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Crystal structure refinement and electron microscopy of arsenopyrite

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Dedicated to the memory of Martin J. Buerger

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Abstract. Arsenopyrite crystals from Håkansboda (Sweden) have been studied by single crystal X-ray diffraction and analytical transmission electron microscopy. The material contains an excess of sulfur and some cobalt. Microprobe analyses gave a mean value of $Fe_{0.87}Co_{0.13}As_{0.88}S_{1.12}$. All crystals examined were twinned; the volume ratio of the twinned individuals was taken into account. The structure was refined from 834 independent diffractometer data in the monoclinic space group $C2_1/d$ and final $R = 0.049$ and $R_w = 0.025$ were obtained. The refined occupation numbers of As and S are in good agreement with the microprobe analysis. Fe–S distances range from 2.239 to 2.257, Fe–As distances from 2.336 to 2.375, the As–S distance is 2.346 Å, where S and As stands for (As,S) with predominant S and As, respectively. A transmission electron microscope study revealed antiphase domains and microtwins. Lamellar exsolution was observed in Co-rich specimens. These submicroscopic defects are interpreted on the base of group-subgroup relationships which relate the marcasite to the arsenopyrite structure.

Introduction

The crystal structure of arsenopyrite (ideal formula FeAsS) was first determined by Buerger (1936) who derived a model by analogy with related compounds. Buerger's work was hampered by crystal twinning. The apparent symmetry of that crystal was orthorhombic, but the structure could not be solved in one of the possible orthorhombic space groups. Buerger concluded that the true symmetry must be monoclinic or even triclinic, and he derived a model by trial and error based on the marcasite and gudmundite (FeSbS) structures and on symmetry considerations. Morimoto and Clark (1961) refined arsenopyrite from Freiberg (Germany) based on 172 *h0l* reflections in space group $P\bar{1}$. The agreement, however, was poor ($R = 0.29$). From additional powder data these authors proposed that an excess of sulfur tends to lower the symmetry to triclinic whereas a high amount of arsenic precludes monoclinic symmetry. They state that the "monoclinic structure" may be attained by minor amounts of Co or Sb. A review of published analyses led the authors to the conclusion that most natural arsenopyrites are sulfur-rich. The influence of the cations was examined by Klemm (1965) based on various natural samples and synthetic specimens. This author elucidated the system FeAsS – CoAsS – NiAsS by microprobe analyses and X-ray patterns.

The structural relationship between the marcasite and the arsenopyrite structure and the conditions of formation of one or the other structure type have been discussed controversely in the literature. Brostigen and Kjekshus (1970a) proposed a model known as the "pair reorientation model" to explain the relative stability for one or the other structure. They state that the alterations associated with a transformation from marcasite to arsenopyrite are relatively small. A ligand field approach has been given by Hulliger and Mooser (1965) based on magnetic and Mössbauer data, which was later criticised by Goodenough (1972). The influence of the electron distribution of the dianion in pyrite, marcasite and arsenopyrite type structures was emphasized by Tossell et al. (1981). They explained the preferred structural type by the number of dianion electrons based on a perturbational MO model.

We shall not discuss the relative stability of the arsenopyrite structure here but report an improved refinement of that structure taking the crystal twinning into account. Furthermore crystal defects and some evidence of exsolution has been obtained from transmission electron microscopy.

Experimental

The material studied was from Håkansboda (Sweden). It was detected during a TEM study of pyrrhotines from that locality. Some of the specimens were Co-rich and had to be classified as glaucodot. Preliminary results on glaucodot were published elsewhere (Töpel-Schadt et al., 1982).

The crystals were checked by precession photographs which, in most cases, apparently gave orthorhombic symmetry but did not indicate macroscopic twinning. Several crystals of those examined by precession and diffractometer techniques were analysed by a CAMEBAX microprobe equipped with a wavelength dispersive crystal spectrometer. The data were corrected for atomic number, absorption and fluorescence. The standards used were from Micro Analysis Consultants Ltd.: pyrite (46.40% Fe, 53.41% S, 0.05% Cu, 0.10% Co, 0.04% As), pure cobalt, nickel, antimon metal, and GaAs. The Fe – Co analyses indicated some substitution of Fe by Co with the amount of cobalt ranging from 4 – 21% with a mean of 10 – 11%. The material is free of Ni and Sb. All analyses gave an excess of sulfur. The composition of the material used in the X-ray structure analysis was $Fe_{0.87}Co_{0.13}As_{0.88}S_{1.12}$. The TEM observations were carried out with a JEOL JEM 100B electron microscope equipped with a side entry goniometer and operating at 100 kV. Suitable thin specimens were prepared from conventional petrographic thin sections by ion bombardment. The chemical composition of the material studied by TEM was directly obtained by an attached energy dispersive X-ray spectrometer. The accuracy of the analyses is about 2 – 3%.

The crystal selected for intensity measurement on an ENRAF-NONIUS CAD4 diffractometer had dimensions of 0.05 × 0.06 × 0.11 mm. The lattice constants were derived from setting angles of 25 reflections. All measurements were performed with Mo$K\alpha$ radiation and graphite monochromator. Intensities were collected up to $2\,\theta_{\max} = 70°$. All possible reflections were registered with h from 0 to 9, k from -9 to 9 and l from -9 to 9. Altogether 1656 reflections were measured, 1153 of them had $I > 3\,\sigma(I)$ with $\sigma(I)$ calculated from counting statistics. Three standard reflections showed intensity fluctuations up to 3% but no systematic trend. Data was collected in an $\omega/2\,\theta$ scan mode and a scan width of 1.2°. An empirical correction for absorption based on ψ-scans [absorption coefficient $\mu(\mathrm{Mo}K\alpha) = 118\ \mathrm{cm}^{-1}$] was carried out. Minimum transmission:maximum transmission was 0.76:1.00. Averaging yielded a final set of 834 reflections ($R_{\mathrm{int}} = 0.04$)[1].

Crystal structure

The crystal structure of arsenopyrite is closely related to the orthorhombic marcasite (FeS_2) structure. Figure 1 represents the unit cell of marcasite ($P\,2/m\,2_1/n\,2_1/n$, lattice constants A, B, C) projected down c together with different settings of the arsenopyrite cell. Numerical values are given in Table 1. Morimoto and Clark (1961) have chosen the primitive cell a'', b'', c'' while the non-conventional C-centered setting allows a direct comparison of the structural parameters in marcasite and arsenopyrite. Buerger (1936)

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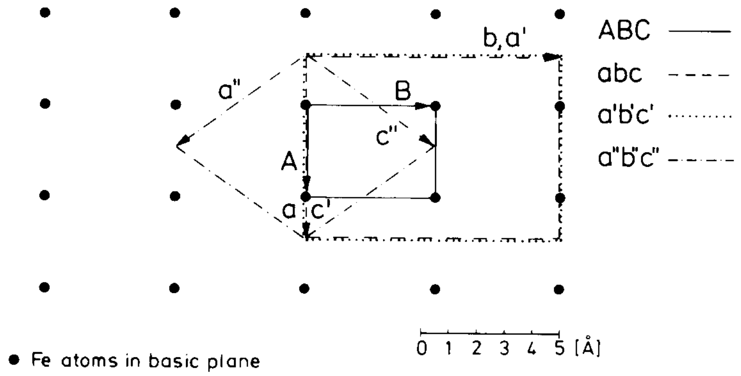
[1] Additional material to this paper can be ordered referring to the no. CSD 52605, names of the authors and citation of the paper at the Fachinformationszentrum Energie, Physik, Mathematik GmbH, D-7514 Eggenstein-Leopoldshafen 2, FRG.



A, B, C	marcasite-cell (FeS_2) Pmnn A, B, C
a, b, c	arsenopyrite-cell $(Fe, Co)(AsS)_2$ $C112_1/d$ monocline, pseudo-orthorhombic a = 2A, b = 2B, c = C, γ = 90°
a', b', c'	arsenopyrite-cell $(Fe,Co)(As,S)_2$ $B12_1/d1$ monocline, pseudo-orthorhombic [Buerger, 1936] a' = 2B, b' = C', c' = 2A, β = 90°
a'', b'', c''	arsenopyrite-cell, primitive setting $P2_1/c$ a'' = A − B, b'' = −C, c'' = A + B

Fig. 1. Projections of the sub- and super cells of arsenopyrite on to the basal plane.

used setting $B12_1/d1$ in order to compare the structure with manganite and rutile. This paper refers to space group $C112_1/d$. Reflections with $h = 2n$, $k = 2n$ coincide with the marcasite lattice while those with $h = 2n + 1$, $k = 2n + 1$ are due to the doubling of the cell volume. Reflections with $h + k = 4n + 2$, forbidden by the d glide were observed on precession photographs for $h = 2n + 1$. There may be allowed $hk0$ reflections of a second individual twinned according to mirror planes ⊥ a and b or twofold axes ∥ a and b of an orthorhombic structure of the marcasite type. These symmetry elements were lost due to symmetry reduction.

If the occurrence of these "forbidden" $h\bar{k}0$ reflections is interpreted by twinning, the ratio of the intensities $I(h\bar{k}0)/I(hk0)$ (the corresponding $hk0$ reflections are allowed) should reflect the volume ratio of the twin individuals, and hence be constant. Within experimental errors this condition is fairly well respected (compare Fig. 2). The ratio of the structure factors is approximately 1:3, therefore the volume ratio should be about 1:9.

Table 1. Unit cell dimensions and space groups for marcasite and arsenopyrite.

Space group	Marcasite		Arsenopyrite			
	Buerger (1931)	Buerger (1936)	this work			Morimoto, Clark (1961)
	Pmnn	$B12_1/d1$	$B12_1/d1$	$C112_1/d$	$P12_1/c1$	$P12_1/c1$ ($P\bar{1}$)
a [Å]	3.39	9.55	9.451(2)	6.5456(7)	5.7405(7)	5.744
b [Å]	4.45	5.71	5.6492(8)	9.451(2)	5.6492(8)	5.675
c [Å]	5.42	6.42	6.5456(7)	5.6492(8)	5.7559(5)	5.782
β, γ	–	90.0	89.84(1)	89.84(1)	110.59(1)	112.17
V [Å^3]	81.76	350.1	349.5(2)	349.5(2)	174.73(8)	174.63
Z	2	8	8	8	4	4
locality	Joplin	Franklin, N.J.	Håkansboda, Sweden			Freiberg, FRG

Table 2. Atomic coordinates and thermal parameters $U_{ij} = 100 \cdot U_{ij}$ for arsenopyrites. S.o.f.'s of As and S refer to scattering factors for the pure elements. Thermal parameters are $T = \exp[-2\pi^2 \cdot (U_{11} \cdot h^2 \cdot a^{*2} + \ldots + 2 \cdot U_{12} \cdot h \cdot k \cdot a^* \cdot b^* + \ldots)$.

	s.o.f.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Fe	1.0	0.2769(1)	0.0042(1)	0.0035(1)	1.26(3)	0.60(3)	0.47(2)	0.06(2)	0.01(2)	−0.07(2)
As	0.842(3)	−0.0067(1)	0.1425(1)	0.1286(1)	0.57(2)	0.70(2)	0.38(2)	0.10(2)	−0.01(2)	−0.04(2)
S	1.233(6)	0.5081(1)	0.1638(1)	0.1309(2)	0.57(4)	0.81(4)	0.41(4)	0.08(3)	0.02(3)	0.07(3)

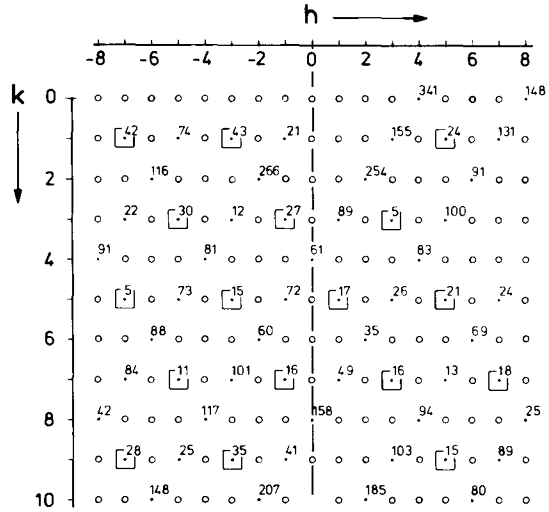


Fig. 2. Structure factors in the *hk*0 plane indicating the volume ratio of the twin individuals.

The volume ratio $q/(1-q)$ of the twin individuals defines the quantity q. $I(+)$ and $I(-)$ are the observed intensities for reflection hkl and $h\bar{k}l$, respectively. The contribution of the twin individuals is expressed by:

$$\begin{aligned} I(+) &= (1-q)\cdot I(hkl) + q\cdot I(h\bar{k}l) \\ I(-) &= q\cdot I(hkl) + (1-q)\cdot I(h\bar{k}l)\,. \end{aligned} \tag{1}$$

The "untwinned" intensities can be derived from these equations:

$$\begin{aligned} I(hkl) &= ((1-q)\cdot I(+) - q\cdot I(-))/(1-2q) \\ I(h\bar{k}l) &= ((1-q)\cdot I(-) - q\cdot I(+))/1-2q)\,. \end{aligned} \tag{2}$$

Refinement started in $C112_1/d$ with parameters transformed from Buerger's values (1936). Scattering factors for Fe^{2+}, As and S calculated from relativistic Hartree-Fock functions, were taken from International Tables, Vol. IV (1974). Weights $1/\sigma^2$, σ from counting statistics, were applied. With anisotropic thermal parameters and free site occupation factors (s.o.f.'s) for As and S, $R = 0.066$, $R_w = 0.037$ was achieved.

The "untwinning" of intensities according to Eq. (2) led to an optimum value $q = 0.10 \pm 0.01$, in good agreement with the estimated ratio, and $R = 0.049$, $R_w = 0.025$. No drastic change in the structural parameters was observed. S.o.f.'s of As and S are 0.842(3) and 1.233(5), respectively. This is interpreted as mixed (As, S) populations at both sites, $As_{0.69}S_{0.31}$ for the

Table 3. Interatomic distances (Å) and angles (°) in arsenopyrite. Standard deviations are 0.001 Å for distances and 0.05° for angles.

Fe	$-S^{ii}$	2.239	Fe	$-As^{iv}$	2.336
	$-S^{iii}$	2.250		$-As^{v}$	2.371
	$-S$	2.257		$-As$	2.375
As	$-S$	2.346			
$S^{ii}-Fe$	$-S^{iii}$	94.42	$S^{iii}-Fe$	$-S$	99.19
	$-S$	89.93		$-As^{iv}$	91.35
	$-As^{iv}$	173.21		$-As^{v}$	87.00
	$-As^{v}$	91.46		$-As$	167.15
	$-As$	83.79	$As^{iv}-Fe$	$-As^{v}$	85.27
$S-Fe$	$-As^{iv}$	92.69		$-As$	89.79
	$-As^{v}$	173.54	$As^{v}-Fe$	$-As$	80.34
	$-As$	167.15			

Symmetry code:	–	x,	y,	z;
	ii	$-1/4+x$,	$-1/4+y$,	$1/2-z$;
	iii	$1-x$,	$-y$,	$-z$;
	iv	$1/4-x$,	$1/4-y$,	$-1/2+z$;
	v	$-x$,	$-y$,	$-z$;

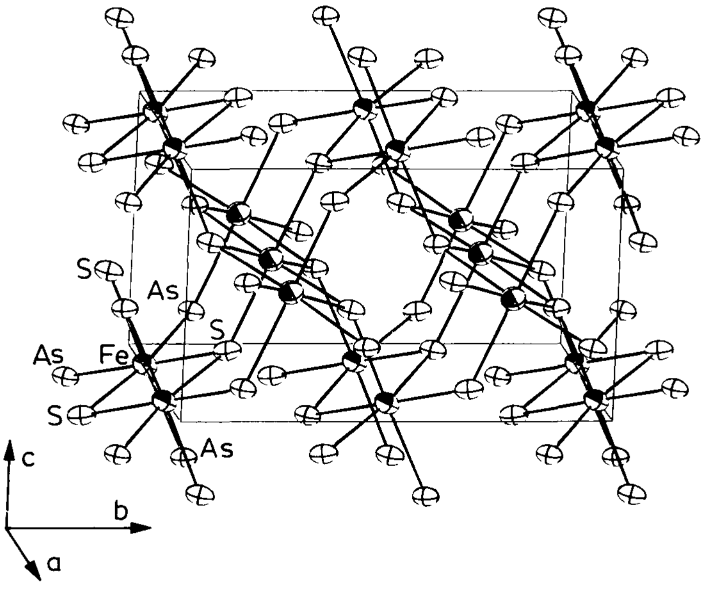


Fig. 3. Crystal structure of arsenopyrite. Probability level 99%.

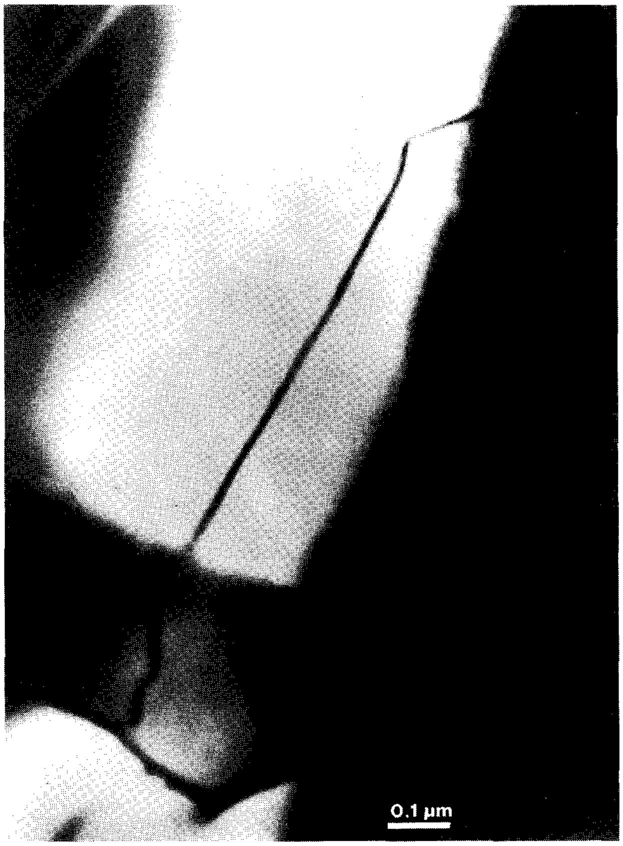


Fig. 4. Twin and antiphase domain boundary in $(Fe_{0.9}Co_{0.1})$ $(As,S)_2$ TEM dark field, $g = 131$. The plane of intergrowth is almost parallel to (001).

As site and $S_{0.78}As_{0.22}$ for the S site, which sums up to a bulk composition $As_{0.91}S_{1.09}$ in fairly good agreement with the chemical analyses. A replacement of the scattering values for Fe by mixed Co – Fe values did not change the refined parameters. The crystal structure of arsenopyrite is basically the same as reported by Buerger (1936). The refined parameters are given in Table 2, interatomic distances and angles are listed in Table 3 and the structure is represented in Figure 3.

Transmission electron microscopy

The twinning in arsenopyrite becomes directly visible in TEM images. The twin domain size varies from microscopic to submicroscopic. Figure 4 gives

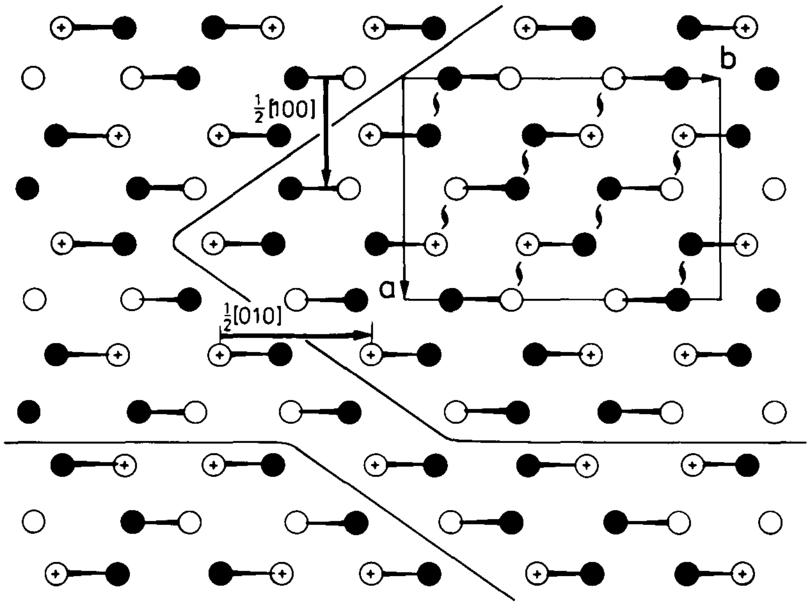


Fig. 5. Formation of antiphase domain boundaries in arsenopyrite by ordering of As and S. Black dots: As, light dots: S; + : center of the connecting line at $z = 0.5$, otherwise at $z = 0$.

an example of a small twin domain and an antiphase domain boundary crossing the interfaces. The twin axis is parallel to [001]. Operating in the dark field mode with a superstructure reflection (h odd, k odd) the antiphase domain boundaries are visible. The displacement vector R was determined as 1/2 [100] and 1/2 [010]. The Co content of the material displaying APB's is about 10 mol%. The observed type of APB's results from the ordering of S and As. This is schematically demonstrated in Figure 5. Regions that are out of phase are brought into phase by application of the antiphase vectors. The equivalence of 1/2 [100] [= *a*(marcasite)] and 1/2 [010] [= *b*(marcasite)] is evident.

Exsolution lamellae are shown in Figure 6. They may be due to an exsolution in Co-rich and Co-poor lamellae. This material is characterized by a higher Co content, varying between 17 and 21 mol% Co. The lamellae are oriented parallel to (110).

Pure CoAsS (cobaltite) crystallizes pseudoisometric in space group $Pca2_1$ ($a = b = c = 5.582$ Å, $\alpha = \beta = \gamma = 90°$, approximately), and above 450°C adopts the pyrite structure ($Pa\bar{3}$) (Giese et al., 1965; Scott et al., 1976). Klemm (1965) found by X-ray powder analysis at room temperature solid solutions with cubic structure from CoAsS to $Fe_{0.47}$ $Co_{0.53}AsS$.

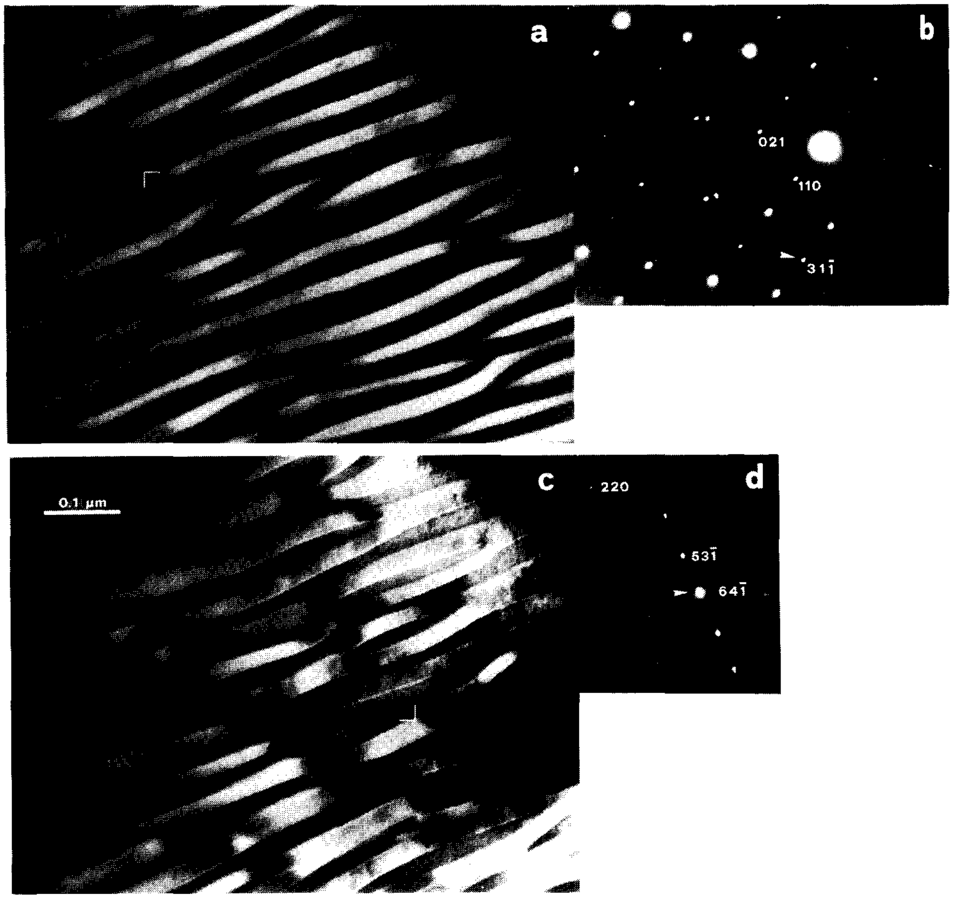


Fig. 6. Exsolution in cobalt containing arsenopyrite on (110): a, b: Co-poor phase (arsenopyrite-type) in contrast. c, d: Co-enriched phase (cobaltite-type) in contrast dark field, the operating reflections are marked by arrows.

Discussion

The structure refinement of the arsenopyrite with formula $Fe_{0.87}Co_{0.13}As_{0.88}S_{1.12}$ was based on data from a twin crystal taking the volume ratio of the two individuals into account. The symmetry is monoclinic according to Morimoto's and Clark's statement that cobalt stabilizes the monoclinic symmetry. The average Fe–S distance in arsenopyrite is 2.249 Å which is almost equal to the mean Fe–S distance in marcasite FeS_2 of 2.246 whereas the average Fe–As distance of 2.367 in FeAsS is considerably shorter than the 2.40 in loellingite $FeAs_2$ (Brostigen and Kjekshus, 1970b). This is due to the sulfur excess in our sample.

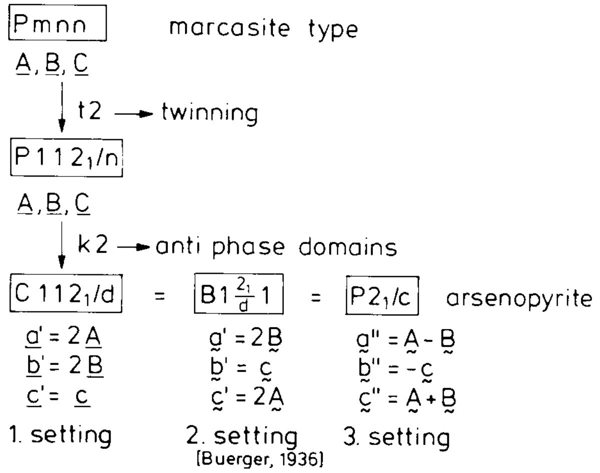


Fig. 7. Group-subgroup relationships between spacegroup of marcasite and the spacegroups of arsenopyrite. *t*2 means "translationengleiche" symmetry reduction and *k*2 stands for "klassengleiche" symmetry reduction.

The occurrence of antiphase and twin domains in arsenopyrite may be interpreted by group-subgroup relationships. The symmetry reduction from marcasite type *Pmnn* and arsenopyrite $C112_1/d$ is demonstrated in the "family tree" (Fig. 7). The loss of symmetry is compensated by characteristic crystal defects. The reduction *t*2 leading from *Pmnn* to $P112_1/n$ causes two kinds of twin domains with twofold twin axes parallel *A* and *B*. $P112_1/n$ is a maximal subgroup of *Pmnn*. The reduction *k*2 is responsible for the formation of antiphase domains with displacement vectors *A* or *B* (lattice vectors of marcasite), which compensate the loss of translational symmetry. $C112_1/d$ is a maximal subgroup of $P112_1/n$.

These group-subgroup relationships are a useful tool to explain the nature of crystal defects observed by TEM (Van Tendeloo and Amelinckx, 1974). General applications to crystal chemistry is given by Bärnighausen (1980). It should be emphasized that the results described here were obtained from specimens which do not correspond to the ideal formula of arsenopyrite. The amount of 10 – 15% cobalt may classify the sample under the mineral name of danaite. The twinning in these samples is, however, typical for the arsenopyrite structure.

The observed exsolutions of Co-rich and Co-poor lamellae in the (Fe,Co) $(As,S)_2$ system is another example of the relationship between pyrite, marcasite and arsenopyrite type structures as discussed previously by Brostigen and Kjekshus (1970a).

It seems therefore, that the microstructure in our system is similar to that in the marcasite-pyrite system. These two polytypes of FeS_2 may occur with {110} of marcasite parallel to {001} of pyrite (Fleet, 1970). A corresponding structural relationship between cobaltite and arsenopyrite was discussed by Klemm (1965), who proposed a model for the transformation of monoclinic arsenopyrite to a cubic phase. This model is based on the similarity of the cobaltite structure projected on (001), and the (110) projection of the arsenopyrite structure. The values $d(220) = 2.712$ Å in arsenopyrite and $d(002) = 2.791$ Å in cobaltite are very similar as well. Our TEM observations confirm that the (110) plane of arsenopyrite is intergrown with parallel (001) planes of cobaltite.

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