

The Crystallography of Eucairite, $CuAgSe$

By A. J. FRUEH JR., G. K. CZAMANSKE and CH. KNIGHT

With 5 figures

(Received October 17, 1956)

Zusammenfassung

Eucairit bildet pseudotetragonale rhombische Kristalle, deren Elementarzellen die Gitterkonstanten $a = 4,105 \text{ \AA}$, $b = 20,35 \text{ \AA}$, $c = 6,31 \text{ \AA}$ haben und sich aus tetragonalen Unterzellen mit a zwischen $4,07 \text{ \AA}$ und $4,105 \text{ \AA}$ und $c = 6,31 \text{ \AA}$ aufbauen; ihre Raumgruppe ist $P4/nmm$. In der Unterzelle sind 2($CuAgSe$) enthalten, mit Ag in $\pm [1/4, 1/4, 0,449]$, Se in $\pm [1/4, 1/4, 0,873]$ und Cu in $\pm [1/4, 3/4, 0,105]$. Die wirkliche Elementarzelle setzt sich aus solchen, in zwei Orientierungen angeordneten, Unterzellen zusammen. Zwischen 190 und 195°C erfolgt Umwandlung in eine Hochtemperatur-Modifikation.

Abstract

Eucairite crystallizes as pseudo-tetragonal orthorhombic crystals having a large supercell of $a = 4.105 \text{ \AA}$, $b = 20.35 \text{ \AA}$; $c = 6.31 \text{ \AA}$ based upon a tetragonal subcell whose a dimension lies somewhere between 4.07 \AA and 4.105 \AA and whose c dimension is equal to 6.31 \AA and which has the space group symmetry of $P4/nmm$. There are 2($CuAgSe$) per subcell with the Ag atoms at $1/4, 1/4, .449$; $3/4, 3/4, .551$. The Se atoms are at $1/4, 1/4, .873$; $3/4, 3/4, .127$ and the Cu atoms are at $1/4, 3/4, .105$; $3/4, 1/4, .895$. The true cell or supercell is a stacked sequence of these subcells in two orientations. At $190-195^\circ\text{C}$ there is an inversion to a high temperature modification.

Introduction

The occurrence, appearance and physical properties of the comparatively rare mineral eucairite, $CuAgSe$, have been adequately described in mineralogical literature, the most recent description being that of J. W. EARLEY in his paper on selenide minerals¹. From a sample from Skrikerum, Sweden (Natural History Museum, Stockholm, yellow 2345), EARLEY found the unit cell of eucairite to be tetragonal, space group $P4/nmm$, with the dimensions $a = 4.075$,

¹ J. W. EARLEY, Description and synthesis of the selenide minerals. Amer. Mineralogist **35** (1950) 345-347.

$c = 6.29$ kX. Allowing 2 (*CuAgSe*) per cell, the calculated density is 7.91 which compares favorably with the measured values of 7.6–7.8.

In the present study material from a sample of the same specimen as noted above was used. The eucairite was disseminated in dendritic-like growths in calcite. To obtain fragments for single crystal work the eucairite was separated from the calcite by dissolving the latter in dilute hydrochloric acid and then fracturing the dendrites in an iron

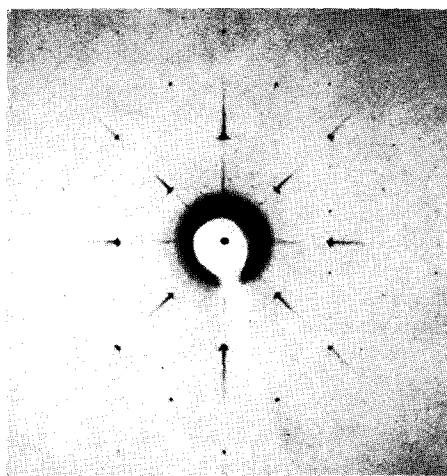


Fig. 1. Zero-level c axis precession picture of eucairite $MoK\alpha$ radiation

mortar at liquid nitrogen temperatures. The low-temperature technique was necessary to prevent the plastic deformation of the selenide. Irregular fragments with the maximum dimension on the order of 0.1 mm. were chosen for diffraction work. Upon first observation it was believed that the unit cell and space group described above could be confirmed. After close inspection of precession and WEISSENBERG diffraction records of several crystals, however, it was discovered that the crystals are not truly single but rather that all observed crystals are intergrowths of orthorhombic crystals which share the c axis while the a axis of one parallels the b axis of the other. It was further discovered that a few very weak superstructure spots existed which quintupled the cell in one dimension (Fig. 1) so that when measured by the BUERGER precession method using $MoK\alpha$ radiation ($\lambda = .710 \text{ \AA}$) the true cell has the dimensions:

$$\begin{aligned} a &= 4.105 \text{ \AA} \\ b &= 20.35 (5 \times 4.07) \text{ \AA} \\ c &= 6.31 \text{ \AA}. \end{aligned}$$

The superstructure reflections can be indexed as (230), (270), (2.13.0), (540), (470), (4.13.0), (322), (382). For all other observed reflections the k index is either 0 or divisible by 5. These superstructure reflections were always found to be present in the diffraction records

of crystals from two other localities: Sierra de Umango, La Rioja, Argentina, (U. S. National Museum # 84, 457); and Cougar mine, Slick Rock district, San Miguel County, Colorado. (U. S. Geological Survey # 68-61.)

Determination of the approximate structure

Neglecting the weak superstructure reflections and using the smaller subcell with the higher symmetry ($P4/nmm$) an approximate structure was determined. The intensities of the diffraction spectra of the intergrown crystals were measured with a single-crystal GEIGER-counter goniometer using $Cu K\alpha$ radiation.

With 2 ($CuAgSe$) per cell all the atoms must be located on twofold special positions: $\begin{pmatrix} 1 & 1 \\ 4 & 4 \end{pmatrix} \begin{pmatrix} 3 & 3 \\ 4 & 4 \end{pmatrix} z$, $\begin{pmatrix} 3 & 1 & 1 \\ 4 & 4 & 2 \end{pmatrix}$, $\begin{pmatrix} 1 & 3 & 1 \\ 4 & 4 & 2 \end{pmatrix}$ or $\begin{pmatrix} 3 & 1 & 0 \\ 4 & 4 & 0 \end{pmatrix}$, $\begin{pmatrix} 1 & 3 & 0 \\ 4 & 4 & 0 \end{pmatrix}$. A comparison of the measured ($h k 0$) intensities with those calculated, assuming all the permutations of the three elements in the special positions, yielded the most reasonable check when Ag and Se atoms were placed at $\begin{pmatrix} 1 & 1 \\ 4 & 4 \end{pmatrix} z$, $\begin{pmatrix} 3 & 3 \\ 4 & 4 \end{pmatrix} \bar{z}$ and the Cu atoms on either $\begin{pmatrix} 3 & 1 & 0 \\ 4 & 4 & 0 \end{pmatrix}$, $\begin{pmatrix} 1 & 3 & 0 \\ 4 & 4 & 0 \end{pmatrix}$ or $\begin{pmatrix} 3 & 1 & 1 \\ 4 & 4 & 2 \end{pmatrix}$, $\begin{pmatrix} 1 & 3 & 1 \\ 4 & 4 & 2 \end{pmatrix}$; (see Table 1).

Table 1

$\sin \theta$	Indices	F calculated	F observed
0.378	200	— 78	78
0.756	400	54	54
0.267	150	— 43	36
0.598	350	31	32
0.534	2.10.0	65	45
0.845	4.10.0	— 50	28

To determine two parameters of the Ag and Se atoms, a PATTERN projection on ($0 k l$) was computed (Fig. 2). An interpretation of this projection gave a z parameter for Ag of .45 and for Se , $z = .84$. It should also be noted that there is no peak at the expected $Cu-Cu$ interaction distance of $\begin{pmatrix} 0 & 1 \\ & 2 \end{pmatrix} 0$. Successive electron density projections on (100), the final of which is shown in Fig. 3, and intensity comparisons fixed the Ag atoms at $\begin{pmatrix} 1 & 1 \\ 4 & 4 \end{pmatrix} .449$ and $\begin{pmatrix} 3 & 3 \\ 4 & 4 \end{pmatrix} .551$ and the Se atoms at $\begin{pmatrix} 1 & 1 \\ 4 & 4 \end{pmatrix} .873$ and $\begin{pmatrix} 3 & 3 \\ 4 & 4 \end{pmatrix} .127$. The Ag and Se atoms conform with

the space group requirements of the higher symmetry cell, but the *Cu* atoms appear to be off the twofold special positions $\begin{pmatrix} 1 & 3 \\ 4 & 4 \end{pmatrix} 0$ $\begin{pmatrix} 3 & 1 \\ 4 & 4 \end{pmatrix} 0$ at a position $\begin{pmatrix} 1 & 3 \\ 4 & 4 \end{pmatrix} .105$ which, according to space group require-

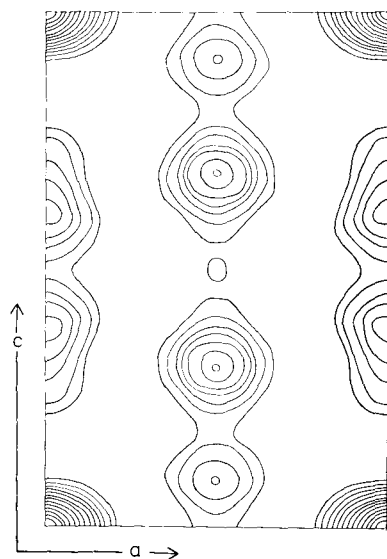


Fig. 2. PATTERSON projection of eucairite on (010)

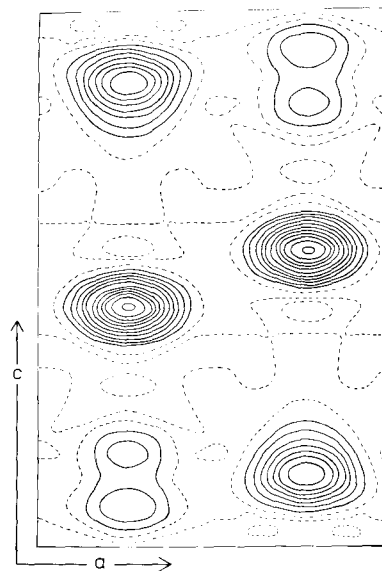


Fig. 3. Electron density projection of eucairite on (010)

ments, is a fourfold position requiring equivalent atoms at $\begin{pmatrix} 1 & 3 \\ 4 & 4 \end{pmatrix} .895$, $\begin{pmatrix} 3 & 1 \\ 4 & 4 \end{pmatrix} .105$ and $\begin{pmatrix} 3 & 1 \\ 4 & 4 \end{pmatrix} .895$. It is here that the use of higher symmetry must be abandoned. The true symmetry of the subcell is evidently orthorhombic, *Pmmm*. The *Ag* and *Se* atoms occupy the positions listed above and the *Cu* atoms are at $\begin{pmatrix} 1 & 3 \\ 4 & 4 \end{pmatrix} .105$ and $\begin{pmatrix} 3 & 1 \\ 4 & 4 \end{pmatrix} .895$.

Note that, if the *a* and *b* axes are interchanged, the parameters of the *Ag* and *Se* atoms remain the same, and the parameters of the *Cu* atoms become $\begin{pmatrix} 1 & 3 \\ 4 & 4 \end{pmatrix} .895$, $\begin{pmatrix} 3 & 1 \\ 4 & 4 \end{pmatrix} .105$. Hence, a random composite of both orientations will produce a statistical structure allowing one half of a *Cu* atom in each of the fourfold positions of the tetragonal (*P4/nmm*) cell discussed above.

The presence of superstructure reflections indicates that eucairite is not a random structure, but rather a structure in which there is a definite sequence to the orientation of the subcells, a sequence that

probably repeats itself periodically every five cells in the b direction. As the Cu positions have the same x and y parameters for both orientations of the subcell, the placement of the Cu atoms alone cannot account for the presence of superstructure reflections on the c axis, zero-level photographs. However, the Cu atom lying within a squashed Se tetrahedron is considerably closer to one pair of Se atoms than to the other pair, thus causing a dimensional distortion of the subcell so that $a \neq b$. The assembled sequence of the subcells in the two orientations that make up the true cell will not have equivalent atoms at $b/5$; $2b/5$; $3b/5$ and $4b/5$ of the true cell, and therefore will allow the additional reflections to appear on the zero level of the c axis photographs.

The actual crystal edifices are made up of domains of these larger true cells that are related to other domains of the edifice by having the c axes parallel, and the a axis of one parallel to the b axis of the other. The sizes of the domains are sufficiently large to produce sharp diffraction spectra. The authors have been unable to separate an edifice having a single domain of sufficient size to handle for diffraction purposes. Therefore the validity of this determination must rest upon the comparison (Table 2) of the observed intensities with the average of the $(h\ 0\ l)$ and the $(05hl)$ calculated intensities. In both Tables 1 and 2 the weak superstructure reflections have been omitted as no attempt has been made to determine the sequence of the orientation of the subcells.

The structure

In order to examine the crystal-chemical properties of eucairite, it is easiest to look at an idealized structure where the little subcells are all oriented in the same manner. Such an idealized structure is illustrated in Fig. 4.

The Ag atoms lie in an almost planar, centered array perpendicular to the c axis. Each Ag atom has four other Ag atoms at a distance of 2.96 Å; one close Se atom at 2.67 Å; four Se atoms at 3.59 Å; and one additional Se atom at 3.64 Å.

The Se atoms form a sheet of squashed tetrahedra in which each corner is shared with similar tetrahedra. Each Se atom has four other Se atoms at a distance of 3.30 Å. The Cu atoms lie within the squashed tetrahedron. The Cu is not located at the center of the tetrahedron but rather close to one of the longer edges, being at a distance of 2.06 Å from two of the Se atoms and a distance of 2.50 Å from the

other two. The closest *Cu-Ag* distance is 2.98 Å. It should be noted that one of the *Cu-Se* distances is closer than would normally be expected, whereas all the other interatomic distances seem reasonable.

A striking feature of the structure is that each *Ag* is bonded closely to only one *Se* atom and the cohesive forces holding the structure together must in part depend upon *Ag-Ag* metallic bonds. This feature

Table 2

Sin θ	Indices	F cal	Indices	F cal	$\frac{1}{2} (F _{h0l} + F _{05a1})$	
					calculated	observed
0.122	001	1	—	—	1	—
0.244	002	37	—	—	37	29
0.366	003	46	—	—	46	58
0.488	004	27	—	—	27	26
0.610	005	26	—	—	26	14
0.732	006	17	—	—	17	19
0.854	007	24	—	—	24	19
0.225	101	7	051	22	14	15
0.309	102	26	052	68	47	41
0.412	103	29	053	6	18	34
0.524	104	19	054	35	27	36
0.639	105	42	055	37	39	53
0.756	106	18	056	1	9	—
0.875	107	14	057	37	26	36
0.378	200	78	0.10.0	78	78	78
0.397	201	0	0.10.1	0	0	—
0.450	202	29	0.10.2	29	29	27
0.526	203	38	0.10.3	38	38	48
0.617	204	24	0.10.4	24	24	25
0.718	205	24	0.10.5	24	24	12
0.580	301	5	0.15.1	14	9	—
0.617	302	20	0.15.2	49	34	39
0.675	303	22	0.15.3	41	31	26
0.748	304	16	0.15.4	29	22	26
0.833	305	36	0.15.5	32	34	37
0.756	400	54	0.20.0	54	54	54
0.766	401	1	0.20.1	1	1	—
0.794	402	22	0.20.2	22	22	21
0.840	403	29	0.20.3	29	29	23

may readily explain the maleable nature of eucairite. (Crystals of eucairite will easily smear into plates while being ground in a mortar).

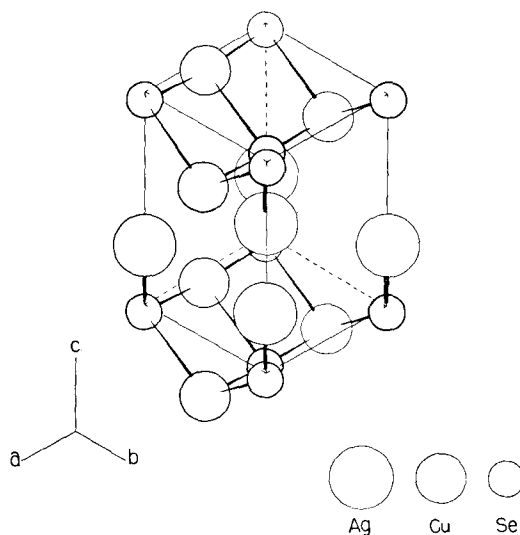


Fig. 4. Crystal structure of eucairite

High temperature modification

At a temperature between $190-195^{\circ}\text{C}$ eucairite inverts to a high temperature form. The pattern, Fig. 5, shows only four lines of the following observed relative intensities and d spacings:

1. very strong	2.15 Å	3. strong	1.84 Å
2. very weak	2.00 Å	4. weak	1.75 Å

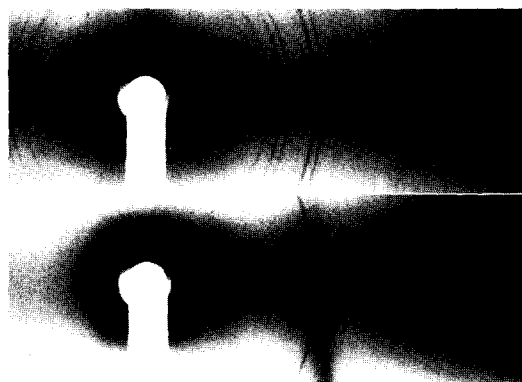


Fig. 5. Powder pattern of eucairite ($CoK\alpha$) (a) room temperature, (b) above 195°C

The crystals return to the low form upon rapid cooling in air. The rapidity and reversibility of this transition should not necessarily lead to the conclusion that eucairite has a polymorphic transformation of the rapid displacive type. The great mobility of both silver and copper in semi-metals such as sulfides and selenides, even at fairly low temperatures will facilitate the ease of reconstruction to stable forms without the aid of a flux.

Acknowledgements

The authors wish to express their appreciation to Prof. FRANZ WICKMAN, Dr. GEORGE SWITZER and Dr. ROBERT COLEMAN for supplying the crystals investigated.

Department of Geology, University of Chicago, USA