

A further crystal structure refinement of cobaltite

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Abstract

Fifteen cobaltite (CoAsS) specimens from localities in North America, Australia, and Sweden were analyzed with electron microprobe, powder diffraction, and precession camera techniques. From each specimen, a sample with a well-developed cube form {100} was selected. Intensity data were collected from 30 reflections, which are mostly forbidden by cubic space group $Pa\bar{3}$, with a single crystal diffractometer. A complete intensity data set was collected from four of these 15 samples. Least-squares refinement shows different degrees of apparent As–S disorder with one sample almost ordered in space group $Pca2_1$ (predominantly one twin-related domain), one sample significantly ordered (predominantly two twin-related domains), one sample partially ordered (unequal amounts of six twin-related domains), and one sample disordered (equal amounts of six twin-related domains). These samples are explained as a sextuplet of orthorhombic ($Pca2_1$) interpenetrating twin-related domains about a $\bar{3}$ twin axis [111]. Therefore cobaltite-low (true As–S order at the atomic level, $Pca2_1$, cobaltite subgroup) has $a \approx b \approx c$. No authentic mineralogical occurrence of cobaltite-high (true As–S disorder at the atomic level, $Pa\bar{3}$, pyrite subgroup) appears to have been recorded.

Introduction

The space group of cobaltite (CoAsS) has been investigated by Mechling (1921), Ramsdell (1925), de Jong (1926, 1928), Peacock and Henry (1948), Bokij and Tsenokov (1954), Onorato (1957a, 1957b), Winterberger (1962), and Oftedal (1963). Giese and Kerr (1965) determined the crystal structure of cobaltite (CU 200-83), and reported R values of 0.10 for $hk0$ and 0.12 for $h0l$. Their crystal structure shows that As occupies four non-metal sites, whereas S occupies the other four non-metal sites in the pyrite-type crystal structure with an orthorhombic (pseudocubic) symmetry of $Pca2_1$. After heat treatment at 800–850° C for two days, the crystal structure model was refined in space group $Pa\bar{3}$ to an R value of 0.05 with the As and S disordered among the eight non-metal sites of the pyrite-type crystal structure. The crystal structure determination of cobaltite by Le Damany (1962) shows a partial disorder of As and S. Cobaltite was reinvestigated in order to compare it with other pseudocubic pyrite-type crystal structures of gersdorffite (Bayliss and Stephenson, 1968), arsenian ullmannite (Bayliss, 1977a) and pyrite (Bayliss, 1977b).

The 010 and 110 reflections may be used to differentiate between space groups $Pca2_1$, $P2_13$ and $Pa\bar{3}$. Berry and Thompson (1962) observed both the 010 and 110 reflections in cobaltite from Hakensbo (ROM M11824) with Straumanis-type powder X-ray diffraction photographs, Fe radiation, and Mn filter. Later Giese and Kerr (1965) also observed both the 010 and 110 reflections in cobaltite from Cobalt, Ontario (CU 200-83) and Tunaberg, Sweden by powder X-ray diffraction photographs with Fe radiation and 20 hours exposure. Long exposures were necessary to show these weak 010 and 110 reflections; they were not observed in USNM 95740 after an 8 hour exposure. Peacock and Henry (1948) did not observe either the 010 or the 110 reflection in ROM M14499 with Cu radiation, but any weak reflection would be hidden in the high fluorescent background caused by the Co in cobaltite. Reflections 010 and 110 were observed in both Debye-Scherrer photographs and powder diffractometer patterns for all six cobaltite specimens by Bayliss (1969a) with Co radiation.

All cobaltite specimens observed by Klemm (1962), Ramdohr (1969), and Cabri and Laflamme (1976) are optically anisotropic. Twinning occurs extensively in all cobaltites examined by Bayliss (1969a). With photomicrographs of polished sec-

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tions under crossed nicols from Hakensbo specimens, Klemm (1962, Fig. 16) shows coarse irregular zoning, whereas Ramdohr (1969, Fig. 495b) shows good twinning, which is comparatively regular on a fine scale but not in a network. Although all the crystal faces exhibited externally by cobaltite are consistent with the cubic system, internally they consist of optically anisotropic lamellae in a somewhat regular arrangement and/or irregular areas. From these data, Ramdohr (1969) speculates that cobaltite is pseudocubic with a sextuplet of orthorhombic lamellae twinned parallel to (110).

Experimental and results

Fifteen cobaltite specimens were obtained for this investigation from the Australian Museum (AM), Columbia University (CU), David New-Minerals (D. New), Royal Ontario Museum (ROM), United States National Museum (USNM), and University of New South Wales (UNSW). Specimens, which have previously been studied, are CU 200-83 and USNM 95740 by Giese and Kerr (1965), ROM M11824 by Berry and Thompson (1962), ROM M14469 by Peacock and Henry (1948), and UNSW, UNSW 61, UNSW 233, UNSW 361, UNSW 362, and AM D24919 by Bayliss (1969a). Specimen numbers and their localities are listed in Table 1, and the same order is also used in Tables 2 and 3.

Powder X-ray diffractometer patterns of all 15 cobaltite specimens show both the 010 and 110 reflections including the six specimens of Bayliss (1969a), two specimens of Giese and Kerr (1965), and one each from Berry and Thompson (1962) and Peacock and Henry (1948). Their reflection shape is similar to that of the other reflections recorded. The presence of these reflections 010 and 110 has been

Table 1. Specimen numbers and their localities

Specimen Number	Locality
UNSW 362	N.S.W., Australia
ROM M14469	Columbus Claim, Cobalt, Ont., Canada
UNSW 61	Bimbowrie, S.A., Australia
CU 200-83	Cobalt, Ontario, Canada
USNM 95740	Cobalt, Ontario, Canada
UNSW	S. Broken Hill, N.S.W., Australia
AM D24919	Mt. Cobalt, Qld., Australia
AM D24922	Cobalt, near Charters Towers, Qld.
ROM M11824	Hakensbo, Sweden
AM D37828	Broken Hill S., N.S.W., Australia
UNSW 361	Cloncurry, Qld., Australia
D. New	Idaho, U.S.A.
UNSW 233	Torrington, N.S.W., Australia
AM D37827	Broken Hill S., N.S.W., Australia
AM D37829	Broken Hill S., N.S.W., Australia

Table 2. Electron microprobe analyses

Specimen Number	Fe	Co	Ni	S	As	Total
CoAsS		35.5		19.3	45.2	100.0
362	1.8	32.6	1.1	20.1	43.8	99.4
M14469	3.2	28.6	3.6	19.7	45.1	100.2
61	1.7	34.2	0.1	20.5	43.0	99.5
95740	3.9	26.6	4.8	18.9	45.3	99.5
UNSW	3.0	32.6	0.6	20.3	43.7	100.2
D24919	2.2	32.6	0.7	20.1	44.0	99.6
D24922	2.0	32.9	0.3	20.2	44.0	99.4
M11824	5.0	30.9	0.9	22.3	40.6	99.7
D37828	2.4	32.6	0.8	20.1	44.2	100.1
361	2.5	31.6	1.2	19.9	44.5	99.7
233	1.9	33.2	0.5	20.1	45.0	100.7
D37827	2.7	31.7	1.5	20.2	44.3	100.4
D37829	2.4	33.2	0.3	20.4	44.2	100.5

confirmed by 114.6 mm Debye-Scherrer powder photographs. Neither powder diffractometer patterns nor Debye-Scherrer powder photographs showed distinct reflection splitting, however the broad reflections near $\theta = 90^\circ$ of all cobaltite specimens may be interpreted as multiple reflections from a pseudo-cubic mineral.

These cobaltite specimens were chemically analyzed for 6 elements (Fe, Co, Ni, S, As and Sb) by electron microprobe as previously described by Stout and Bayliss (1975). Standards used were Fe, Co, Ni, As, Sb, FeS, FeS₂, CoS₂, NiS, Sb₂S₃, As₂S₃, (Ni,Co)As₃ and FeAsS. The As standard was repolished and recoated to avoid oxidation. Data were refined with a modified version of the computer program SLAVE (Nicholls *et al.*, 1977). Detection limits were determined to be about 0.5 wt.%. The analytical results are presented in Table 2.

Calculation of the stoichiometry from electron microprobe results in Table 2 based upon a 4MX_n structural formula indicates that n varies between 1.97 and 2.03. Since the electron microprobe data contain random errors, no evidence is available to indicate deviations from stoichiometric MX₂. Klemm (1965) accepts the MX₂ formula for cobaltite based upon a literature survey, chemical syntheses and analyses. Also no deviation from stoichiometric MX₂ is indicated by Klemm and Weiser (1965). Therefore it appears logical to accept a stoichiometric MX₂ formula.

The cobaltite specimens (Table 2) show a minor range of substitution of Co by Fe and Ni, which falls within the solid solution limits of the ternary diagram FeAsS-CoAsS-NiAsS at 400° C of Klemm (1965). Metal chemical zoning is observed in speci-

men UNSW, where a 10% Co variation is inversely proportional to a 9% Fe and 1% Ni variation; and also in specimen 95740, where a 6% Co variation is inversely proportional to a 1% Fe and 5% Ni variation. All other specimens show metal chemical zoning between 1% and 3%. The specimens also show a minor range of substitution of As by S, which falls within the solid solution limits at 550° C of Bayliss (1969b). Non-metal chemical zoning is observed in specimen 362, where a 2% As variation is inversely proportional to a 1% variation.

From each cobaltite specimen, a sample was selected with an approximately equidimensional well-developed cube form {100}. The preliminary alignment along an *a* axis was made on a precession camera using unfiltered Mo radiation. These precession photographs *hk0* and *h0l* confirmed the presence of reflections 010 and 110, which are forbidden by space group *Pa3*. Simple twinning was not observed by either reflection splitting or the presence of strong 210 and strong 120 reflections. Strong 210 and 120 reflections may result from a (110) twin plane as shown by the iron-cross twinning in pyrite (Tennyson, 1980).

Each sample except D24919 was accurately centered on a Weissenberg two circle automatic diffractometer with reflections 800, 080 and 008, so that an *a* axis coincided with the diffractometer ω axis. Integrated intensities of 30 reflections, which includes 27 reflections forbidden by space group *Pa3*, were collected. These integrated intensities were corrected for background and scaled so that the maximum observed relative intensity (*I*) is 1000. Values of 1 are approximately equal to the limit of detection at the one standard deviation confidence level. Manual rotation about the scattering vector of some *h00* reflections with $h = 2n + 1$ shows a continuous high intensity, and their reflection shapes are similar to those of other reflections, so that these reflections are not caused by the Renninger effect. Sample D24919 was treated similarly, except that this sample was accurately centered on a manual four circle diffractometer with reflections 800, $\bar{8}00$ and 080 so that an *a* axis coincided with the diffractometer ϕ axis. Integrated intensities of 26 reflections, which includes 24 reflections forbidden by space group *Pa3*, were collected.

The crystallographic axes of each sample were chosen so that $I_{120} \gg I_{210}$, and if possible $I_{010} > I_{001} > I_{100}$. This is satisfied by only one of the six possible orthogonal orientations. If $I_{010} = I_{001} = I_{100}$, then three different orthogonal orientations are

possible. Each column of Table 3 has been arranged in sets of three reflections, which are equivalent in the cubic space groups *P2₁3* and *Pa3*. The observed relative intensities (*I*) of the 15 samples have been arranged from left to right across Table 3 with $I_{010} > I_{001} > I_{100}$ to $I_{010} = I_{001} > I_{100}$ to $I_{010} = I_{001} = I_{100}$. Other similar observed relationships from left to right across Table 3 are as follows:

$$I_{110} > I_{011} > I_{101} \text{ to } I_{110} = I_{011} > I_{101} \text{ to } I_{110} = I_{011} = I_{101}.$$

$$I_{310} > I_{031} > I_{103} \text{ to } I_{310} = I_{031} > I_{103} \text{ to } I_{310} = I_{031} = I_{103}.$$

$$I_{130} > I_{013} > I_{301} \text{ to } I_{130} = I_{013} > I_{301} \text{ to } I_{130} = I_{013} = I_{301}.$$

$$I_{330} > I_{033} > I_{303} \text{ to } I_{330} = I_{033} > I_{303} \text{ to } I_{330} = I_{033} = I_{303}.$$

Reflections that would be extinct in the untwinned crystal structure with space group *Pca2₁* are 001, 100, 011, 101, 031, 103, 013, 301, 033 and 303.

The values of F_{calc} given in Table 4 from four of these 15 cobaltite samples show that F_{120} , F_{012} and F_{201} are approximately equal. The variability between the values of I_{120} , I_{012} and I_{201} in Table 3 for these 15 cobaltite samples is a factor of about two, which takes into account the fact that these observed relative intensities have not been corrected for absorption. Therefore for these cobaltite samples, the relative intensity of a reflection from one sample must be at least double the relative intensity of the same reflection from another sample to be considered different. With this limitation, there are differences across Table 3, so that it is not essential to correct all the relative intensities for absorption and calculate their standard deviations.

In order to investigate these differences, samples at various positions across Table 3 were selected for crystal structure analysis. These are 362 ($I_{010} \gg I_{001} = I_{100}$), D24919 ($I_{010} > I_{001} > I_{100}$), M11824 ($I_{010} = I_{001} > I_{100}$), and D37829 ($I_{010} = I_{001} = I_{100}$), which are marked by * in Table 3. There is neither systematic chemical variation nor chemical zoning variation across Table 3. Their derived chemical formulae based upon a 4MX_2 structural formulae are as follows:

362	$(\text{Fe}_{0.05}\text{Co}_{0.92}\text{Ni}_{0.03})\text{As}_{0.97}\text{S}_{1.03}$
D24919	$(\text{Fe}_{0.06}\text{Co}_{0.92}\text{Ni}_{0.02})\text{As}_{0.97}\text{S}_{1.03}$
M11824	$(\text{Fe}_{0.14}\text{Co}_{0.84}\text{Ni}_{0.02})\text{As}_{0.88}\text{S}_{1.12}$
D37829	$(\text{Fe}_{0.07}\text{Co}_{0.92}\text{Ni}_{0.01})\text{As}_{0.96}\text{S}_{1.04}$

Table 3. Observed relative intensities from 15 cobaltite samples

<i>hkl</i>	*						*						*			
	362	14469	61	200-83	95740	UNSW	24919	24922	11824	37828	361	D.New	233	37827	37829	
010	195	122	273	179	79	168	154	85	90	192	158	76	85	68	56	
001	0	0	20	0	1	11	46	66	150	27	25	76	97	60	40	
100	1	0	2	4	8	14	7	2	7	58	47	29	46	39	56	
030	37	22	55	37	15	33	30	18	19	36	28	14	16	15	11	
003	0	0	4	0	0	2	19	13	29	5	5	14	19	11	7	
300	0	0	0	2	0	3	17	1	1	11	8	6	9	7	10	
050	35	21	50	37	14	33	33	17	17	34	25	13	15	15	12	
005	3	0	7	0	1	3	39	13	28	8	5	16	23	9	8	
500	0	1	0	1	1	3	2	2	1	11	9	5	9	8	10	
070	20	12	31	22	7	18	29	9	9	20	12	9	9	7	6	
007	0	0	3	0	0	1	22	6	17	4	4	8	13	4	4	
700	0	0	0	2	1	2	2	0	1	5	5	2	4	5	6	
110	100	46	129	61	25	71	124	41	39	99	48	39	45	27	26	
011	1	2	11	5	1	8	39	25	54	15	14	29	52	33	29	
101	0	0	1	2	1	5	2	1	6	19	18	19	23	20	24	
120	649	675	1000	1000	561	601	905	506	864	1000	1000	608	1000	646	623	
012	649	1000	792	543	1000	1000		507	768	771	435	610	743	1000	1000	
201	1000	513	658	685	557	763	1000	1000	1000	941	595	1000	888	485	552	
210	4	0	2	4	2	2	16	3	2	5	1	1	4	2	1	
021	0	1	0	1	0	2	2	2	0	1	0	0	1	3	2	
102	0	1	0	0	0	5	1	1	0	2	0	0	1	4	2	
310	32	10	41	18	4	19	59	16	9	38	11	16	16	6	7	
031	0	0	4	0	1	1	8	8	15	5	5	8	17	8	6	
103	0	1	0	5	0	6	2	0	1	4	4	4	5	9	11	
130	30	15	37	24	10	20	40	13	13	27	23	10	10	9	8	
013	1	1	3	0	1	1	14	10	20	5	4	11	15	15	11	
301	0	0	0	0	2	4	1	1	2	8	6	9	9	6	6	
330	30	15	34	22	10	24		12	10	30	15	12	14	10	9	
033	4	1	6	1	0	4		10	20	8	5	10	19	10	9	
303	1	0	1	3	1	3		1	2	7	7	5	7	6	9	

All reflections, which were recorded by powder diffractometer patterns, Debye-Scherrer and precession photographs, may be indexed on a cubic unit cell with a between 5.57 and 5.59 Å, which is similar to 5.576 Å of CoAsS by Bayliss (1969b). Therefore no deviation from $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$ was detectable. For each of the four cobaltite samples, the angular position of about 20 strong reflections at high 2θ values were measured. All samples showed $a = b = c$ and $\alpha = \beta = \gamma = 90^\circ$; except 362 where b is significantly longer than c , and there is some indication that b is shorter than a (Table 5).

Integrated intensities of all reflections from one hemisphere were collected under the conditions listed in Table 5. For D24919, when the total counts of a reflection were less than 500, the background counts were remeasured for 60 seconds to obtain better integrated intensities. A standard 020 reflec-

tion, which was measured every 50 reflections throughout the data collection, showed satisfactory experimental stability, so that no correction was applied for instrumental drift. Background, Lorentz, polarization, and absorption corrections were made with the programs SHELX from Cambridge University for 362, M11824, and D37829, while the method of Wuensch and Prewitt (1965) was used for D24919. Data correction conditions are listed in Table 5.

All reflections were included in the refinement of the crystal-structure model by the least-squares program (REFINE 4) of Finger and Prince (1975). All observations were weighed according to $\omega = 1/\sigma_f^2$, where σ_f is the standard deviation based on counting statistics. Initial positional parameters were taken from Giese and Kerr (1965). Neutral atomic scattering factors and anomalous dispersion corrections were taken from the *International Tables of X-*

Table 4. Structure factors from five cobaltite samples

<i>hkl</i>	362		24919		11824		37829		362
	F_{obs}	F_{calc}	F_{obs}	F_{calc}	F_{obs}	F_{calc}	F_{obs}	F_{calc}	F_{obs}
010	38.3	32.7	28.2	20.2	14.8	8.6			22.9
001	1.4	3.7	19.6	15.5	16.7	5.6	17.1	1.3	20.5
100			7.1	2.6			16.5	1.6	16.7
030	29.1	23.9	20.9	15.6	11.0	6.4			17.9
003	0.8	4.2	15.1	12.4	13.2	3.7	12.8	2.0	16.0
300			4.4	2.5			12.2	3.7	13.7
050	36.6	37.8	28.4	24.8	13.6	12.9			22.9
005	9.4	2.8	18.6	15.5	17.2	14.8	16.8	2.1	20.4
500			5.3	1.8			17.7	4.1	16.9
070	35.4	36.8	24.8	24.6	13.4	12.5			21.6
007	3.0	4.5	18.3	15.0	16.1	14.7	15.3	2.9	19.4
700			5.6	3.0			14.9	3.3	16.6
110	27.3	25.1	18.8	15.5	8.2	7.7	9.6	2.0	
011	1.4	3.2	16.2	10.6	12.9	4.6	10.7	3.2	
101	1.9	0.5	5.4	2.9	1.9	4.3	11.0	1.3	
120	94.1	91.0	88.4	83.2	61.3	48.4	59.7	63.8	
012	94.5	91.2	90.7	80.9	58.4	48.3	70.8	63.5	
201	90.3	95.1	83.3	83.1	37.5	49.3	76.7	63.4	
210	5.9	4.9	3.0	2.9	2.5	2.4	3.1	1.6	
021	1.1	1.0	5.9	1.7	2.0	3.9	3.7	6.1	
102	1.8	1.0	2.1	2.4	1.1	1.7	2.8	7.8	
310	17.1	22.1	16.9	12.6	5.7	7.7	9.1	4.0	
031	0.8	2.5	12.7	10.0	11.0	2.1	7.4	3.8	
103	2.1	1.2	3.6	2.2	2.8	2.6	10.1	9.7	
130	24.5	24.4	17.7	14.9	8.7	8.1	7.2	1.2	
013	0.9	2.3	14.0	10.3	11.6	8.7	11.0	3.3	
301	1.3	1.7	3.7	0.5	1.1	2.5	10.8	6.8	
330	28.3	26.8	21.0	18.0	10.3	10.1	11.0	0.7	
033	9.0	2.7	16.0	12.1	13.8	9.7	12.4	2.6	
303	5.3	0.7	6.6	2.4	3.9	1.9	13.4	1.7	

ray Crystallography (1974). The crystal-structure model of 362 was first refined in space group $Pca2_1$, which indicates that the pyrite-type crystal-structure is correct. The observation of reflections forbidden by space group $Pca2_1$ may be explained by either complex twinning or further ordering of the Fe, Co, Ni, As and S atoms among the twelve sites. In order to investigate these possibilities, the crystal structure model was refined in space group $P1$ with atom M_1 fixed at (0, 0, 0). Full matrix least-squares refinement of the S occupancies of the eight non-metal sites were undertaken with seven site occupancies varied and the eighth site automatically reset to maintain the overall chemical composition. No significant correlation problems were encountered in the refinement of the non-metal site occupancies and temperature factors for 362, D24919 and M11824. The strong correlation between site occupancies, extinction parameter, and

temperature factors for D37829 means that site occupancy refinement is not possible. Difference fouriers show that there are no other atomic positions in these four crystal-structures, which confirms that a simple (110) twin plane does not exist.

Crystal structure description

The positional parameters in Table 6 are listed for 362 in space group $Pca2_1$ with atoms of $M(0, 1/4, 0)$, $X(3/8, 5/8, 3/8)$ and $X(5/8, 7/8, 5/8)$. Only one of the six orthogonal orientations is possible for 362, D24919 and M11824, but three different orthogonal orientations are possible for D37829. These positional parameters are then similar to those generated by space group $Pa3$ after reduction by the vector (0, $-1/4$, 0) with axes yxz and atoms of $M(0, 0, 0)$ and $X(3/8, 3/8, 3/8)$.

The total amount of As in the four non-metal sites (Table 7) related by $Pca2_1$ symmetry (X_1 to X_4 , and

Table 5. Data collection and correction conditions, extinction parameters, and *R* values

Specimen Number	362	D24919	M11824	D37829
Crystal size μm	X 125(3) Y 55(3) Z 55(3)	107(3) 127(3) 98(3)	77(3) 43(3) 53(3)	53(3) 198(3) 53(3)
Unit cell \AA	<i>a</i> 5.592(4) <i>b</i> 5.587(3) <i>c</i> 5.567(3)	5.578(3)	5.572(3)	5.570(3)
Radiation	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Monochromator	Graphite	Graphite	Graphite	Graphite
Diffractometer	2 circle	4 circle	2 circle	2 circle
Layers	0 to 4		0 to 4	0 to 4
Background sec	50	10	50	60
Scan mode	$\theta:2\theta$	$\theta:2\theta$	$\theta:2\theta$	$\theta:2\theta$
type	step	continuous	step	step
width $^{\circ}2\theta$	2.0	$1.9+0.69\tan\theta$	2.0	2.4
interval $\theta:2\theta$	0.01:0.02		0.01:0.02	0.01:0.02
speed	1sec/step	1 $^{\circ}$ /min	1sec/step	1sec/step
range $^{\circ}2\theta$	5 to 60	5 to 65	5 to 60	5 to 60
Measurement	$\times 1$	$\times 3$	$\times 1$	$\times 1$
No. of unique reflections	756	1096	824	797
Absorption coefficient (cm^{-1})	301	303	284	302
grid points	1024	364	1280	1024
Transmission factors max.	0.26	0.14	0.34	0.26
min.	0.20	0.06	0.23	0.20
Extinction parameter $\times 10^7$	0.034(2)	-200(10)	1.15(2)	0.39(2)
<i>R</i> value (<i>P</i> 1)	0.049	0.074	0.111	0.128

X_5 to X_8) for the four cobaltite samples were calculated. Sample 362 appears to be almost ordered; D24919 appears to be significantly ordered; M11824 appears to be partially ordered; and D37829 appears to be disordered. The As occupancy sequence of the eight non-metal sites is $X_7 = X_6 > X_5 = X_8 > X_4 = X_1 > X_2 = X_3$. This As occupancy sequence correlates with the average interatomic distances, since the longer average interatomic distances correlate with the higher As site occupancies. Also this As occupancy sequence correlates with the temperature factors, since the lower temperature factors correlate with the higher As site occupancies.

The occupancies of the metal sites were refined, although no meaningful refinement was expected since the atomic scattering factors of Fe, Co and Ni are similar. There may be a chemical reason for this type of As-S ordering. Since Fe (borderline hard acid) may be classified as harder than Ni, and S (base) is probably harder than As, it is possible that

Ni may occur in an As-rich environment and Fe in a S-rich environment. Longer interatomic distances are expected for Ni-As, since As is larger than S, and Ni is larger than Fe because NiS_2 ($a = 5.7\text{\AA}$) is larger than FeS_2 ($a = 5.4\text{\AA}$). The average interatomic distances about the octahedral metal sites are not only affected by the substitution of Ni and Fe for Co, but also by the amount of As in the six non-metal sites coordinated with each octahedral metal site. Therefore the total number of As atoms in these six non-metal sites coordinated with each octahedral metal site were calculated. An overall analysis of the metal site occupancy refinement, temperature factors, average interatomic distances, and total number of As atoms in the six non-metal sites coordinated with each octahedral metal site shows no systematic trend. Therefore the Ni and Fe are randomly distributed among the four metal sites.

The pyrite-type crystal structure may be described as similar to the halite crystal structure with the metal atom (M) replacing Na and the non-metal pair (X_2) replacing Cl. A summation of the As atoms in the non-metal pair (X_2) shows that each non-metal pair contains approximately one As atom. The variation of the non-metal pairs interatomic distances reflects the amount of As in the non-metal pair sites.

The interatomic angles (Table 8) indicate that the coordination of the non-metal atoms has been distorted from a regular tetrahedron (109° angles) to a trigonal pyramid with average interatomic angles of 102° (M-X-X) and 116° (M-X-M). The coordination of the metal atoms has been distorted from a regular octahedron (90° angles) to a trigonal prism with average interatomic angles of 85° ($X_A\text{-M-X}_A$ or $X_B\text{-M-X}_B$) and 95° ($X_A\text{-M-X}_B$). The X_A atoms occupy the S sites and the X_B atoms occupy the As (or Sb) sites in the $P2_13$ ordering that occurs in gersdorffite (Bayliss and Stephenson, 1967) and ullmannite (Pratt and Bayliss, 1980).

Since 362 approaches orthorhombic symmetry ($\alpha = \beta = \gamma = 90^\circ$), a least-squares refinement of the

Table 6. Positional parameters and isotopic temperature factors for 362 in space group $Pca2_1$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$B(\text{\AA})^2$
Co	.9955(4)	.2596(3)	.0000	.35(3)
S	.3845(7)	.6314(5)	.3809(8)	.64(7)
As	.6195(3)	.8694(2)	.6168(6)	.23(3)

Table 7. Non-metal site occupancies

	362		D24919		M11824	
	S	As	S	As	S	As
X ₁	0.96(1)	0.04	0.65	0.35(2)	0.69(1)	0.31
X ₂	0.93(1)	0.07	0.89	0.11(2)	0.69(2)	0.31
X ₃	1.00(1)		1.00		0.81(2)	0.19
X ₄	0.93(1)	0.07	0.59	0.41(2)	0.50(2)	0.50
X ₅	0.12(1)	0.88	0.42	0.58(2)	0.37(2)	0.63
X ₆	0.04(1)	0.96		1.00(2)	0.54(1)	0.46
X ₇		1.00	0.04	0.96(2)	0.41(2)	0.59
X ₈	0.13(1)	0.87	0.52	0.48(2)	0.47	0.53

data (374 unique reflections) were made in space group $Pca2_1$ with a resultant R value of 0.057, which is significantly higher than the later refinement made in space group $P1$ with a R value of 0.049 based upon the significance test of Hamilton (1965) at the 0.005 level. However such statistics may not work correctly, if there are systematic errors in the intensity data.

The absorption correction to D24919 is poor, because one side of the cube was not a perfect cleavage, the cube was too large as shown by its low transmission factors, and too few grid points were used (Table 5). The X_4 - X_8 interatomic distance of D24919 is too long or the amount of As in this non-metal pair is too low. The unfortunate choice of this poor sample from specimen D24919 and the intensity data collection and refinement were made a number of years ago, but since D24919 falls at a useful position in Table 3 it is included here.

One inconsistency in the As occupancy sequence of the eight non-metal sites, where $X_7 = X_6 > X_5 = X_8 > X_4 = X_1 > X_2 = X_3$, is the small amount of As in X_6 of M11824 compared to 362 and D24919. The long interatomic distances indicate a greater As content, however its low temperature factors indicate a smaller As content. This inconsistency is possibly explained by the large experimental errors in the intensity data of M11824 as shown by the high R value of 0.111.

The average interatomic distances of D37829 show M to X_1 , X_2 , X_7 and X_8 of 2.35Å are greater than M to X_3 , X_4 , X_5 and X_6 of 2.30Å, which indicates non-metal atom ordering based on a $P2_13$ model. The strong correlation between site occupancies and temperature factors indicates that site occupancy refinement is not possible. Therefore the As and S are equally distributed among the eight non-metal sites with only a single temperature factor for the eight non-metal sites. Similar observed

structure factors to D37829 (Table 4, column 8) had previously been observed from a second sample of 362 (Table 4, column 10). With about 2000 absorption corrected four-circle diffractometer data of this second sample of 362, the crystal structure model was refined by least-squares to an R value of 0.21 in space group $P1$, which gave an apparently disordered crystal structure similar to that of D37829. Since this result has been repeated, it appears consistent.

Twinning

Least-squares refinement shows different As-S order-disorder from left to right across Table 5 with one sample almost ordered in space group $Pca2_1$, one sample significantly ordered, one sample partially ordered, and one sample disordered. The R values increase from left to right across Table 5 (0.049; 0.074, 0.111; 0.128), and this is illustrated by the increased difficulty of refinement. Eight recently published crystal structure refinements by the author (Bayliss 1977a, b; Bayliss and Nowacki 1972; Pratt and Bayliss 1979, 1980; Stout and Bayliss 1975, 1980) with similar methods show an R value range of 0.015 to 0.044. With these methods, one would expect to obtain an R value of about 0.03 for a disordered cobaltite crystal structure rather than the values of 0.128 and 0.21 recorded in this paper. Therefore the high R values of these cobaltites can not be attributed to experimental error, but must be attributed to the present samples, so that the possibility of complex twinning should be investigated.

Of the 30 reflections recorded in Table 3, the reflections forbidden by space groups are 27 by $Pa3$, 18 by $Pca2_1$, 12 by $P2_13$ and zero by $P1$. The observed relative intensity data in the left hand

Table 8. Interatomic distance (Å) and angles (°) for 362 in space group $Pca2_1$

Co-S	2.306	S-Co-S	87	Co-S -Co	115
Co-S	2.285	S-Co-S	87	Co-S -Co	116
Co-S	2.288	S-Co-S	96	Co-S -Co	117
Co-As	2.362	As-Co-As	83	Co-S -As	101
Co-As	2.359	As-Co-As	84	Co-S -As	102
Co-As	2.363	As-Co-As	93	Co-S -As	103
As-S	2.284	S-Co-As	85	Co-As-S	100
		S-Co-As	86	Co-As-S	101
		S-Co-As	94	Co-As-S	103
		S-Co-As	94		
		S-Co-As	95	Co-As-Co	115
		S-Co-As	95	Co-As-Co	117
				Co-As-Co	117

columns of Table 3 are almost consistent with space group $Pca2_1$. Whereas Table 3 shows that all the reflections become observable as the columns are viewed from left to right. A crystal structure with the As and S disordered should have space group $Pa3$ like the cobaltite-high of Giese and Kerr (1965). However the reflections that are systematically absent in space group $Pa3$ are clearly observable (Tables 3 and 4).

The total average intensity has been calculated for sets of three reflections, which are equivalent in the cubic space groups $Pa3$ and $P2_13$, from the observed relative intensities (I) of the 15 cobaltite crystals listed in Table 3 as follows:

$$\begin{aligned} I_{100} + I_{010} + I_{001} &= 195 \\ I_{300} + I_{030} + I_{003} &= 39 \\ I_{500} + I_{050} + I_{005} &= 40 \\ I_{700} + I_{070} + I_{007} &= 23 \\ I_{101} + I_{110} + I_{011} &= 92 \\ I_{103} + I_{310} + I_{031} &= 29 \\ I_{301} + I_{130} + I_{013} &= 30 \\ I_{303} = I_{330} = I_{033} &= 29 \end{aligned}$$

Each cobaltite sample has a similar total average intensity for each set of three reflections, which are equivalent in space groups $Pa3$ and $P2_13$, within the limitation established earlier in this paper for these cobaltite samples that an intensity of a reflection from one sample must be at least double the intensity of the same reflection from another sample to be considered different. Table 3 shows significant differences between the intensities of the same reflection from different samples.

The pyrite-type crystal structure with completely ordered As-S in space group $Pca2_1$ may be twinned to produce a total of six different orthogonal orientations with similar although not exactly identical atomic parameters for the metal and non-metal sites, because $a \approx b \approx c$ (Table 5) and $x \approx y \approx z$ (Table 6). The four As and four S atoms will each occupy different sets of four out of eight non-metal sites in each of the six orientations, although the four Co atoms will occupy the same four metal sites in each of the six orientations. These six orientations are I(x, y, z), II($\bar{x}, \bar{y}, \bar{z}$), III(y, z, x), IV($\bar{y}, \bar{z}, \bar{x}$), V(z, x, y) and VI($\bar{z}, \bar{x}, \bar{y}$).

The amount of each twin pair (I + II, III + IV, V + VI) may be calculated from the summation of

F_{hk0} with k odd, F_{0kl} with l odd, and F_{h0l} with h odd from Table 4.

$$e.g. \quad I + II = \frac{\Sigma F_{hk0}}{\Sigma F_{hk0} + \Sigma F_{0kl} + \Sigma F_{h0l}}$$

The difference between each twin pair (I - II, III - IV, V - VI) may be calculated by the summation of As occupancy factors in Table 7 in four non-metal sites related by $Pca2_1$ symmetry minus the total amount of As in the other four non-metal sites divided by four. Three orientations (II, IV and V) are not possible for 362 and D24919, because As is absent from non-metal site X_3 (Table 7). The results in Table 9 are similar by the two methods of calculation for 362 and D24919, and are compatible by the two methods of calculation for M11824 and D37829.

The cobaltite specimen CU 200-83 of Giese and Kerr (1965) was obtained from Dr. P. F. Kerr. Reflections that are systematically absent in $Pca2_1$ are observed (Table 3). Therefore their specimen appears to be a twin, which may partly account for their high R values of 0.10 ($hk0$) and 0.12 ($h0l$). The crystal structure with partial disorder of As and S by Le Damany (1962) may also be explained by twinning.

The formation temperatures given by Ramdohr (1969) for cobaltite are medium for Cobalt, Ontario, and high for Broken Hill, N.S.W. and Hakensbo. Cobaltite specimens (M11469, CU 200-83, and 95740) from Cobalt (medium temperature) are twinned less than specimens (UNSW, M11824, D37828, D37827, D37829) from Broken Hill and Hakensbo (high temperature).

Conclusions

These cobaltite samples are a sextuplet of orthorhombic ($Pca2_1$) interpenetrating twin-related domains about a $\bar{3}$ twin axis $[\bar{1}\bar{1}\bar{1}]$. This explains (1) the R value increase from left to right across Table 5 (362 < D24919 < M11824 < D37829), which is illustrated by the increased differences between

Table 9. Twin percentages

Sample Number	I x, y, z	II $\bar{x}, \bar{y}, \bar{z}$	III y, z, x	IV $\bar{y}, \bar{z}, \bar{x}$	V z, x, y	VI $\bar{z}, \bar{x}, \bar{y}$
362	84	0	9	0	0	7
24919	53	0	38	0	0	9
11824	32	9	31	17	3	8
37829	16	16	17	17	17	17

F_{obs} and F_{calc} in Table 4, by the increase of the standard deviations of the coordinates, and by the increase of As-S disorder; (2) why the R value of the disordered crystal structure is significantly above 0.03; (3) the presence of strong reflections forbidden by the disordered crystal structure ($Pa3$); (4) the similar total average intensities for sets of three reflections, which are equivalent in space groups $Pa3$ and $P2_13$, from each cobaltite sample; (5) why different samples from 362 may have different structure factors (Table 4); (6) why the almost ordered sample (362) is orthorhombic ($\alpha = \beta = \gamma = 90^\circ$), whereas the apparently less ordered samples (D24919, M11824 and D37829) are pseudo-cubic ($a = b = c$, $\alpha = \beta = \gamma = 90^\circ$); (7) why the non-metal site occupancies of the apparently disordered crystal structure (D37829) do not refine; and (8) the poor crystallinity of D37829 as indicated by the longer scan range ($2.4^\circ 2\theta$) required. Therefore, the refinement of the crystal structure model in space group $P1$ is unjustified.

The poor quality of these four crystal-structure refinements is attributed to twinning, since the positional parameters of the six orthorhombic orientations are slightly different, because neither x , y , and z nor a , b , and c are exactly equal. Systematic errors caused by twinning indicates that the standard deviations of the positional parameters in Table 6, and hence also of the interatomic distances and angles, are underestimated. Although it is possible to refine crystal structure models based on twinned crystals, such a refinement is unlikely to provide an excellent quality refinement, because the exact values of a , b , and c are unknown. Therefore a single crystal without twinning should be used to obtain an excellent quality refinement of cobaltite in space group $Pca2_1$ with true As-S order at the atomic level.

No authentic mineralogical occurrence of cobaltite-high (true As-S disorder at the atomic level, $Pa3$, pyrite subgroup) appears to have been recorded.

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