THE CRYSTAL STRUCTURES OF ORDERED AND DISORDERED COBALTITE

R. F. Giese, Jr.[1] and P. F. Kerr, *Department of Geology, Columbia University, New York.*

Abstract

Single crystal x-ray studies indicate that the mineral cobaltite (CoAsS) is orthorhombic with the arsenic and sulfur partially disordered. Heating in vacuum to 850° C. completely disorders the arsenic and sulfur. The space group of this form is $Pa3$ and the structure is that of pyrite. Annealing in vacuum from 450° C. orders the arsenic and sulphur completely. The space group is $Pca2_1$ (pseudoisometric). Examination of the related mineral gersdorffite (NiAsS) shows that it belongs to space group $P2_13$ and has an ullmanite (NiSbS) structure.

Introduction

The mineral cobaltite is a sulfarsenide of cobalt, CoAsS, in which minor amounts of iron and nickel substitute for cobalt, and antimony substitutes for arsenic (Beutell, 1911). It is found in high temperature veins or as a constituent of disseminated deposits in metamorphosed rocks. Crystals are common and the most frequent forms are the cube and pyritohedron, and, less frequently, the octahedron (Palache *et al.* 1944).

On the basis of crystal morphology, cobaltite has generally been assumed to have the symmetry of the pyrite group. This symmetry is isometric-diploidal $- 2/m \ \overline{3}$ (see for example, Dana, 1892). With the determination of the pyrite structure (Bragg, 1914) it became clear that cobaltite must have a lower symmetry, since the substitution of an As-S unit for the S-S unit of pyrite would destroy the symmetry centers of the S-S units. This lower symmetry was thought to be tetartoidal -23, and minerals similar to cobaltite (ullmanite and gersdorffite) were placed in the "cobaltite group" (Palache *et al.* 1944).

The first x-ray study of cobaltite was done by Mechling (1921). From the symmetry of Laue photographs, he proposed a structure based on the space group $P2_13$. Shortly after, Schneiderhöhn (1922) examined a single specimen of cobaltite with the reflecting microscope and found it to be anisotropic in polarized light. He suggested that cobaltite had undergone an inversion after formation and was actually orthorhombic (the symmetry by analogy with pyrite and marcasite). This optical anisotropy has been confirmed by several others (Sampson, 1923; Flörke, 1923, 1926; Ramdohr, 1950; Onorato, 1957). When heated above 850° C. and quenched, cobaltite was reported to be optically isotropic (Flörke, 1926).

[1] Present Address: Research and Development Division, The Carborundum Company, Niagara Falls, New York.

Ramsdell considered the question in 1925 and confirmed the apparent isometric character of powder photographs. He suggested that the optical anisotropy might be either (1) the result of deformation twinning caused by grinding and polishing the specimen, or (2) evidence that cobaltite is pseudoisometric. Peacock and Henry (1947) on the basis of intensity measurements of powder photographs decided that cobaltite had a disordered structure in which the arsenic and sulfur were substituting for each other. This is identical with the structure of pyrite. Onorato (1957) using intensity data obtained from Weissenberg photographs, proposed the symmetry $P2_1/c$. The agreement between observed and calculated intensities was poor. It has recently come to the authors' attention, through the kindness of Dr. Winterberger, that an x-ray study of cobaltite was done by Le Damany in 1962. The study concerned only natural cobaltite and indicated a partial disorder of arsenic and sulfur.

PRELIMINARY INVESTIGATION

Several of the previous investigations (Peacock and Henry, 1947; Onorato, 1957) used copper radiation. This resulted in a very high fluorescent background from the cobalt. As an initial check on the accuracy of the space group determination, several samples of cobaltite were examined by powder diffraction techniques with iron radiation and a very small sample. The results (Table 1) clearly showed several reflections forbidden by the space group assigned by Peacock and Henry. A small sample and long exposure were necessary to show these weak lines. All such lines were indexable using the cobaltite unit cell, indicating that they were probably not caused by impurities. To resolve the apparent contradictions in cobaltite, it was decided to do a structure determination using single crystal techniques.

SPACE GROUP DETERMINATION

The cobaltite samples used in the single crystal studies were from Cobalt, Ontario (Columbia Collection No. 200-83) and were in the form of small cubes (1–2 mm edge), some being modified by octahedra. Using a small cleavage fragment, the precession camera was used to take orthogonal zero layer and first upper layer photographs with filtered molybdenum radiation. The photographs indicated a primitive cell and orthogonal glide planes as in space group $Pa3$. However, several weak odd order prism reflections were present which should have been extinguished by the glide planes. It was later learned that these "forbidden reflections" were also observed by Takéuchi (1956). These reflections suggested the possibility of some sort of disorder. One natural form of disorder would be a partial substitution of sulfur and arsenic. Complete

TABLE 1. VALUES FOR SOME COBALTITE SPECIMENS

hkl	1			2		3		4	
	d obs.	d calc.	I	d obs.	I	d obs.	I	d obs.	I
100[1]	5.56	5.58	2	5.58	2				
110[1]	3.94	3.95	1	3.94	1				
111	3.30	3.22	2	3.31	2	3.35	3	3.28	$\frac{1}{2}$
200	2.77	2.79	8	2.79	8	2.78	7	2.83	6
210	2.49	2.50	10	2.50	10	2.49	10	2.54	10
211	2.27	2.28	9	2.28	9	2.28	9	2.29	8
220	1.973	1.974	6	1.972	3	1.970	2	1.988	2
300, 221	1.856	1.861	1						
310[1]	1.762	1.765	$\frac{1}{2}$						
311	1.680	1.683	10	1.682	10	1.681	10	1.690	9
222	1.608	1.611	1	1.610	$\frac{1}{2}$	1.608	$\frac{1}{2}$	1.609	$\frac{1}{2}$
320	1.545	1.548	4	1.547	4	1.548	2	1.559	3
321	1.490	1.492	8	1.490	6	1.491	8	1.496	4
400	1.393	1.400	$\frac{1}{2}$					1.403	$\frac{1}{2}$
410, 322	1.350	1.354	$\frac{1}{2}$						
411, 330	1.310	1.316	$\frac{1}{2}$						
331	1.277	1.281	$\frac{1}{2}$			1.276	$\frac{1}{2}$		
420	1.246	1.248	3	1.247	$\frac{1}{2}$	1.249	$\frac{1}{2}$	1.253	$\frac{1}{2}$
421	1.216	1.218	5	1.217	3	1.218	4	1.222	1
332	1.189	1.190	3	1.189	1	1.189	1	1.198	$\frac{1}{2}$
422	1.139	1.139	3	1.139	$\frac{1}{2}$	1.141	$\frac{1}{2}$	1.148	$\frac{1}{2}$
500, 430	1.115	1.116	$\frac{1}{2}$						
510, 431	1.093	1.095	$\frac{1}{2}$						
511, 333	1.073	1.074	8	1.074	6	1.076	6	1.080	4
520, 432	1.033	1.037	5	1.036	6	1.038	5	1.042	2
521	1.018	1.019	3	1.019	1	1.021	3	1.022	1
440	.987	.987	5	.987	6	.988	7	.989	3

1. Cobalt, Ont., 20 hrs., 0.3 mm. glass capillary.

2. Tunaberg, Sweden, 18 hrs., very small fiber.

3. Cobalt, Ont., 8 hrs., 0.3 mm. glass cap. (USNM 95740).

4. Cobalt, Ont., ?, ?(Peacock and Henry, 1947).

[1] Reflections forbidden in space group proposed by Peacock and Henry (1947).

disorder would yield the structure suggested by Peacock and Henry (1947) and have the space group $Pa3$.

DISORDERED STRUCTURE DETERMINATION

Crystals of cobaltite were sealed under vacuum in fused quartz tubes. These were placed in a muffle furnace and held at an elevated temperature for one or two days and then quenched in cold water. After quenching, a small fragment was examined by precession methods. It was hoped

that an increase in temperature would permit the arsenic and sulfur to randomly substitute for each other to a greater degree than in the natural material. As the temperature prior to quenching increased, the forbidden reflections became weaker.

At the highest temperatures ($>700°$ C.), decomposition became a problem. After quenching, the crystal surfaces were found to be coated with a mixture of decomposition products. However, in the center of the crystal, there appeared to be little alteration. Precession photographs indicated the central material was still cobaltite. This method was used by Florke (1926) in his high temperature optical studies.

A sample held at $800–850°$ C. for two days showed only the systematic extinctions of space group *Pa3*. This crystal was used to collect (hko) intensity data. It was a roughly orthogonal cleavage fragment with the dimensions $.20 \times .13 \times .04$ mm. It was mounted (on the precession camera) with the smallest dimension parallel to the *x*-ray beam. No correction was made for absorption errors. Diffraction intensities were estimated by comparison with a standard scale. The usual Lorentz and polarization corrections were made.

Assuming the structure to be of the pyrite type with arsenic and sulfur substituting for each other, the structure is determined by one positional parameter, that of the (arsenic+sulfur) atom. Structure factors were calculated using various values for this parameter and the normal R-factor was plotted against the parameter. The atomic scattering factors were taken from the Internationalle Tabellen, V. 2. The results are shown in Fig. 1 and Table 2. The best fit is obtained when x = .380. No temperature factor was used in the calculations.

ORDERED STRUCTURE DETERMINATION

A single crystal from the same locality was sealed in a quartz tube and heated to $450°$ C. It was cooled slowly to room temperature over a period of ten hours in an attempt to order the arsenic and sulfur. Weissenberg and precession photographs indicated that the space group was either *Pca2₁* or *Pbcm*. The cell dimensions remained essentially the same (5.582 $\pm .002A$) and the cell was isometric within measurement errors. A cleavage fragment ($.25 \times .10 \times .07$ mm.) was used to collect (hko) intensity data with a precession camera and (hol) data were collected with a Weissenberg camera. Intensities were estimated as before and reduced to structure factors in the usual way.

Regarding this as an order-disorder mechanism, the space group of the ordered form must be a subgroup of the disordered form (Buerger, 1947). This rules out the centrosymmetric space group *Pbcm*.

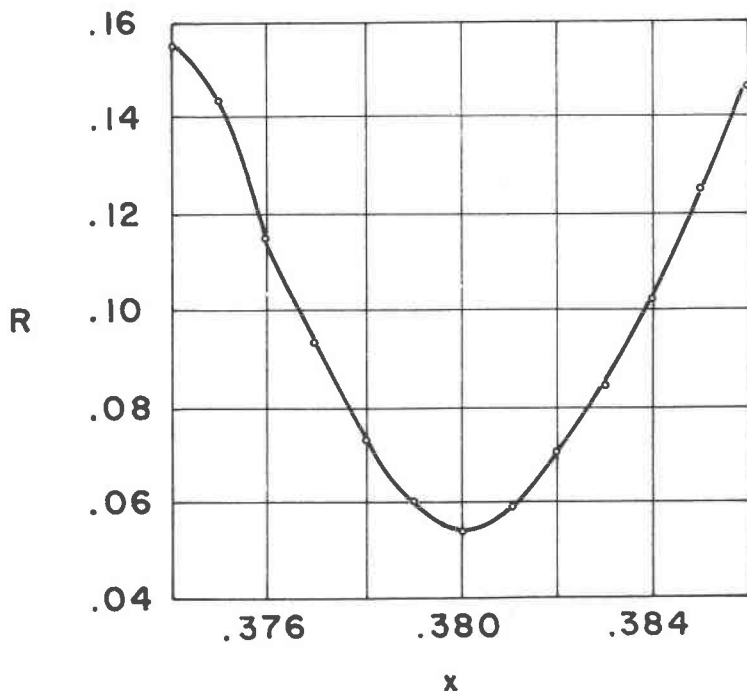A trial structure was found in space group *Pca2₁* based upon an order-

Fig. 1. Plot of the R-factor *versus* the variable parameter, x, in disordered cobaltite.

ing of the arsenic and sulfur atoms. The parameters were refined using least squares methods and the scattering tables in Volume 3 of the International Tables for X-ray Crystallography. The final R factors for (hko)

TABLE 2. DISORDERED CoAsS—SPACE GROUP *Pa3*

hkl	F Calc.	F Obs.	hkl	F Calc.	F Obs.
200	91.0	85.0	420	49.9	51.8
400	−48.4	52.5	430	8.8	8.9
600	30.3	27.2	440	134.3	129.0
210	97.7	95.2	450	− 5.9	X
220	72.1	70.0	460	52.4	56.9
230	88.6	93.5	610	−56.4	52.4
240	49.9	53.8	620	42.7	40.5
250	−54.4	59.3	630	−60.6	62.2
260	42.7	39.5	640	52.4	52.1
270	−62.0	61.2	650	40.6	40.8
410	8.8	13.6			

X = not observed.

and (hol) are .10 and .12. The observed and calculated intensities are listed in Table 3.

POLISHED SECTION STUDY

To verify the results obtained from the x-ray studies, two samples were prepared for microscopic study. Both came from Sweden (locality unknown) and appeared to be single crystals; one a cube and the other a pyritohedron.

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS FOR ORDERED CoAsS

hkl	F Obs.	F Calc.	hkl	F Obs.	F Calc.	hkl	F Obs.	F Calc.
020	93.4	−97.8	340	19.6	12.5	004	57.8	54.6
030	33.7	30.7	350	35.2	−31.6	006	45.1	59.7
040	56.1	−55.0	360	69.5	67.3	200	99.1	100.2
050	44.9	43.9	400	52.5	−53.5	201	121.2	113.2
060	30.8	−27.3	410	40.2	38.7	202	92.9	78.8
070	49.7	−46.7	420	58.5	−52.7	203	109.8	102.3
120	99.2	−102.6	430	47.3	−44.5	204	52.4	52.3
130	31.4	27.5	440	143.5	147.8	205	47.8	65.0
140	15.6	11.0	450	11.7	−8.6	206	38.2	46.7
150	30.4	−26.5	460	59.9	−56.1	400	52.5	53.5
160	67.2	63.1	510	35.2	−27.9	401	29.2	20.4
170	13.5	−11.3	520	64.0	56.0	402	91.6	75.0
200	99.1	100.2	530	8.8	−4.6	403	20.7	12.3
220	73.6	−78.4	540	7.8	−4.6	404	143.4	148.3
230	12.3	−8.5	550	6.8	6.7	405	16.9	9.9
240	52.9	50.4	600	31.0	25.4	600	31.0	25.4
250	21.8	18.0	610	10.3	10.2	601	78.0	65.8
260	48.0	−42.7	620	48.0	−44.3	602	59.1	46.6
310	32.1	24.6	640	62.0	60.2	603	82.8	77.7
320	90.4	−99.2	710	33.5	−33.8	604	78.3	61.2
330	37.6	33.1	002	84.9	113.4			

The anisotropy of both was weak and difficult to photograph using a normal lighting arrangement. The photographs (Figs. 2, a–c) were taken using a very high intensity xenon light source. Figure 2a shows the cube cobaltite and Fig. 2b the pyritohedral cobaltite. These clearly show the previously reported anisotropy. Some small fragments of the latter were sealed in an evacuated silica tube and heated to 825° C. for one hour and quenched in water. Figure 2c shows a small fragment of this material which is almost completely isotropic. X-ray diffraction confirmed that the material was still cobaltite.

DISCUSSION

Electron density projections of the ordered and disordered forms of cobaltite are shown in Fig. 3. The contour interval is on an arbitrary scale. The final atomic parameters, atomic radii and interatomic dis-
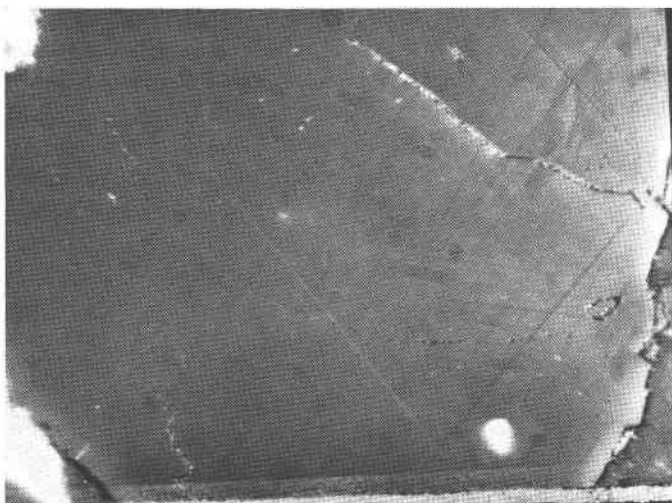
Fig. 2. Polished section photographs of cobaltite (150×). Figs. 2a, b—natural material. Fig. 2c—material quenched from 850°C.

FIG. 3. Electron density projections of disordered (3a) and ordered cobaltite (3b, 3c). The contours are drawn with an arbitrary interval. The first solid contour is at height zero. Figure 3a is projected onto (001). Figures 3b and 3c are projected onto (001) and (010) respectively.

tances are listed in Table 4. To more easily compare the ordered and disordered forms, the parameters of the ordered form have been transformed to coincide with the disordered cell. It is seen that the shifts, caused by ordering, are small.

TABLE 4. ATOMIC PARAMETERS, BOND LENGTHS AND ATOMIC RADII IN ORDERED
AND DISORDERED COBALTITE

| | Parameters | | | | | |
| | Ordered | | | Disordered | | |
	X	Y	Z	X	Y	Z
Cobalt	$-.010$	.006	.011	0	0	0
Arsenic	.380	.381	.383	.380	.380	.380
Sulfur	$-.380$	.380	$-.382$	$-.380$	$-.380$	$-.380$

| Bond Lengths | | |
	Ordered	Disordered
Cobalt—Arsenic	2.31 A	
Cobalt—Arsenic	2.39	
Cobalt—Arsenic	2.36	
Cobalt—Sulfur	2.36	
Cobalt—Sulfur	2.26	
Cobalt—Sulfur	2.29	
Arsenic—Sulfur	2.30	
(Arsenic+Sulfur)—(Arsenic+Sulfur)		2.31
Cobalt—(Arsenic+Sulfur)		2.31

| Atomic Radii | | | |
	Disordered Cobaltite	Ordered Cobaltite	Arsenopyrite (Morimoto and Clark, 1961)
Iron			1.14 A
Cobalt	1.16 A	1.17 A	
Arsenic		1.18	1.21
Sulfur		1.12	1.11
(Arsenic and Sulfur)	1.16	1.15 (Av.)	1.16 (Av.)

The disordered structure, as mentioned before is the pyrite structure (Fig. 4a). The cobalt atoms (smaller spheres) have a face-centered arrangement and the eight (arsenic+sulfur) atoms (larger spheres) are in the eight subcubes of the unit cell. In each subcube, the (arsenic+sulfur) atom lies on a line joining opposite corners of the subcube (heavy dotted line). These body diagonals are axes of 3-fold symmetry. This arrangement
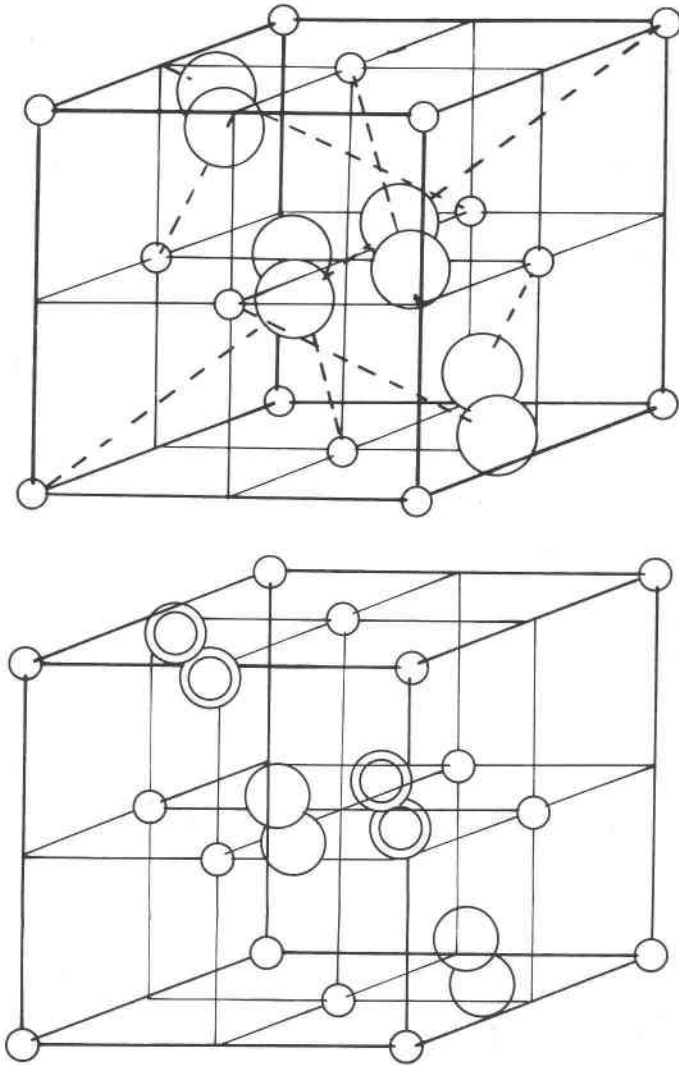
FIG. 4. Structure of cobaltite. 4a. Disordered cobaltite. The smaller spheres are cobalt and the larger spheres are (arsenic+sulfur). 4b. Ordered cobaltite. The smaller spheres are cobalt and the larger spheres are arsenic (plain) and sulfur (double circles).

places a cobalt atom at the center of an octahedron whose corners are (arsenic+sulfur) atoms. Each (arsenic+sulfur) atom is coordinated by three cobalt atoms and one (arsenic+sulfur) atom in a distorted tetrahedral arrangement.

The ordered structure (Fig. 4b) has the same spatial arrangement as shown in Fig. 4a. The eight (arsenic+sulfur) atoms become four sulfur and four arsenic atoms. The larger spheres in the lower four subcubes become sulfur and the larger spheres in the upper four subcubes become arsenic (or *vice-versa*). All atoms move slightly away from their positions in the disordered structure. A cobalt atom in the ordered form is coordinated by three arsenic and three sulfur atoms in an octagonal arrangement. An arsenic atom is coordinated by three cobalt atoms and one sulfur atom and similarly a sulfur atom is coordinated by three cobalt atoms and one arsenic atom in a distorted tetrahedral arrangement.

The ability of arsenic and sulfur to substitute for each other suggests the possibility of similar behavior in arsenopyrite (FeAsS) and gersdorffite (NiAsS).

In a restudy of the crystal structure of arsenopyrite, Morimoto and Clark (1961) conclude that the space group is $P\bar{1}$ approaching $P2_1/c$ as the arsenic content increases. This is equivalent to saying that replacement of sulfur by arsenic increases the symmetry. In fact, the authors concluded that from the evidence of electron density maps, 30 per cent of the sulfur substituted for arsenic and *vice-versa*. It is unfortunate that their quenching experiments were not done at temperatures above 600° C. since this is approximately the lower limit for observable symmetry changes in cobaltite.

Crystals of gersdorffite are rather rare and no report could be found in the literature regarding its space group and structure based on single crystals. Powder photographs indicated space group $Pa3$ and a pyrite structure based on a disordering of arsenic and sulfur (Peacock and Henry, 1947). Previous reports indicated space group $P2_13$ (Palache *et al.* 1944).

Three small octahedral crystals (origin unknown) were found in the Columbia Collection. They were identified as gersdorffite by a comparison of the d values with those of Peacock and Henry and an emission spectrographic analysis which showed: trace—iron, copper, silver, antimony; moderate—gold, bismuth, cobalt; major—nickel, arsenic. Sulfur was not included in the analysis. Precession and Weissenberg photographs of a fragment of one of the crystals clearly showed space group $P2_13$. Very long exposures failed to show any reflections violating this space group. A comparison of the (hko) intensities with those of ullmanite (Takéuchi, 1956) showed them to be isostructural. Hence, there seems to be no evidence of substitution between arsenic and sulfur in gersdorffite. The sample available was insufficient to allow any quenching experiments.

Conclusions

We are now in a position to explain the apparently contradictory properties of cobaltite.

1. The optical anisotropy results from the non-isometric symmetry of natural cobaltite.
2. The complete transformation to isometric symmetry at 800–850° C. confirms Flörke's observation of the optical isotropy of cobaltite above 830° C.
3. The isometric appearance of the powder photographs of cobaltite results from the near identity of the two structures in terms of atomic positions and the close similarity in interatomic distances in both forms.
4. The forbidden x-ray reflections observed in natural cobaltite are those which occur in the ordered form and result from the partial disordering of the natural material.

Acknowledgments

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