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THE CRYSTAL STRUCTURE OF ALLOCLASITE, CoAsS, AND THE ALLOCLASITE-COBALTITE TRANSFORMATION*

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ABSTRACT

Alloclasite, CoAsS, crystallizes in the monoclinic space group $P2_1$ with lattice constants *a* 4.661(2), *b* 5.602(2), *c* 3.411(1)Å, β 90°2(5)′, $Z=2$. Full-matrix least-squares refinement of 600 observed reflections with anisotropic temperature factors and an ordered arrangement of As and S resulted in an *R* factor of 0.029. The systematic extinction of 00*l* with *l* odd has been found to be structural in nature. Because alloclasite has a marcasite-type structure it may be readily transformed to either the ordered orthorhombic or the disordered cubic form of cobaltite. The structure of ordered cobaltite was refined on the basis of an absorption-corrected version of previously published data for purposes of comparison.

SOMMAIRE

L'alloclasite CoAsS cristallise dans le groupe spatial monoclinique $P2_1$, avec constantes réticulaires: *a* 4.661(2), *b* 5.602(2), *c* 3.411(1)Å, β 90°2(5)′, $Z=2$. Sa structure cristalline a été affinée sur six cents réflexions observées, par la méthode des moindres carrés à matrice entière, avec coefficients d'agitation thermique anisotrope et une mise en ordre de As et S, jusqu'à un résidu *R* de 0.029. L'absence systématique de 00*l* avec *l* impair s'est avérée structurale. Du fait que sa structure est du type marcasite, l'alloclasite peut se transformer facilement en l'un eou l'autre des formes de la cobaltite: orthorhombique ordonnée ou cubique désordonnée. A titre de comparaison, la structure de la cobaltite ordonnée a été affinée au moyen de données déjà publiées, corrigées cette fois pour les erreurs d'absorption.

(Traduit par la Rédaction)

INTRODUCTION

According to Krenner (1929), alloclasite was first named and described in 1866 by G. Tschermak, who believed the new mineral to be very similar to glaucodot but to contain bismuth as an essential constituent. Tschermak later concluded, however, that alloclasite was not after all a distinct species but a bismuthian variety of cobaltite. A re-examination of material from the Elizabeth mine, Oravicza, Roumania (Tschermak's type locality for alloclasite) was made by Krenner, who concluded that the mineral was a high-cobalt glaucodot on the basis of a new analysis which showed only 0.1% Bi. In 1963 Polushkina & Sidorenko described a mineral, from an unnamed locality in the Tuva autonomous region, U.S.S.R., which from their reported analysis and powder pattern is certainly alloclasite. They did not, however, suggest this identification in their paper, referring to the mineral as a structural variety of cobaltite.

Although the early literature on alloclasite casts considerable doubt on its validity as a distinct mineral species, its powder pattern was sufficiently unique that Berry & Thompson (1962) included the mineral as a valid species in the Peacock Atlas. Subsequent work has tended to confirm its validity, although there has existed considerable confusion about its space group and symmetry. Polushkina & Sidorenko (1963) suggested unit-cell parameters and the space group *Pnnm* for their 'structural variety of cobaltite' on the basis of a graphical indexing of their powder pattern by analogy with that of marcasite, but made no single-crystal studies of their material. Borishanskaya *et al.* (1965) reported an analysis and powder pattern for alloclasite from an iron-ore deposit at South Dashkesan, Azerbaydzhan S.S.R., and suggested that it was a modification of glaucodot with a distinctive composition, intrinsic structure and optical properties, although again no single-crystal work was done. The first reported single-crystal study of alloclasite was that of Kingston (1971), who used material from the type locality and defined the space group as $P22_12_1$. Almost simultaneously, Petruk *et al.* (1971) reported single-crystal data on alloclasite from the 4th level, Silverfields mine, Cobalt, Ontario, giving the space group $P222_1$. More recently, alloclasite analyses and powder pat-

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terns have been reported for material from Bou-Azzer, Morocco (Johan *et al.* 1972) and from Lautaret, France (Maurel & Picot 1973); however, no further single-crystal studies have been reported.

The present study was undertaken in order to determine the true space group and crystal structure of alloclasite, and to explain the nature of the structural transformation alloclasite-cobaltite (both with formula CoAsS). The same specimen of type material as was used by Kingston (1971) (USNM 62855, Elizabeth mine, Oravicza, Roumania) was borrowed from the United States National Museum. As noted by Kingston, this specimen consists of compact radiating bundles of alloclasite crystals in a blocky, white calcite gangue with minor intergrown wire gold; this description compares favorably with that given by Krenner (1929) for his material from this locality. All results given here were obtained from crystal fragments selected from a single such bundle.

EXPERIMENTAL

The results of new microprobe analyses and density determinations are given in Table 1, together with those reported by Kingston (1971) and Petruk *et al.* (1971). Weissenberg photographs appeared initially to confirm the orthorhombic space group $P22_12_1$ ($0k0$ absent for k odd, $00l$ absent for l odd). The slight variation occasionally observed between $\bar{h}kl$ and hkl was attributed to absorption, as $\mu R \simeq 14$ for the crystal used. Double-radius zero-level Weissenberg photographs, calibrated with superimposed Si powder lines, were taken in order to refine the unit-cell parameters on the basis of measured values of θ for high-angle resolved reflections (program LAPA, T. Ito, unpublished); the results of the final such refinement are given in Table 1.

A complete sphere of intensities was collected using Cu$K\alpha$ radiation and the ω-scan technique, for a crystal in the form of a tetragonal prism mounted on a Supper-Pace autodiffractometer. The intensities were corrected for Lorentz and polarization effects and for absorption, and then averaged to give 98 independent observed reflections.

TABLE 1. ANALYSES AND CELL PARAMETERS REPORTED FOR ALLOCLASITE

	Present work		Kingston(1971)		Petruk *et al.*(1971)*	
	Wt.%	Atoms	Wt.%	Atoms	Wt.%	Atoms
Co	25.1	1.36	25.4	1.45	26.5	1.52
Fe	6.7	0.38	8.4	0.49	6.0	0.36
Ni	1.0	0.05			tr	
As	47.5	2.02	44.3	1.99	49.0	2.20
S	19.9	1.98	18.7	1.96	17.0	1.80
	100.2		96.8		98.5	
a	4.661(2)Å		4.641		4.658	
b	5.602(2)		5.606		5.621	
c	3.411(1)		3.415		3.399	
β	90°2(5)'					
Space group	$P2_1$		$P22_12_1$		$P222_1$	
Z	2					
D(meas.)	5.95(2) gcm^{-3}		5.91		6.02	
μ_lMoKα	228 cm^{-1}					

*Sample #9570

All attempts to solve the structure in space group $P22_12_1$ failed, even for severely disordered models. Because of the similarity in their cell parameters and their analogous compositions, it was decided to investigate a possible relationship between the structures of alloclasite and costibite (CoSbS—Rowland *et al.* 1975). This would require that all atoms of alloclasite occupy 2(*a*) special positions in the space group $Pn2_1m$. The extinction condition for this, $0kl$ absent for $k+l$ odd, was violated by several reflections, which were therefore removed from the data set. Refinement of a costibite-like model terminated at $R \simeq 0.15$ and gave unreasonably short Co-As/S bonds. It was then noted that the well-resolved Patterson map could also be interpreted in terms of a Co-As/S octahedral structure in the space group $P2_1nm$. Reflections of type $h0l$ with $h+l$ odd were removed from the data set and the cell contents transformed to the new origin. Refinement of a model in which Co was ordered with As plus S statistically occupying the other two sites terminated at $R=0.088$. Five of the six Co-As/S bonds, as well as the As/S-As/S bond, fell in the range 2.322 to 2.346Å. The remaining Co-As/S distance of 2.190Å was, however, unreasonably short for an octahedral bond.

It appeared that this structure must be essentially correct, even though it was not crystallographically satisfactory, being in an obviously incorrect space group. The atomic positions were therefore re-examined to determine whether there was a possible monoclinic space group which would accept the $P2_1nm$ sites, remove the extinction condition imposed, and allow an ordered arrangement of As and S. With a suitable origin transformation, the space group $P2_1$ (second setting) fulfils these conditions. The cobalt sites remain unchanged and the four As/S sites may be split into a pair for each of As and S. The only extinction condition of $P2_1$ ($0k0$ with k odd) is already present, and therefore the condition of $00l$ absent with l odd must be structural in nature.

A second crystal, in the form of a trigonal prism elongate [010] and bounded by $\{101\}$, $\{10\bar{1}\}$, $\{\bar{4}01\}$, $\{010\}$ and $\{0\bar{1}0\}$ cleavage faces (crystal volume $= 0.126 \times 10^{-5}$ cm^3), was selected for the collection of a new data set. In this case monochromatized Mo$K\alpha$ radiation

TABLE 2. ATOMIC COORDINATES AND TEMPERATURE FACTORS ($x10^4$) FOR ALLOCLASITE

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B_{equiv}
Co	0.24824(20)	0.0	0.24480(28)	113(2)	84(1)	222(3)	0(1)	0(2)	-2(2)	1.02(2)
As	0.04766(13)	0.37149(24)	0.25547(19)	154(2)	112(1)	259(3)	-4(2)	-5(2)	-2(3)	1.37(2)
S	0.44104(22)	0.62236(37)	0.24239(29)	159(4)	117(3)	320(8)	6(4)	-9(4)	4(7)	1.45(4)

was used and intensities were measured to $\theta_{max}=45°$. The raw intensities were corrected for Lorentz and polarization effects appropriate to this geometry by a local program (P. Engel, unpublished) and for absorption by the analytic method of Alcock (1970); maximum and minimum values of the transmission factor were 0.547 and 0.354. This resulted in 759 independent reflections of which 159 were classified as unobserved and omitted from the refinement.

STRUCTURE REFINEMENT

Starting coordinates for all atoms in $P2_1$ were obtained by shifting the origin to –¼,¼,¼ in the $P2_1nm$ cell. The initial assignment of As and S sites was arbitrary, but proved to be correct in subsequent refinement. The origin was defined by fixing the Co y-coordinate at zero. Six cycles of least-squares refinement with anisotropic thermal parameters for all atoms reduced R from its initial value of 0.13 to 0.029 for the 600 observed reflections, or 0.044 for all data, with no unobserved reflection calculating at greater than 1.5 times its input value. The final positional and anisotropic thermal parameters are given in Table 2.

The analysis given in Table 1 is essentially stoichiometric for As and S; however, the Co+Fe+Ni sum at 1.79 atoms is significantly low. Therefore, after all other parameters had converged, several additional cycles of least-squares refinement were run in which the occupancy parameters alone were varied. The As site converged at 1.967(4) As+0.033 S, and the S site at 1.963(5) S+0.037 As, for a total cell content of 2.004 As and 1.996 S atoms. The Co site remained under-occupied throughout the refinement, final values being 1.404(3) Co + 0.451 Fe.

Finger's (1969) least-squares program RFINE was used throughout, with bond length and angle errors calculated by his linking program BADTEA. Atomic scattering factors used were those given by Cromer & Mann (1968) for neutral atoms, together with the anomalous dispersion coefficients of Cromer (1965). The final atomic and thermal parameters are listed in Table 2, the calculated bond lengths and angles in Table 3. The table containing observed and calculated structure factors for alloclasite has been deposited with the National Science Library.*

TABLE 3. INTERATOMIC DISTANCES AND BOND ANGLES FOR ALLOCLASITE

Co OCTAHEDRON		As TETRAHEDRON		S TETRAHEDRON	
		DISTANCES(Å)			
Co-As	2.282	As-Co	2.282	S-Co(h)	2.299
-As(a)	2.308	-Co(f)	2.308	-Co(i)	2.309
-As(b)	2.309	-Co(g)	2.309	-Co(j)	2.372
-S(c)	2.299	-S	2.311	-As	2.311
-S(d)	2.309	mean	2.303	mean	2.323
-S(e)	2.372				
mean	2.313				
		ANGLES			
As-Co-As(a)	91.59°	Co-As-S	103.25	Co(h)-S-Co(i)	121.41
-As(b)	92.96	-S(f)	122.77	-Co(j)	120.13
-S(c)	178.63	-S(g)	121.15	-As	104.45
-S(d)	89.88	Co(f)-As-S	107.40	Co(i)-S-Co(j)	93.56
-S(e)	88.55	-Co(g)	95.26	-As	109.35
As(a)-Co-As(b)	95.26	Co(g)-As-S	105.65	Co(j)-S-As	107.11
-S(c)	87.10	mean	109.24	mean	109.34
-S(d)	177.81				
-S(e)	84.86				
As(b)-Co-S(c)	86.77				
-S(d)	86.29				
-S(e)	178.48				
S(c)-Co-S(d)	91.45				
-S(e)	91.72				
S(d)-Co-S(e)	93.56				
mean	89.72				

EQUIVALENT SITES IF Co, As AND S ARE AT x, y, z

(a)	$-x, -\frac{1}{2}+y, -z+1$	(f)	$-x, \frac{1}{2}+y, -z+1$
(b)	$-x, -\frac{1}{2}+y, -z$	(g)	$-x, \frac{1}{2}+y, -z$
(c)	$x, -1+y, z$	(h)	$x, 1+y, z$
(d)	$-x+1, -\frac{1}{2}+y, -z$	(i)	$-x+1, \frac{1}{2}+y, -z$
(e)	$-x+1, -\frac{1}{2}+y, -z+1$	(j)	$-x+1, \frac{1}{2}+y, -z+1$

DISCUSSION OF THE ALLOCLASITE STRUCTURE

It has now been confirmed that alloclasite has a structure closely related to that of costibite, i.e., of marcasite type. If the costibite origin (in $Pn2_1m$) is translated to 0,0,–¼, and Sb is replaced with As, the result is a very close approximation of the alloclasite structure. This origin shift destroys both the mirror and the glide planes of the orthorhombic space group, leaving only the 2_1 screw-axis parallel to b. The apparent extinction of $00l$ with l odd is structural in nature and was confirmed by the refinement, in that all reflections $00l$ with l odd calculated at essentially zero.

As alloclasite has a marcasite-type structure, an origin shift of ¼,½,¼ may be applied to the data of Table 2 for a direct comparison of

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*This table is available, at a nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada, K1A 0S2.

the two sets of atomic coordinates. The sites occupied by an ordered set of As and S in alloclasite are equivalent to the four-fold site occupied by S in marcasite. This results in staggered layers of Co octahedra with As and S atoms occupying planes at $x \simeq 0$ and $x \simeq 1/2$, respectively. Each octahedron (Fig. 1) shares an As-S edge with two other octahedra in the same layer, forming octahedral chains in the *c* direction. Its six corners are shared with corners of four octahedra above and four below the layer. Each As or S atom is tetrahedrally coordinated to three Co plus either an S or As atom (Fig. 2); the tetrahedra are interpenetrating with the As-S bond (2.311Å) shared.

Given that alloclasite has a marcasite-type structure, the observed transformation of alloclasite into cobaltite (Maurel & Picot 1973; 1974) is not as exceptional as was previously supposed, and can be readily explained as a transformation of the marcasite-into-pyrite type (Fleet 1970). In order to settle several problems relating to the published structure of ordered cobaltite (Giese & Kerr 1965), a refinement of an absorption-corrected version of their data was made and is presented in the following section.

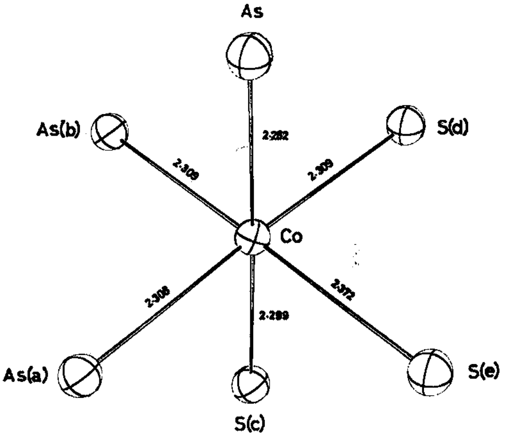

FIG. 1. Cobalt octahedron of alloclasite, showing interatomic distances in Å.

REFINEMENT OF THE ORDERED COBALTITE STRUCTURE

Structures for both the disordered cubic ($Pa3$) and the ordered orthorhombic ($Pca2_1$) polymorphs of cobaltite have been reported by Giese & Kerr (1965). A careful consideration of their Table 4 suggested the existence of two probable errors in the atomic parameters given for ordered cobaltite; first, the *z* coordinates for all atoms appear to have been refined, and second, the *y* coordinate of S should presumably be negative. Moreover, since no transformation equations are given, it is unknown which setting in $Pca2_1$ was used.

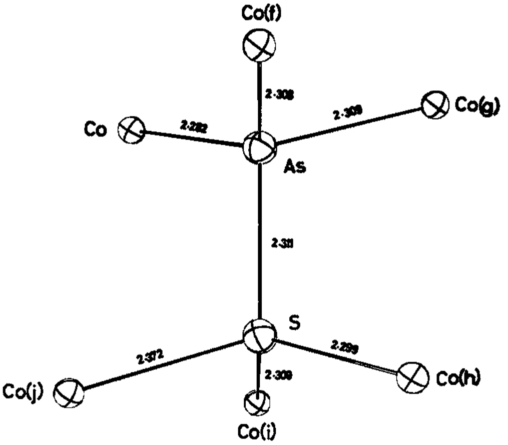

FIG. 2. Arsenic and sulfur coordination in alloclasite, showing the orientation of the two interpenetrating tetrahedra. Interatomic distances are given in Å.

The observed *F* values of Giese & Kerr (1965) were corrected for absorption, using the analytic program of Alcock (1970), on the basis of information given in their paper. It was necessary to assume that $\mu = 27.5°$ for their precession data (given the areal extent of reflections in their structure-factor list and the further assumption that $F = 60$mm). Starting parameters used in the subsequent refinement were those given for PtGeSe (Entner & Parthé 1973) in $Pca2_1$. These refined very rapidly to the values given in Table 4. The final *R* factor for all data was 0.102 or, with the badly underestimated 200 and 201 reflections omitted, 0.072. The 210 reflection, which should have been observable on the original films, was not given in the published structure-factor table of Giese & Kerr;

TABLE 4. REFINED ATOMIC PARAMETERS FOR ORDERED COBALTITE AND THE ASSOCIATED INTERATOMIC DISTANCES

Atom	x	y	z	B
Co	0.00575(140)	0.74091(147)	0.0	0.17(10)
As	0.38278(94)	0.13019(97)	0.61309(285)	0.24(9)
S	0.61633(322)	-0.36886(264)	0.38054(442)	0.61(26)

Interatomic distances

	Present work	Giess & Kerr(1965)
Co-As	2.347(21)Å	2.31
-As	2.371(21)	2.36
-As	2.378(21)	2.39
-S	2.285(35)	2.26
-S	2.295(35)	2.29
-S	2.296(35)	2.36
As-S	2.271(51)	2.30

it was treated as unobserved in the refinement and returned a calculated value near zero.

Given the large errors inherent in the refinement of such a limited data set (only *hk*0 and *h*0*l* reflections were available), the revised interatomic distances given in Table 4 should be regarded merely as approximations. There is a clear tendency, however, for the Co-As/S octahedron to be more regular and for the individual Co-As and Co-S distances to be much closer to their averages than in the original structure. The following transformations relate the reported structures of Giese & Kerr to the present refined structure; subscript *c* refers to the cubic (*Pa*3) disordered polymorph, subscript *g* to the ordering arrangement proposed by Giese & Kerr, and subscript *o* to the ordering arrangement of the present refinement:

$$\begin{aligned} x_o &\simeq y_c \simeq x_g \\ y_o &\simeq x_c - 1/4 \simeq y_g - 1/2 \\ z_o &\simeq -z_c \simeq -z_g \end{aligned}$$

If either *o* or *g* is transformed to *c*, a random arrangement of both the As and S atoms is required to fill one 8(*c*) special position in the disordered *Pa*3 structure. The implication of Giese & Kerr's Table 4, however, is that the disordered 8(*c*) position is split into two ordered 4(*a*) positions, at *x*, *x*, *x* and -*x*, -*x*, -*x* in terms of the *Pa*3 site. Such an ordering arrangement would imply that the ordering process in cobaltite proceeds via an ullmanite-type structure (Takeuchi 1957), which is clearly not the case.

THE ALLOCLASITE-COBALTITE TRANSFORMATION

On the basis of this refined cobaltite structure, it is possible to show that a transformation of the marcasite-into-pyrite type (Fleet 1970) will lead directly from the ordered alloclasite to the ordered cobaltite arrangement with a minimum of structural disturbance. The work of Johan *et al.* (1972) supports the proposal that this transformation can produce in nature the ordered orthorhombic form of cobaltite instead of the disordered cubic variety. Their Figure 1 shows a crystal of alloclasite which contains lamellae of cobaltite accompanied by a network of fine cracks. Similar networks of healed cracks are visible also in the figures of Maurel & Picot (1973) for completely transformed crystals, and such a stress pattern is implicit in the transformation theory of Fleet. Moreover, in the powder pattern for their alloclasite, Johan *et al.* list a strong (010) line at d=5.63Å. This reflection is space-group forbidden for both the alloclasite and the disordered cobaltite structures, but is intense for the ordered cobaltite structure. An ordered arrangement of As and S can be maintained during a transformation from alloclasite to the orthorhombic cobaltite modification; however, this ordering is lost upon its inversion to the cubic form. The confusion in the literature, due to reports of what are obviously mixtures of these phases, can be somewhat clarified by applying the following structure-related diagnostic. The powder patterns of the three phases contain essential differences: alloclasite ($P2_1$) has $d(110) \simeq 3.58$Å; ordered cobaltite ($Pca2_1$) has $d(010) \simeq 5.60$Å; disordered cobaltite (*Pa*3) may be distinguished from both of them by the absence of these two lines. In addition, arsenopyrite, which is frequently associated with all of these minerals, is differentiated from them by the presence of a strong line at d=2.664Å.

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