	0.3823	0.0798	Cu (18)	0.1816	0.1337	0.7545	Cu (49)	0.1453	0.2554	0.6100
S (19)	0.1824	0.6235	0.0790	Cu (19)	0.1890	0.3852	0.7412	Cu (50)	0.1443	0.5029	0.6162
S (20)	0.1836	0.8687	0.0737	Cu (20)	0.1931	0.8773	0.7385	Cu (51)	0.1420	0.5960	0.9293
S (21)	0.1892	0.0037	0.3209	Cu (21)	0.0161	0.1536	0.0656	Cu (52)	0.2241	0.2886	0.1852
S (22)	0.1926	0.2555	0.3401	Cu (22)	0.0169	0.3899	0.1376	Cu (53)	0.2303	0.4620	0.1977
S (23)	0.1876	0.4955	0.3382	Cu (23)	0.0180	0.6341	0.1245	Cu (54)	0.2346	0.1367	0.4227
S (24)	0.1949	0.7471	0.3278	Cu (24)	0.0148	0.8770	0.1250	Cu (55)	0.2346	0.3904	0.4062
S (25)	0.1827	0.1241	0.5768	Cu (25)	0.0146	0.2896	0.3053	Cu (56)	0.2308	0.5872	0.4358
S (26)	0.1829	0.3774	0.5737	Cu (26)	0.0164	0.4645	0.3179	Cu (57)	0.2344	0.5411	0.6927
S (27)	0.1900	0.6224	0.5799	Cu (27)	0.0177	0.7394	0.3335	Cu (58)	0.2325	0.7142	0.6811
S (28)	0.1870	0.8784	0.5743	Cu (28)	0.0140	0.1048	0.5903	Cu (59)	0.2306	0.4097	0.9373
S (29)	0.1847	0.9991	0.8254	Cu (29)	0.0112	0.3880	0.5622	Cu (60)	0.2373	0.6349	0.8738
S (30)	0.1875	0.2605	0.8288	Cu (30)	0.0176	0.8598	0.6328	Cu (61)	0.2359	0.8561	0.9123
S (31)	0.1923	0.5086	0.8385	Cu (31)	0.0143	0.9668	0.8129	Cu (62)	0.1270	0.2612	0.2454
S (32)	0.1913	0.7527	0.8256								

Table 1. Atomic coordinates in djurleite in unit cell fractions. The structure is monoclinic, space group $P2_1/n$, a = 26.897 Å, b = 15.745 Å, c = 13.565 Å, and $\beta = 90.13^\circ$; all atoms are in general positions. Positional error for sulfur is 0.011 Å; for copper 0.007 Å.

and $Z = 128 \text{ Cu}_{r}\text{S}$ molecules. According to an electrochemical study by Potter (11), x may range from 1.934 to 1.965.

A set of intensities was measured with a Picker automatic diffractometer using Mo K α radiation, all within an asymmetric sector in the range of 2θ from 5° to 45° (where θ is the Bragg angle). These intensities were converted to a data set of 5687 observed independent structure amplitudes, including corrections for Lorentz, polarization, absorption, anomalous dispersion, and isotropic extinction effects. The structure problem was approached from the substructure, which is based on the reported structure of high chalcocite (7). Phases were calculated for substructure reflections and extended to the superstructure reflections by the symbolic addition method (12).

In the substructure space group $P6_{3^{\prime}}$ mmc, there are three possible origins at symmetry centers for the supercell in $P2_1/n$, one of which can be ruled out as being incompatible with the hexagonalclose-packed sulfur framework and the supercell symmetry. The remaining two can each have the monoclinic a axis lying along either the + or - hexagonal aaxis. The four possible orientations each led to a twofold ambiguity in the symbolic addition process, which otherwise proceeded smoothly. Thus, eight different phase models had to be tested and studied by Fourier methods. Each gave a clear image of the sulfur framework and a tantalizing image of large numbers of copper atoms in reasonable locations. Attempts to refine the eight structure models succeeded for only one, however. This model dropped to R = 0.20 in the first three least-squares cycles, whereas none of the others could be reduced below R = 0.50. The refined electron density map showed 32 sulfur and 62 copper atoms in the asymmetric unit, sharply delineated with appropriate peak heights, all in crystal chemically reasonable locations. Isotropic refinement leads to an average thermal motion for sulfur of $\tilde{u} = 0.07$ Å and for copper of $\tilde{u} = 0.11$ Å. The structure is currently being refined in anisotropic mode (846 parameters); at present R = 0.12. The latest set of atomic coordinates is given in Table 1.

No evidence has so far been found of disorder or partial occupancy in the structure. The revealed unit cell content corresponds to x = 62/32 = 1.9375 in the formula Cu_xS, indicating that the composition is near the low end of the homogeneity range found by Potter (11). If one copper atom were added to the asymmetric unit, x would be 1.9688, close to Potter's upper limit. Such an additional possible copper site has not yet been found in the crystal under study.

Of the 62 copper atoms in the asymmetric unit, 20 are in triangular coordination with sulfur in the hexagonal-closepacked sulfur layers lying normal to the a axis; the remaining 42 copper atoms are between the sulfur layers, 32 in triangular and 9 in tetrahedral coordination, often in severely distorted environments. A single copper atom, Cu(62), is in linear, twofold coordination. The structure contains two kinds of sulfur layers (S-1 and S-2), each containing 16 sulfur atoms; one contains 9 and the other 11 copper atoms. Thus, there are three different interlayer copper arrangements. The distribution of atoms is shown schematically in Fig. 1. Figure 2 shows the coordination arrangement of the structure viewed along the a axis in three sections. By contrast, the low chalcocite structure contains one type of hexagonal-close-packed sulfur layer and two different interlayer copper arrangements. So far, no extensive similarity between the two structures beyond these general features has become apparent.

Each copper atom has two, three, or four sulfur neighbors at distances ranging from 2.15 Å (for the twofold copper) to 2.8 Å. Most bond distances lie between 2.25 and 2.35 Å. Each copper atom also has two to six other copper atoms at distances less than 3 Å, some as close as 2.45 Å. These distances are most commonly in the range 2.70 to 2.80 Å. (The Cu-Cu distance in the metal is 2.556 Å.) Thus, the predominant coordination of sulfur about copper is triangular as in low chalcocite, similar to the typical triangular group in covellite (13) but having considerably longer average bond length (the triangular Cu-S distance in covellite is 2.191 Å). Most probably, bonding interactions between copper atoms are present and contribute to the stability of this structure and also to that of low chalcocite.

HOWARD T. EVANS, JR. U.S. Geological Survey, National Center 959, Reston, Virginia 22092

References and Notes

- 1. H. T. Evans, Jr., Nature (London) Phys. Sci. 232, 69 (1971).
- S. Djurle, Acta Chem. Scand. 12, 1415, (1958).
 E. H. Roseboom, Am. Mineral. 47, 1181 (1962);

- E. H. Roseboom, Am. Mineral. 47, 1181 (1962); N. Morimoto, Mineral. J. 3, 338 (1962).
 A. Putnis, Philos. Mag. 34, 1083 (1976).
 J. Lewis, Jr., and V. Kupčík, Acta Crystallogr. Sect. B 30, 848 (1974).
 H. Takeda, J. D. H. Donnay, E. H. Roseboom, D. E. Appleman, Z. Kristallogr. 125, 1 (1967).
 B. J. Wuensch and M. J. Buerger, Mineral. Soc. Am. Spec. Pap. 1 (1963), p. 164; R. Sadanaga, M. Ohmasa, N. Morimoto, Mineral. J. 4, 275 (1965).
- 1965). This was possible through the kindness of D. E. Appleman of the Smithsonian Institution. 8.
- I thank Ozark Lead Co. and R. W. Potter, II, of the U.S. Geological Survey for their generous
- the U.S. Geological survey for their generous help in obtaining this material.
 10. R. W. Potter, II, and H. T. Evans, Jr., J. Res. U.S. Geol. Surv. 4, 205 (1976).
 11. R. W. Potter, II, Econ. Geol. 72, 1524 (1977).
 12. J. Karle and I. L. Karle, Acta Crystallogr. 21, 240 (1966).
- 13. H. T
- H. T. Evans, Jr., and J. A. Konnert, Am. Miner-al. 61, 996 (1976).

7 September 1978

Intraventricular Carbachol Mimics the Effects of Light on the Circadian Rhythm in the Rat Pineal Gland

Abstract. Environmental lighting regulates numerous circadian rhythms, including the cycle in pineal serotonin N-acetyltransferase activity. Brief exposure of rats to light can shift the phase of this enzyme's circadian rhythm. Light also rapidly reduces nocturnal enzyme activity. Intraventricular injections of carbachol, a cholinergic agonist, can mimic both of these effects. Light and carbachol presumably act on the suprachiasmatic nucleus of the hypothalamus. These experiments demonstrate the feasibility of using a neuropharmacologic approach to the mechanisms underlying mammalian circadian rhythms.

The enzyme serotonin N-acetyltransferase, which is involved in the synthesis of the hormone melatonin (1), displays a circadian rhythm in the rat pineal gland (2). At night, there is 30- to 50-fold more activity in the gland than during the day. The endogenous nature of this rhythm is indicated by its persistence in constant darkness or in blinded animals (2); that is, the rhythm can "free run." Enzyme activity rises and falls with a period slightly longer than 24 hours (3). Although the rhythm is endogenous to the organism, it does not appear to be endogenous to the rat pineal itself. Rather, like other circadian rhythms, the oscillations are determined by the central nervous system.

The rat pineal gland is innervated by sympathetic nerve fibers with cell bodies in the superior cervical ganglia (4). These fibers release the neurotransmitter norepinephrine. During the night, more norepinephrine is released than during the day (5). This rhythm in adrenergic stimulation drives the rhythm in enzyme activity. If the connection between the gland and the brain is cut, for example, by bi-

SCIENCE, VOL. 203, 26 JANUARY 1979