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STRUCTURE AND TWINNING OF COBALTITE

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ABSTRACT

The common twinning in cobaltite has been re-interpreted on the basis of observations of polished sections in reflected light and the distribution of space-group-forbidden reflections, and attributed to a 3-fold [111] twin axis with incoherent twin boundaries. The visibility of twin domains in reflected light is enhanced by staining with a solution of potassium permanganate in dilute sulfuric acid. The structure of cobaltite has been refined to an acceptably low R value using intensity measurements from a twinned crystal. The crystal data for the refinement are: CoAsS, M_r = 165.92, cubic, $Pca2_1$, a 5.5833(7), b 5.5892(6), c 5.5812(8) Å, V 174.17 Å^3, Z = 4, D_x 6.328 g.cm^{-3}, λ(MoKα) 0.71069 Å, μ = 296.1 cm^{-1}, F(000) = 304, room temperature, 870 unique reflections, final R = 0.016. The $AsSCo_3$ and $SAsCo_3$ tetrahedral clusters both closely approach C_3 symmetry. Average Co–As and Co–S bond distances are 2.362 Å and 2.294 Å, respectively.

Keywords: cobaltite, twin microstructure, crystal structure.

SOMMAIRE

Nous avons ré-interprété la macle répandue de la cobaltite à la lumière d'observations de sections polies et de la distribution de réflexions non permises dans le groupe spatial choisi antérieurement. Nous attribuons la macle à une rotation d'ordre 3 autour de l'axe [111]; les interfaces entre les domaines maclés seraient incohérents. La visibilité de ces domaines en lumière réfléchie est améliorée par traitement avec une solution de permanganate de potassium dans l'acide sulfurique dilué. La structure de la cobaltite a été affinée jusqu'à un résidu R suffisamment faible en utilisant les mesures d'intensité obtenues sur cristal maclé. Les données nécessaires pour l'affinement sont: CoAsS, M_r = 165.92, cubique, $Pca2_1$, a 5.5833(7), b 5.5892(6), c 5.5812(8) Å, V 174.17 Å^3, Z = 4, D_x 6.328 g.cm^{-3}, λ(Mo$K\alpha$) = 0.71069 Å, μ = 296.1 cm^{-1}, F(000) = 304, température ambiante, 870 réflexions uniques, R final = 0.016. Les regroupements $AsSCo_3$ et $SAsCo_3$ possèdent une symétrie très proche de C_3. La longueur moyenne des liaisons Co–As et Co–S est de 2.362 et 2.294 Å, respectivement.

(Traduit par la Rédaction)

Mots-clés: cobaltite, microstructure d'un cristal maclé, structure cristalline.

INTRODUCTION

Cobaltite, CoAsS, has a pyrite-derivative structure with orthorhombic (pseudocubic) symmetry (space group $Pca2_1$) and an ordered distribution of As and S atoms (Giese & Kerr 1965, Bayliss 1982). Other crystallographic studies on cobaltite are referenced and reviewed in Bayliss (1982).

Refinements of the structure of cobaltite characteristically result in R values significantly higher than those anticipated from the precision of the intensity measurements. The X-ray-diffraction pattern of cobaltite contains reflections not permitted by space group $Pca2_1$ (Berry & Thompson 1962, Giese & Kerr 1965, Bayliss 1982). Reflections forbidden in $Pca2_1$ are $0kl$, $l \neq 2n$ and $h0l$, $h \neq 2n$. When the intensities of reflections $hk0$ ($k \neq 2n$), $0kl$ ($l \neq 2n$), and $h0l$ ($h \neq 2n$) are compared in triplets that are equivalent in the cubic space group of pyrite ($Pa3$; *e.g.*, 310, 031, 103), it becomes clear that one or both of the two classes of space-group-forbidden reflections are always present (Tables 3 and 4 of Bayliss 1982). Following earlier speculation on the twinning of cobaltite (Ramdohr 1969), Bayliss (1982) attributed the systematic presence of space-group-forbidden reflections to a sextuplet of interpenetrating, twin-related, orthorhombic domains about a $\bar{3}$ twin axis [111]. He derived a composite partly disordered structure with $P1$ symmetry and eight nonequivalent (As,S) positions per unit cell. The proportions of the six twin orientations in a composite crystal were calculated from knowledge of the observed structure-factors and the refined site-occupancies of As. However, it was recognized that the final R values for refinement in space group $P1$ remained unacceptably high (0.05 to 0.13; Bayliss 1982).

In this paper, the twinning in cobaltite is reinterpreted, and the crystal structure of cobaltite is refined in space group $Pca2_1$ to an R value of 0.016 using intensity measurements from a twinned crystal.

EXPERIMENTAL

Two specimens of cobaltite were obtained from the Dana Mineral Collection at The University of Western Ontario and characterized by reflected light microscopy, electron-microprobe analysis, and X-ray powder and single-crystal diffraction. Specimen 1692 is from an unknown locality and consists of coarse polyhedral crystals within a quartz matrix. Specimen 3174 is from the Frood mine, Sudbury, Ontario, and

TABLE 1. ELECTRON-MICROPROBE COMPOSITIONS FOR COBALTITE

	1692		3174	
	wt%	at%	wt%	at%
Fe	2.8	2.7	6.5	6.5
Co	29.6	27.6	14.7	13.9
Ni	2.1	2.0	12.6	12.0
As	44.8	32.9	45.2	33.7
S	20.3	34.8	19.4	33.8
Total	99.6	100.0	98.4	99.9

Specimen 1692 is from unknown locality: 3174 is from Frood mine, Sudbury, Ontario

is in the form of separated large cubo-octahedra containing lamellar inclusions of niccoline. Electron-microprobe analyses were made with a JEOL JXA-8600 system at The University of Western Ontario, with synthetic FeS and NiS, Co metal, arsenopyrite and chalcopyrite as standards. Average compositions are given in Table 1; Cu was not detected. The chemical composition of specimen 1692, with only minor substitution by Fe and Ni, is similar to that of the cobaltite specimens surveyed by Bayliss (1982). Its diffraction pattern is similar to that of specimen AM D24919, from Mount Cobalt, Queensland, Australia (Tables 4 and 9 of Bayliss 1982), and was interpretable on the basis of just two twin-related crystal orientations. Therefore, specimen 1692 was selected for X-ray structure analysis. Specimen 3174 is a cobaltite–gersdorffite solid solution (Table 1) and is complexly twinned.

A crystal of specimen 1692 was reduced to an approximately cubic shape (by cleaving with a scalpel and grinding with 600 mesh abrasive paper), and had approximate dimensions of 0.10 × 0.07 × 0.07 mm and a calculated volume of 0.52×10^{-3} mm^3. All single-crystal measurements were made with an Enraf–Nonius CAD-4F diffractometer, using graphite-monochromatized Mo*Kα* X radiation. The unit-cell parameters [*a* 5.5833(7), *b* 5.5812(8), *c* 5.5892(6) Å] were refined from 20 reflections in 2Θ range 61.0–66.8°. Intensity data were collected by Θ–2Θ scan with a scan angle (2Θ) = 2.4° and corrected for dispersion. The 3063 *hkl* reflections allowed by space group $Pca2_1$ out to $2\theta = 90°$ were measured ($-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $0 \leq l \leq 11$). There was no significant variation in intensity ($R_{int} < 0.02$) of the standard reflections 200, 020, and 002. Background, Lorentz, polarization and absorption corrections were applied; transmission factors (calculated by Gaussian integration with a 12 × 12 × 12 grid and μ = 296.1 cm^{-1}) varied from 0.116 for 010 to 0.237 for $\bar{6}, \bar{9}, 2$. There were 870 unique reflections, with 294 considered unobserved

TABLE 2. POSITIONAL AND ISOTROPIC THERMAL PARAMETERS (A^2) FOR COBALTITE

	Equi-point	x	y	z	B_{eq}
Co	4(a)	0.99504(8)	0.25909(6)	0.0	0.239(4)
As	4(a)	0.61885(4)	0.86935(5)	0.61668(13)	0.353(4)
S	4(a)	0.38266(12)	0.63129(12)	0.37996(19)	0.316(7)

$$B_{eq} = \frac{4}{3} \Sigma_i \Sigma_j B_{ij} a_i \cdot a_j$$

TABLE 3. ANISOTROPIC THERMAL PARAMETERS (x10^3 A^2) FOR COBALTITE

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	298(7)	167(7)	251(6)	-3(6)	8(7)	14(8)
As	426(7)	288(7)	346(6)	-19(8)	-2(9)	-26(11)
S	359(18)	242(17)	346(17)	27(19)	-39(17)	60(20)

Anisotropic temperature factors have the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + \ldots + 2B_{23}klb^*c^*\cos\alpha^*)]$

TABLE 4. SELECTED INTERATOMIC DISTANCES (A) AND BOND ANGLES (°) IN COBALTITE

Co-As^1	2.364(1)	Co-S^1	2.296(1)
Co-As^2	2.361(1)	Co-S^2	2.290(1)
Co-As^3	2.360(1)	Co-S^3	2.295(1)
S-As	2.292(1)		
As^1-Co-As^2	83.65(2)	Co^1-As-Co^2	116.74(2)
As^1-Co-As^3	83.70(2)	Co^1-As-Co^3	115.12(2)
As^1-Co-S^2	94.85(3)	Co^1-As-S	100.93(2)
As^1-Co-S^3	94.35(3)	Co^2-As-Co^3	116.86(2)
As^2-Co-As^3	92.77(2)	Co^2-As-S	102.81(2)
As^2-Co-S^1	94.55(2)	Co^3-As-S	100.22(2)
As^2-Co-S^3	85.28(3)	As-S-Co^1	101.85(3)
As^3-Co-S^1	94.92(3)	As-S-Co^2	100.79(3)
As^3-Co-S^2	85.63(3)	As-S-Co^3	102.73(3)
S^1-Co-S^2	86.91(3)	Co^1-S-Co^2	115.53(4)
S^1-Co-S^3	86.98(3)	Co^1-S-Co^3	116.71(4)
S^2-Co-S^3	96.28(3)	Co^2-S-Co^3	115.56(4)

Symmetry code: (1) $-x, -y, 1/2+z$; (2) $1/2-x, y, 1/2+z$; (3) $1/2+x, -y, z$.

TABLE 5. OBSERVED REDUCED INTENSITIES FOR GROUPS OF REFLECTIONS THAT REVEAL TWINNING IN COBALTITE

hkl	Ir	Twin (%)	hkl	Ir	Twin (%)	hkl	Ir	Twin (%)
010	101	34	430	103	32	350	42	36
001	51		043	48		035	24	
100	4		304	0		503	0	
110	52	33	410	77	31	070	95	32
011	26		041	35		007	44	
101	0		104	0		700	0	
030	61	31	050	102	31	710	35	33
003	28		005	45		071	17	
300	0		500	0		107	0	
310	35	31	510	39	30	870	27	--
031	16		051	17		087	0	
103	0		105	0		708	0	
130	44	32	150	38	32	490	26	35
013	21		015	18		049	14	
301	0		501	0		904	0	
330	51	31	250	16	33			
033	23		025	8				
303	0		502	0				

Specimen 1692: Ir is reduced observed intensity (x10^{-1}): reflection triplets are equivalent in Pa3 (pyrite group): in untwinned cobaltite ($Pca2_1$), hk0 is present, 0kl ($l \neq 2n$) and h0l ($h \neq 2n$) are absent: Twin (%) is contribution of crystal in twin orientation to diffracted intensity, given by $[Ir_{lhk}/(Ir_{hkl} + Ir_{lhk})]$

on the basis of I $<3\sigma(\mathrm{I})$ [$\sigma(I) = \{I_\mathrm{m} + 0.002^2(I_\mathrm{m} - \mathrm{B})^2 + 0.005^2(I - I_\mathrm{m})^2\}^{1/2}$, I_m, measured intensity and B, background].

Structure refinement proceeded from the positional parameters of Bayliss (1982). The quantity $\Sigma w(\Delta \mathrm{F})^2$ was minimized ($w = 1/\sigma^2$), and unobserved reflections were given a low weight ($\sigma = 1000$). Refinement in $Pca2_1$, with no allowance for twinning, partial disorder of As and S, and isotropic thermal parameters, converged to $R = 0.056$. Refinement in $P1$ (as in Bayliss 1982) did not converge properly, and the minimum value of R with isotropic thermal parameters was found to be 0.055. The final refinement was made in $Pca2_1$, with the observed structure-factors corrected for the contribution from twinning (as described below); we used all reflections out to $2\Theta = 90°$ and 27 variable parameters. The refinement converged to $R = 0.016$, $R_\mathrm{w} = 0.019$ [for reflections with $I \geq 3\sigma(I)$], $\mathrm{S} = 0.653$, $(\Delta/\sigma)_\mathrm{max} = 6\times10^{-5}$, $\Delta\rho = -1.0$ eÅ^{-3} (at 0.00,0.75,0.63) to 1.6 eÅ^{-3} at (0.25,0.15,0.13)]. The isotropic extinction parameter for type-I extinction (g; Coppens & Hamilton 1970) is $0.077(5)\times10^{-4}$. Scattering factors for neutral atomic species and f′, f″ were taken, respectively, from Tables 2.2B and 2.3.1 of the International Tables for X-ray Crystallography (1974). All computations were carried out with DATAP77 and LINEX77 (State University of New York at Buffalo). Final parameters are given in Tables 2 and 3; a list of observed and calculated structure-factors is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2. Selected interatomic distances and bond angles are given in Table 4.

TWINNING IN COBALTITE

The X-ray-scattering contributions to Bragg reflections from twin domains may be summed on the basis of either F^2 or F, where F is the structure factor. The summation $\Sigma(\mathrm{pF}^2)$, where p is the twin proportion, applies to twin boundaries that are "incoherent toward X-ray diffraction", as is the case in most twinned crystals. For coarse-scale domains, the X-ray-diffraction pattern is simply a composite of the superimposed diffraction patterns of the individual domains. The summation $(\Sigma \mathrm{pF})^2$ applies to twin boundaries that are "coherent toward diffraction". The crystal structure within the diffraction volume is modified by the twin mechanism and, with fine-scale twin intergrowths, a new composite crystal-structure results (as in some polytypes).

Observed reduced X-ray intensities for triplets of the reflections $hk0$ ($k\neq2n$), $0kl$ ($l\neq2n$), and $h0l$ ($h\neq2n$) (*e.g.*, 310, 031, 103; *etc.*) of specimen 1692 are given in Table 5. If the fact that these are weak reflections with fairly high standard deviations is taken into account, it is clear that reflections of the class $0kl$ ($l\neq2n$) are present, but those of the class $h0l$ ($h\neq2n$) are absent. Thus specimen 1692 appears to be a relatively simple twin, with a single twin-axis (and, as noted earlier, analogous to specimen AM D24919 of Bayliss 1982). In contrast, precession photographs of specimen 3174 revealed reflection triplets to have similar intensities, which therefore indicates a complex twin.

Twin domains in cobaltite are resolved by reflected light microscopy (*e.g.*, Figs. 495a,b of Ramdohr 1969), and therefore their boundaries are almost certainly incoherent toward X-ray diffraction. In the present study, it was observed that optical resolution of twin domains in cobaltite is greatly enhanced by staining the polished surface with a solution of $\mathrm{KMnO_4}$ in dilute (1:1) $\mathrm{H_2SO_4}$ (a technique that has been used recently to resolve optical microstructures in arsenian pyrite from gold deposits: Fleet *et al.* 1989). The enhancement in resolution appears to result from precipitation of a reaction product (possibly $\mathrm{MnO_2}$) at twin boundaries. Examination of numerous grains of specimen 1692 revealed the apparent presence of only two twin orientations (Fig. 1), which appear as lamellae of one orientation within a matrix of the other. The twin lamellae are lozenge-shaped, and are similar to the flame textures of two-phase hexagonal pyrrhotite (*e.g.*, Fleet & MacRae 1969). The twin microstructure of specimen 1692 is consistent with the presence of a single 3-fold [111] twin axis. On the other hand, specimen 3174 revealed a complex twin microstructure in a stained polished section, not unlike that illustrated in Figure 495b of Ramdohr (1969).

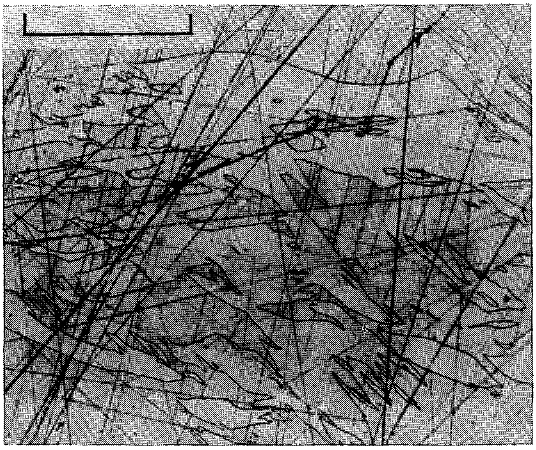

FIG. 1. Flame-textured twin domains resolved in cobaltite specimen 1692; examined in reflected light, stained with $\mathrm{KMnO_4}$ in 1:1 $\mathrm{H_2SO_4}$. Scale bar is 0.05 mm.

The distribution of $Pca2_1$-forbidden reflections in the diffraction pattern of specimen 1692 can be attributed now to unequal proportions of two twin domains, the minor twin-domain being related to the reference orientation by a single counterclockwise rotation of 120° about [111]. Thus reflection triplets of the reference orientation (*hkl, lhk,* and *klh,* which are equivalent in space group *Pa*3) become $k'l'h'$, $h'k'l'$, and $l'h'k'$ of the twin orientation. Because the unit cell of cobaltite is dimensionally pseudocubic, $k'l'h'$ overlaps with *hkl,* $h'k'l'$ with *lhk,* and $l'h'k'$ with *klh*. For example, for the triplet (310, 031, 103; Table 5), the reduced intensities of *hkl, lhk,* and *klh* are 35, 0, and 0, respectively, and for $k'l'h'$, $h'k'l'$, and $l'h'k'$ they are 0, 16, and 0, respectively. The sums of the reduced intensities for *all* triplets that include $Pca2_1$-forbidden reflections [$0kl$ ($l \neq 2n$), $h0l$ ($h \neq 2n$); see footnote to Table 5] gave an average ratio for the proportion of reference to twin orientation of 0.68:0.32. This is approximately consistent with the proportion observed in stained polished section (Fig. 1). The least-squares refinement of the crystal structure of cobaltite was carried out by first sorting the list of reflections into reflection triplets (*hkl, lhk, klh*) equivalent in space group $Pca2_1$. The least-squares program (LINEX77) was modified so that after the first cycle of refinement, the observed structure-factors and standard deviations were corrected for the effect of twinning using the magnitudes of the calculated structure-factors from the preceding cycle. Thus, $|\mathrm{Fobs}_{hkl}|^2(\mathrm{corrected}) = [|\mathrm{Fcalc}_{hkl}|^2/(0.68\times|\mathrm{Fcalc}_{hkl}|^2+0.32\times|\mathrm{Fcalc}_{klh}|^2)]\times|\mathrm{Fobs}_{hkl}|^2$, and so on. The twin proportion was refined by iteration: *R* was minimized with a twin ratio of 0.68:0.32, thus confirming the twin proportion obtained from triplets with $Pca2_1$-forbidden reflections.

The least-squares refinement proceeded without difficulty for this simplest possible model for twinning of orthorhombic ($Pca2_1$) symmetry about a [111] axis. As 1) a single 3-fold [111] axis gives a maximum of two additional twin-domain orientations and 2) there are four equivalent [111] axes, the maximum number of nonequivalent twin orientations in a complex crystal is six (namely, in terms of unit-cell axes, *XYZ, ZXY, YZX, YXZ, ZYX,* and *XZY*). The crystal structure of cobaltite could not be refined by the present procedure using intensities from such a complexly twinned crystal. In fact, even with just three twin orientations and a single twin axis, the corrected values for the observed structure-factors would have to be extracted from three simultaneous equations.

DISCUSSION

The present interpretation of the twinning in cobaltite, with a 3-fold [111] twin axis and conventional incoherent twin-boundaries, is consistent with the appearance of the twin microstructure in reflected light microscopy, and the distribution of $Pca2_1$-forbidden reflections. Furthermore, it results in a significant reduction in the *R* value for least-squares refinement of the structure of cobaltite with the present specimen, from 0.056 (with partial disorder of As and S) to 0.016.

The origin of the twinning in cobaltite has not been addressed. It may be attributable to ordering of a high-temperature precursor phase with the pyrite structure (disordered As and S atoms and *Pa*3 symmetry). However, the heterogeneous distribution of twin domains and the high temperature of the transformation (≈700°C, Bayliss 1969; which may be higher than the temperature of crystallization of cobaltite in many parageneses) suggest otherwise.

The coherent twin mechanism proposed by Bayliss (1982) does not appear to be appropriate for cobaltite, although the twin proportions calculated from *F* values for *pairs* of the twin orientations he identified [I(xyz), II($\bar{x}\bar{y}\bar{z}$); III(yzx), IV($\bar{y}\bar{z}\bar{x}$); and V(zxy), VI($\overline{zxy}$)] are approximately correct. The eight non-metal site occupancies obtained from refinement of the structure of cobaltite in space group *P*1 are merely artifacts of the twinned crystals. The diffraction pattern of twinned cobaltite is indeed composite, but it does not represent the Fourier transform of a composite crystal-structure with superimposed As and S atoms. It results from the superimposed diffraction-effects from separate incoherent domains of $Pca2_1$ structure. Bayliss (1982) had recognized that the *P*1 refinement for twinned cobaltite was unjustified based largely on the results obtained. These observations may not have direct bearing on the refinement of the structure of anisotropic pyrite (FeS_2) in space group *P*1 (Bayliss 1977), but they do question its recent suggested interpretation (Bayliss 1989) as a sextuplet of interpenetrating, twin-related, orthorhombic (space group $Pca2_1$) domains about a $\bar{3}$ twin axis [111].

The present refinement of the structure of cobaltite, which is based on intensity measurements from a twinned crystal, has resulted in improved precision of the positional and thermal parameters (Tables 2, 3). The average Co–As and Co–S bond distances are 2.362 Å and 2.294 Å, respectively (Table 4), and are similar to the values for the refinement of Bayliss (1982). However, there is less divergence between the three nonequivalent Co–As and Co–S distances in the present refinement. In fact, the $AsSCo_3$ and $SAsCo_3$ tetrahedral clusters both closely approach C_3 symmetry. The displacement of the Co atom from its ideal position (0,0,0) optimizes the average Co–(As,S) bond distances (long for Co–As and short for Co–S).

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