The crystallography of djurleite*, Cu$_{1.97}$S

BY HIROSHI TAKEDA ** and J. D. H. DONNAY

The Johns Hopkins University, Baltimore, Maryland

and EUGENE H. ROSEBOOM and DANIEL E. APPLEMAN


Dedicated to Prof. Dr. G. Menzer on the occasion of his 70th birthday

(Received April 6, 1967)

Auszug

Djurleit ist ein gültiger Mineralname. Das Mineral ist orthorhombisch oder pseudo-orthorhombisch mit der Zusammensetzung Cu$_{1.97}$S, dem Beugungsaspekt $P^h*$ und den Gitterkonstanten: $a = 26.92$; $b = 15.71$; $c = 13.56$ Å (alle $\pm 0.2\%$). Für $Z = 128$, d. h. für einen Zellinhalt Cu$_{252}$S$_{128}$, beträgt $D_\lambda$ 5.81 g cm$^{-3}$ gegenüber $D_m = 5.747 \pm 0.007$. Einkristalle sind selten. Die Intensitätsverteilung für eine stark hervortretende, pseudo-hexagonale Unterkelle spiegelt die annähernd hexagonal-dichteste Packung der Schwefelatome wider.

Abstract

Djurleite is a valid species, orthorhombic or pseudo-orthorhombic, with composition Cu$_{1.97}$S, diffraction aspect $P^h*$, and cell dimensions: $a = 26.92$ Å, $b = 15.71$, $c = 13.56$, all $\pm 0.2\%$. For $Z = 128$, or Cu$_{252}$S$_{128}$ per cell, $D_\lambda = 5.81$ g cm$^{-3}$; $D_m = 5.747 \pm 0.007$. Single crystals are rare. A strongly marked pseudo-hexagonal subcell has an intensity distribution reflecting the hexagonal close-packed arrangement of the sulfur atoms.

I. Historical introduction

DJurle (1958) was the first to recognize that a phase distinct from chalcocite exists near the composition Cu$_{1.96}$S at room temperature. He called this phase "Cu$_{1.96}$S III," and published an unindexed

* Work supported in part by the National Science Foundation through a grant to the Johns Hopkins University (GP 1565). Publication authorized by the Director, U. S. Geological Survey.

** On leave of absence from the Mineralogical Institute, University of Tokyo, Hongo, Tokyo, Japan.
The crystallography of djurleite

powder pattern which he described as showing “low symmetry”. Previously N.W. Buerger (1941) and subsequent workers had thought that a chalcocite solid solution extended from Cu$_2$S to about Cu$_{1.96}$S, because of the similarity of the powder patterns of the two phases.

Rosseboom (1962) and Morimoto (1962) independently established the existence of a mineral identical to Djurle’s phase “Cu$_{1.96}$S III.” Both of them identified the mineral, which they named djurleite, on the basis of the x-ray powder patterns. Neither was able to derive the symmetry or cell parameters. Morimoto showed a precession pattern which he believed was that of djurleite, but the present work has shown that this pattern is actually that of a digenite-like phase.

In 1960 Takeda, working in Prof. Sadanaga’s laboratory at the University of Tokyo, began an investigation of mineral specimens labelled “boulangerite” (Pb$_2$Sb$_2$S$_4$) from Neudorf, Harz, Germany. It soon became clear that this material had been mislabelled, and that it consists of at least two crystallographically distinct phases, neither of which could be identified. In October 1963, at the Geophysical Laboratory of the Carnegie Institution of Washington, G. Kulle-Rud, R. Brett, and N. Morimoto (private communication) examined a polished section of the Neudorf material and concluded that it resembles djurleite and contains lamellae indicating twinning, unmixing, or both. P. Iber (private communication) at the Marshall Space Flight Center, Huntsville, Alabama kindly performed a qualitative electron-probe microanalysis of the same material and confirmed that it contained only Cu and S as essential elements; he did not find Sb or Pb.

Sadanaga, Morimoto, and Ohmasa (1963), on the basis of their examination of material from the Ani Mine, had suggested that djurleite might be a mixture of mutually-oriented crystals of two species: “djurleite I,” similar to digenite, and “djurleite II,” similar to chalcocite. This suggestion has now been shown to be unwarranted, but at the time it cast some doubt on the legitimacy of djurleite as a single phase.

Takeda and Donnay (1964) presented a paper at the 1964 Annual Meeting of the American Crystallographic Association in Bozeman, Montana, in which they gave the space group, cell dimensions and an interpretation of the twinning of an orthorhombic phase present in the Neudorf material. They referred to this phase as “chalocite IV” because its cell dimensions closely approximate multiples of those of hexagonal chalcocite. The same cell dimensions and space group had
been found by Sadanaga and Ohmasa (private communication, November 1963) for an unidentified phase associated with chalcocite on a specimen from St. Ives, Cornwall. At the same meeting Appleman recognized the cell dimensions and the precession patterns of twins, which Takeda and Donnay had obtained for "chalcocite IV", as being identical with those which he had obtained earlier from material known to be djurleite. Thus he was able to inform Takeda and Donnay of the identity, composition and density of this phase.

Appleman and Roseboom had begun single-crystal x-ray studies of djurleite in 1962, with the object of obtaining crystal-chemical explanations for some of the phase equilibria observed by Roseboom in the system Cu—S. Roseboom had already confirmed Djurle's observation that djurleite is a phase distinct from chalcocite with a characteristic powder pattern. Unfortunately he could not make single crystals of synthetic djurleite large enough for x-ray study. However, untwinned single crystals were obtained from massive natural djurleite by a method described below. From these crystals Appleman determined the cell of djurleite in 1962, but he was unable to confirm the space group. He later studied large natural specimens, which appeared to be single crystals of pure djurleite, but proved to be intimately twinned. Roseboom subsequently determined the density of djurleite on this material and he obtained a more accurate estimate of its composition from synthetic samples.

When the precession films taken by Takeda and Donnay were compared with those obtained by Appleman, it was obvious that they represented the same substance. The comparison showed that Appleman's original crystals were indeed untwinned, and provided an additional check on the validity of the twin laws which Takeda and Donnay had derived. As a result of this cooperation, djurleite has been confirmed to be a valid species and its cell dimensions and space group have been determined. The present paper sets forth the results of this joint investigation.

II. Chemistry

Although Djurle assigned the composition Cu$_{1.96}$S to his new phase, he never synthesized it by itself. His samples of Cu$_{1.96}$S composition produced a mixture of djurleite (Cu$_{1.96}$S III) and a tetragonal phase (Cu$_{1.86}$S II), which he believed to be a polymorph of djurleite. Samples annealed at 400°C and at 70°C yielded the two phases in different proportions, suggesting that both phases had the Cu$_{1.96}$S
composition. As it has now been shown that the tetragonal phase can vary from at least Cu$_{1.96}$S (JANOSI, 1964) to Cu$_2$S (SKINNER, BOYD, and ENGLAND, 1964), the above argument is no longer valid.

Both ROSEBOOM (1962) and MORIMOTO (1962) had identified the mineral, djurleite, as DJURLE'S low-symmetry phase Cu$_{1.96}$S III from powder patterns alone. Chemical analyses were of doubtful value because of impurities in the samples and the small differences in composition between chalcocite (20.15 wt.\% S), djurleite (about 20.4 wt.\% S), and digenite (22.0 wt.\% S). An x-ray fluorescence analysis, reported by ROSEBOOM, indicated only a composition intermediate between those of digenite and chalcocite. About 0.8 percent Fe was present, probably as pyrite. MORIMOTO gave a chemical analysis indicating the formula Cu$_{1.91}$Fe$_{0.02}$S, but he noted that this analysis had been made on a djurleite-digenite mixture.

While investigating the phase equilibria in the system Cu—S, ROSEBOOM (1966) tried several ways of synthesizing pure djurleite. Its low decomposition temperature of 93° and the nearly ubiquitous tetragonal phase made this a difficult task. The only completely successful synthesis was accomplished with a sample containing 20.40 ± 0.03 wt.\% S (Cu$_{1.90}$S±0.01S). Because it would be possible for nearly 10 wt.\% chalcocite to go undetected, the composition of the djurleite in this sample can be shown only to lie between Cu$_{1.96}$S (20.46 wt.\% S) and Cu$_{1.97}$S (20.37 wt.\% S). This particular synthesis involved: (a) annealing a mixture of Cu and S at 125°C for 2 months, (b) regrinding, (c) rapid reheating to 260°C, (d) slow cooling (10 degrees/day in 2-degree decrements) to room temperature, followed by (e) an eighteen-month wait while the tetragonal phase comprising two thirds of the sample slowly inverted to djurleite. Similar experiments on other compositions obviously cannot be performed overnight. Djurleite synthesized in other runs, the products of which contain various amounts of other copper sulfides, is compatible with the above composition range but does not delimit it more precisely.

III. Crystallography

Experimental

(A) Neudorf material.—The specimens from Neudorf, Harz, Germany which were used in this study came from the private collection of Dr. K. SAKURAI, Tokyo. In these specimens almost all of the djurleite is twinned. Some of the twins simulate hexagonal single
crystals; they are short prismatic with perfect basal cleavage. Striations parallel to the trace of the cleavage plane are observed on the faces of the hexagonal prism. In all, eleven specimens were investigated, ranging from 0.13 to 0.25 mm in their largest dimension.

Precession photographs were first taken of the zero- and upper-level reciprocal-lattice nets parallel to the cleavage plane. On these nets the strong reflections show hexagonal symmetry, but the complete patterns show orthorhombic symmetry. Zero- and upper-level precession photographs were then taken of the reciprocal-lattice nets perpendicular to the cleavage plane and parallel to the orthorhombic symmetry directions. The nets perpendicular to the cleavage plane but at 30° to the symmetry directions were also photographed. In addition to the precession photographs, cone-axis, rotation, and Weissenberg photographs were taken around each orthorhombic symmetry direction.

When the twin laws of the Neudorf material had been interpreted, as described in an accompanying paper by TAKEDA, DONNAY and APPLEMAN (1967), it was discovered that the specimens consist primarily of an orthorhombic phase twinned according to two twin laws: pseudo-hexagonal and pseudo-tetragonal. Another unidentified phase is also present. The orthorhombic phase was subsequently identified as djurleite.

(B) Butte material.—The djurleite showing the least twinning was extracted from a massive sample from Butte, Montana, said to come from the Kelly Mine. When examined under the ore microscope and by the x-ray powder method, the sample was found to be approximately 90% djurleite, 5% digenite, and 5% bornite, with a trace of pyrite. A number of individual djurleite grains, 0.5 to 0.8 mm in diameter, show no twinning.

A portion of the sample was chilled in liquid nitrogen to prevent deformation and shattered in a percussion mortar. The fine-grained fraction was mounted in cement on a glass slide and polished for observation with the ore microscope. Several apparently homogeneous grains were removed by dissolving the cement with acetone, and were then remounted, polished on a second surface and again examined for chemical homogeneity and lack of twinning. The most suitable fragments were then photographed by the precession method.

Large macrocrystalline specimens of pure djurleite were obtained from Butte through the kindness of Mr. LESTER G. ZEIHEN of the Geological Research Laboratory of the Anaconda Co. These specimens
are pseudo-hexagonal plates up to 10 mm in width and 2 mm in thickness. Examination under the ore microscope shows that all of them consist of the same phase. Faint color differences between crossed nicols are suggestive of twinning. The edges of the plates are bevelled by curved, striated faces, many with re-entrant angles. Precession photographs of small fragments broken from the large plates show intimate twinning according to the pseudo-hexagonal twin law found in the Neudorf material. The patterns are in fact identical with those obtained from the hexagonally twinned Neudorf specimens, with the difference that in the Butte material the relative volumes of the individual crystals making up the twin are approximately equal.

Density

The best density measurements were obtained on two of the large twinned specimens of pure djurleite from Butte, Montana. The density was determined on a Berman balance by weighing the samples in air and in toluene whose density was accurately known. The two specimens, weighing 243 and 360 mg respectively, gave densities of 5.751 ± 0.01 and 5.744 ± 0.01 g cm⁻³, at 25°C, with 3 determinations on each specimen. The average is \( D_m = 5.747 ± 0.007 \) g cm⁻³ (standard deviation).

Morimoto's density determination of 5.63 g cm⁻³ for djurleite (MORIMOTO, 1962) is so low as to suggest that his sample was either digenite or a digenite-djurleite mixture. He describes the crystals as cubic with octahedral faces, "apparently pseudomorphs after galena".

Single-crystal data

The cell dimensions of djurleite, independently determined on material from both localities, are: \( a = 26.95, b = 15.71, c = 13.56 \) Å (Neudorf); \( a = 26.90, b = 15.72, c = 13.57 \) Å (Butte); all approximately ± 0.2%\). The diffraction aspect is orthorhombic \( P_{n} \) with the additional criterion: 0k0 present only with \( k \) even. This aspect is compatible with the orthorhombic space groups \( D_{2h}^{12} = Pmnmm \) and \( C_{2h}^l = P2_{1}nm \) or \( Pmn2_1 \). In this case the 0k0 extinctions are structural. The diffraction aspect is also compatible with the monoclinic space group \( C_{2h}^l = P2_1/n \) with \( \beta = 90^\circ \) and an intensity distribution very close to orthorhombic.

There is a strongly marked pseudo-hexagonal subcell. All strong sublattice reflections obey the conditions \( \bar{h} = 0 \mod 4, k = 0 \mod 4, \)
$l = 0 \mod 2$. The converse is not true: some reflections whose indices obey these criteria are not strong. The very strong reflections all obey additional conditions (Table 1). This intensity distribution is similar to that of a hexagonal close-packed structure.

Table 1. Criteria for strong sublattice reflections

<table>
<thead>
<tr>
<th>$h$, $k$, $l$ = $(p \mod 8, q \mod 8, r \mod 12)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$ $q$ $r$</td>
</tr>
<tr>
<td>0 0 0</td>
</tr>
<tr>
<td>0 4 2</td>
</tr>
<tr>
<td>0 4 6</td>
</tr>
<tr>
<td>0 4 10</td>
</tr>
</tbody>
</table>

The smallest subcell deduced from the patterns has dimensions: $a' = a/4$, $b' = b/4$, $c' = c/2$. Metrically it is pseudo-tetragonal, $a_1(T) = c'$, $a_4(T) = a'$, $c(T) = b'$, and can be obtained from the orthorhombic crystal cell $abc$ by the transformation $00\bar{1}/000/0\bar{1}0$. Provided it is face-centered on $b'c'$, it is also pseudo-hexagonal, $a_1(H) = b'$, $a_4(H) = [(b'/2)^2 + (c'/2)^2]^{1/2}$, $c(H) = a'$, in which case it is obtained from $abc$ by the transformation $010/0\bar{1}1/0\bar{1}0$. This subcell, as was pointed out to us by Professor Sadanaga and Dr. Ohmaza (Tokyo), is very close to the cell of hexagonal $(\beta)$ chalcocite: $a = 3.961$, $c = 6.722 \, \AA$, at $152^\circ C$ (DJURLE, 1958). For the sake of comparison (Table 2), we use the orthohexagonal cell $a''b''c''$ of hexagonal chalco-

Table 2. Orthohexagonal cell $a''b''c''$ of hexagonal chalcocite as subcell of djurleite and orthorhombic chalcocite

<table>
<thead>
<tr>
<th>Hexagonal chalcocite $^1$</th>
<th>Djurleite subcell $^2$</th>
<th>Hexagonal chalcocite $^2$</th>
<th>Djurleite cell $^2$</th>
<th>Hexagonal chalcocite $^2$</th>
<th>Orthorhombic chalcocite $^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a''$</td>
<td>$b'$</td>
<td>$4a''$</td>
<td>$b$</td>
<td>$3a''$</td>
<td>$a$</td>
</tr>
<tr>
<td>3.961 \AA</td>
<td>3.92 \AA</td>
<td>15.844 \AA</td>
<td>15.71 \AA</td>
<td>11.883 \AA</td>
<td>11.881 \AA</td>
</tr>
<tr>
<td>$b''$</td>
<td>$c'$</td>
<td>$2b''$</td>
<td>$c$</td>
<td>$4b''$</td>
<td>$b$</td>
</tr>
<tr>
<td>6.881</td>
<td>6.82</td>
<td>13.722</td>
<td>13.56</td>
<td>27.444</td>
<td>27.323</td>
</tr>
<tr>
<td>$c''$</td>
<td>$a'$</td>
<td>$4c''$</td>
<td>$a$</td>
<td>$2c''$</td>
<td>$c$</td>
</tr>
</tbody>
</table>

$^1$ DJURLE, 1958.
$^2$ This paper. Neudorf.
The crystallography of djurleite

cite. The present orientation of the djurleite cell is chosen in such a way that its b axis coincides with the unique b of the monoclinic interpretation. This is the reason for the cyclic permutation of the cell edges in Table 2.

### Table 3. X-ray powder data for djurleite

<table>
<thead>
<tr>
<th>hkl</th>
<th>2θ (deg)</th>
<th>I (%)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>101</td>
<td>2θ</td>
<td>I (%)</td>
<td></td>
</tr>
</tbody>
</table>

Calculated from the following cell: orthorhombic, *P*2_12_2, a = 26.90 Å, b = 15.72 Å, c = 13.57 Å; α = 90°, β = 90°, γ = 90°. Calculated values are listed only in the vicinity of observed values to save space. Omission of seven values would be indicated — (7) —.

Relative intensity estimated from single crystal data where available. Order of decreasing intensity is vs, s, m, w, v, f.

1 Average from two diffractometer patterns, CuKα radiation.

2 Average peak height, uncorrected, scaled to a maximum value of 100.
Powder data

X-ray powder data for djurleite (Table 3) are indexed on the basis of the cell found in this study. The data are average values from two diffractometer patterns of the twinned crystals of pure djurleite from Butte, Montana. The patterns were run at 4°2θ per minute. The diffractometer was calibrated with respect to the silicon used as an x-ray standard at the Geophysical Laboratory. The silicon cell edge was taken as 5.4306 Å.

Cell content

The cell volume of djurleite, calculated from the average cell dimensions obtained in the present study, is 5734.7 Å³. The most probable composition, as discussed above, is Cu₁₉⁹⁰S. The djurleite cell contains 64 nodes of the sublattice corresponding to the lattice of hexagonal chalcocite, which contains 2 Cu₃S per cell. If, as seems probable, the packing of sulfur atoms is similar in the two minerals, then the djurleite cell contains 128 sulfur atoms, and the total cell content is Cu₃₂₂S₁₂₈. If the number of Cu atoms is reduced to 251, the corresponding formula is Cu₁₉⁶¹S; if it is increased to 253, the formula is Cu₁₉⁷₃S. Both formulae are outside the range of possible composition found above.

The calculated density corresponding to a cell content of Cu₃₂₂S₁₂₈ is 5.81 g cm⁻³. This is somewhat higher than the observed density of 5.747 g cm⁻³.

IV. Conclusions

The work reported in this paper shows that djurleite is a valid mineral species, with crystallographic parameters and composition distinct from those of chalcocite, digenite, or other copper sulfides. The uncertainty felt by previous workers regarding the true identity of djurleite is due largely to the presence of a phase of unknown composition which occurs, associated with djurleite, in many natural and synthetic specimens. Precession patterns of this phase from the Neudorf material resemble those of the digenite-like phase found by SADANAGA, MORIMOTO and OHMASA (1963) in specimens from the Ani Mine. These patterns can be interpreted as showing that the digenite-like phase is twinned, with the pseudo-hexagonal axis of its twin lattice parallel to that of djurleite. On precession patterns taken of specimens in which both phases occur, a strong reflection...
of the digenite-like phase falls in a position that violates the $n$-glide extinction rule of djurleite. The occurrence of these two phases in mutual intergrowth in many specimens, combined with the effects of twinning in both phases, makes interpretation of the patterns difficult.

References

N. W. Buerger (1941), The chalcocite problem. Econ. Geol. 36, 19–44.
E. H. Roseboom (1962), Djurleite, $\text{Cu}_1.96\text{S}$, a new mineral. Amer. Mineralogist 47, 1181–1184.
E. H. Roseboom (1966), An investigation of the system Cu–S and some natural copper sulfides between 25° and 700°C. Econ. Geol. 61, 641–672.