KIEFTITE, CoSb$_3$, A NEW MEMBER OF THE SKUTTERUDITE GROUP FROM TUNABERG, SWEDEN

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ABSTRACT

Kieftite, CoSb$_3$, is a new mineral species from the Tunaberg Cu–Co-sulfide skarn ores, southeastern Bergslagen, Sweden. It occurs as large (up to 400 µm) tin-white subhedral to euhedral crystals in chalcopyrite, associated with bornite, galena, native bismuth, native silver, dyscrasite, gudmundite and tetrahedrite. The mineral is opaque with a highly metallic luster, grey streak, and conchoidal fracture. The calculated density D_x for CoSb$_3$ is 7.63 g cm^{-3} ($Z = 8$); VHN_{100} is in the range 420–514. In reflected plane-polarized light, the mineral is white and isotropic. Reflectance values (nm, %) are 470, 59.0; 546, 58.7; 589, 58.7; 650, 58.7. The average of 30 electron-microprobe analyses gives (in wt.%): Co 12.8, Ni 0.7, Fe 0.3, Cu 0.2, Sb 85.8, Cl 0.3, sum 100.1. The average chemical formula is (Co$_{0.91}$Ni$_{0.05}$Fe$_{0.02}$Cu$_{0.02}$)$_{\Sigma 1.00}$(Sb$_{2.97}$Cl$_{0.03}$)$_{\Sigma 3.00}$ or, ideally, CoSb$_3$. A crystal-structure determination shows kieftite to be isostructural with synthetic CoSb$_3$ and skutterudite CoAs$_3$; the cell is cubic, space group *Im3* (No. 204), a 9.0411(3) Å, V 739.03(4) Å^3. The strongest eight X-ray powder-diffraction lines [d in Å (I) (hkl)] are 2.859(10)(310), 2.416(6)(321), 2.022(8)(420), 1.773(6)(510), 1.551(6)(530), 1.333(7)(631), 1.051(6)(750), and 0.933(8)(932). The name honors Dr. Cornelis Kieft for his contributions to ore mineralogy.

Keywords: kieftite, new mineral species, Sb analogue of skutterudite, reflectance data, electron-microprobe analyses, crystal structure, Tunaberg, Sweden.

SOMMAIRE

La kieftite, CoSb$_3$, nouvelle espèce minérale, provient des skarns à sulfures de cuivre et de cobalt de Tunaberg, dans le secteur sud-est du Bergslagen, en Suède. Elle se présente en cristaux blanc-étain sub-idiomorphes à idiomorphes atteignant 400 µm dans la chalcopyrite, en association avec bornite, galène, bismuth et argent natifs, dyscrasite, gudmundite et tétraédrite. C'est un minéral opaque dont l'éclat est fortement métallique, la rayure, grise, et la fracture, concoïdale. La densité calculée est 7.63 ($Z = 8$), et la dureté VHN_{100}, entre 420 et 514. En lumière réfléchie polarisée, la kieftite est blanche et isotrope. Les valeurs de réflectance (nm, %) sont: 470, 59.0; 546, 58.7; 589, 58.7, 650, 58.7. Trente analyses à la microsonde électronique ont donné la composition moyenne suivante, exprimée en % (poids): Co 12.8, Ni 0.7, Fe 0.3, Cu 0.2, Sb 85.8, Cl 0.3, total 100.1. La formule chimique correspondante serait (Co$_{0.91}$Ni$_{0.05}$Fe$_{0.02}$Cu$_{0.02}$)$_{\Sigma 1.00}$(Sb$_{2.97}$Cl$_{0.03}$)$_{\Sigma 3.00}$, ou, plus simplement, CoSb$_3$. Une détermination de la structure cristalline montre que la kieftite est isostructurale avec le CoSb$_3$ synthétique et la skutterudite (CoAs$_3$). La maille est cubique, groupe spatial *Im3* (no. 204), a 9.0411(3) Å, V 739.03(4) Å^3. Les huit raies les plus intenses du tracé de diffraction X [méthode des poudres; d en Å(I)(hkl)] sont: 2.859(10)(310), 2.416(6)(321), 2.022(8)(420), 1.773(6)(510), 1.551(6)(530), 1.333(7)(631), 1.051(6)(750) et 0.933(8)(932). Le nom honore Cornelis Kieft pour ses nombreuses contributions à la minéralogie des minerais.

(Traduit par la Rédaction)

Mots-clés: kieftite, nouvelle espèce minérale, analogue antimonifère de la skutterudite, réflectance, analyses à la microsonde électronique, structure cristalline, Tunaberg, Suède.

INTRODUCTION

Kieftite, of ideal formula CoSb$_3$, is a new mineral species from the Tunaberg Cu–Co-sulfide skarn ores. The mineral is named for Dr. Cornelis Kieft (born 1924), in recognition of his important contributions to ore mineralogy. The mineral and the mineral name kieftite have been approved by the Commision on New Minerals and Mineral Names, IMA. The type material, consisting of several hand specimens, polished sections and polished thin sections, is preserved in the mineral collection of the Instituut voor Aardwetenschappen, Vrije Universiteit, Amsterdam.

OCCURRENCE AND ASSOCIATED MINERALS

The Tunaberg polymetallic sulfide deposits, Sweden, are located in the southeastern part of the Bergslagen ore province, about 20 km south of Nyköping, at longitude 16°55′ and latitude 58°39′ Mineralization occurs in a metatuffite formation, in the upper part of an Early Proterozoic (1.9–1.8 Ga) volcanosedimentary sequence metamorphosed to the upper amphibolite facies. A central zone of Cu–Co-sulfide skarn ores is hosted by "skarned" marble, and a peripheral zone of Zn–Pb-sulfide ores hosted by metatuffite, graphitic slate and marble.

Kieftite was found in polished sections of chalcopyrite-rich ore collected from dumps and exposed rocks at the abandoned mine, in Cu–Co-sulfide skarn ores of the central zone. Kieftite forms subhedral to euhedral crystals up to 400 μm across in aggregates enclosed in chalcopyrite (Fig. 1) that occurs associated with bornite, galena, native bismuth, native silver, gudmundite and tetrahedrite. The kieftite may contain inclusions of chalcopyrite,

native bismuth and dyscrasite. Other minerals identified in kieftite-bearing specimens include allargentum, antimony, arsenopyrite, breithauptite, cobaltite, (para)costibite, covellite, cubanite, electrum, graphite, molybdenite, nisbite, safflorite, sphalerite, stannoidite and uraninite.

CHEMICAL COMPOSITION

Electron-microprobe analyses were performed with a Cambridge Instruments Microscan-9 electron microprobe equipped with a Link energy-dispersion X-ray analyzer operated at an acceleration potential of 15 kV and at a beam current of 40 nA. Counting times were 15 s. $K\alpha$ lines were measured for Co, Ni, Fe, Cu, Cl and S, $L\alpha$ lines for Sb and As, $M\alpha$ lines for Bi. Pure metals (Co, As), heazlewoodite (Ni), troilite (Fe), chalcopyrite (Cu), stibnite (Sb, S), bismuthinite (Bi, S), and marialite (Cl) were used as standards. A ZAF correction procedure was applied using Wilson's J/Z and Yakowitz's absorption correction (Reed 1993). To avoid errors in the determination of
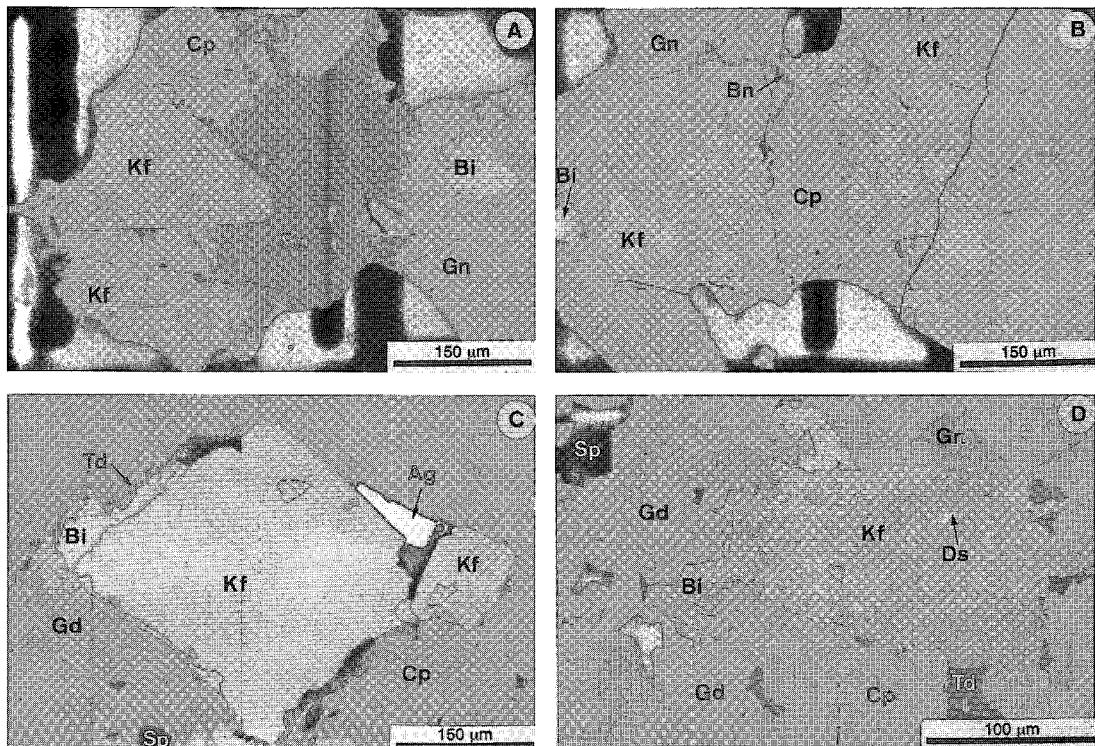

FIG. 1. (A,B) Kieftite (Kf) crystals in chalcopyrite (Cp). Symbols: Bn bornite, Gn galena, Bi native bismuth. (C) Kieftite in chalcopyrite is rimmed by native bismuth, native silver (Ag), gudmundite (Gd) and tetrahedrite (Td). Sp: sphalerite. (D) Kieftite with inclusions of native bismuth and dyscrasite (Ds).

TABLE 1. CHEMICAL COMPOSITION OF KIEFTITE

	1	2	3	4	5	6	7	8	Avg.*
Co, Wt%	12.4	12.8	12.4	13.2	13.3	11.6	12.1	9.8	12.8
Ni	0.7	0.6	0.7	0.3	0.4	1.6	1.4	2.6	0.7
Fe	0.2	0.4	0.3	0.3	0.2	0.2	0.2	1.7	0.3
Cu	0.3	0.4	0.2	0.3	0.2	0.2	0.1	0.4	0.2
Sb	84.7	84.8	85.0	86.5	86.0	86.2	85.2	85.3	85.8
Cl	0.5	0.4	0.2	n.d.	0.3	0.1	0.9	0.4	0.3
Total	98.8	99.4	98.8	100.6	100.4	99.9	99.9	100.2	100.1
Co, form. unit	0.90	0.92	0.90	0.94	0.95	0.84	0.86	0.69	0.91
Ni	0.05	0.04	0.05	0.02	0.03	0.12	0.10	0.19	0.05
Fe	0.02	0.03	0.02	0.02	0.01	0.01	0.01	0.12	0.02
Cu	0.02	0.03	0.01	0.02	0.01	0.01	0.01	0.03	0.02
Sb	2.96	2.94	3.00	3.00	2.96	3.01	2.92	2.92	2.97
Cl	0.06	0.04	0.02		0.04	0.01	0.10	0.05	0.03

Anal. 1, 2, 3 refer to spot analyses of Fig. 2; (*) number of analyses = 30;
S, As, Bi not detected; n.d. = not detected

As concentrations due to overlap of As$L\alpha$ peaks with the second-order Sb$L\beta_1$ lines, the apparent concentration of As in a pure stibnite (Sb$_2$S$_3$) standard was carefully measured; this gave an apparent concentration of 1.10 wt.% As for 71.73 wt.% Sb. After correction for this overlap of lines, the arsenic content of kieftite was found to be below the detection limit of about 0.03 wt.%. Selected results of analyses illustrating the range in composition of kieftite are presented in Table 1. Kieftite has the ideal formula CoSb$_3$; Co shows substitution by Ni (up to 0.19 atoms per formula unit, apfu), Fe (up to 0.12 apfu), Cu (up to 0.04 apfu), whereas Sb shows substitution by Cl (up to 0.10 apfu). Chlorine usually shows an irregular distribution, with Cl-rich patches and rims,

but also with Cl-rich domains in the kieftite (Fig. 2). Schmidt *et al.* (1987) noted that the unit cell of synthetic CoSb$_3$ crystals appear somewhat enlarged compared to that of synthetic CoSb$_3$ in powder form (*a* 9.0385 Å *versus* 9.0356 Å). They ascribed this enlargement of the unit cell to the structural incorporation of Cl, used as a transport agent in the experiments; the unit cell of kieftite from Tunaberg (*a* 9.0411 Å; see below) is still larger than that of synthetic CoSb$_3$ powder. On the basis of 4 atoms in the unit cell and assuming that Cl substitutes for Sb, the average composition of kieftite from Tunaberg is (Co$_{0.91}$Ni$_{0.05}$Fe$_{0.02}$Cu$_{0.02}$)$_{\Sigma1.00}$(Sb$_{2.97}$Cl$_{0.03}$)$_{\Sigma3.00}$. Kieftite is isomorphic with skutterudite CoAs$_3$ (see below), and is its antimonian analogue.
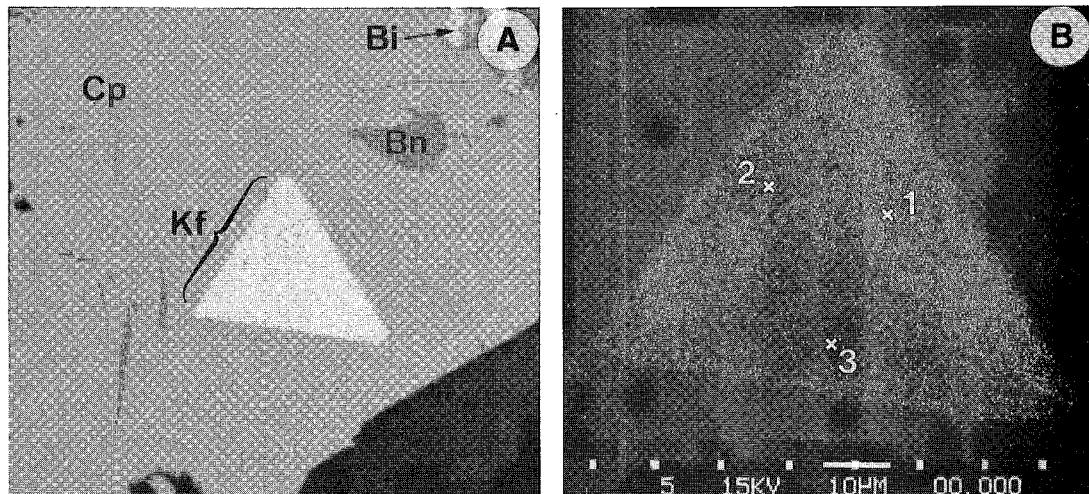

FIG. 2. (A) Euhedral kieftite (Kf) crystal in chalcopyrite (Cp). Other symbols: Bn bornite, Bi native bismuth. (B) Electron microprobe Cl *K*α X-ray image showing domains with different Cl-contents in kieftite crystal shown in Figure 2A. Numbers refer to spot analyses in Table 1.

PHYSICAL AND OPTICAL PROPERTIES

In hand specimen, kieftite is opaque, with a highly metallic luster and tin-white color. The mineral is characterized by a grey streak, and brittle, conchoidal fracture without cleavage. The equant crystals show {100}, {110}, {111} as the most common crystal faces; twinning is not observed. The calculated density D_x for stoichiometric $CoSb_3$ ($Z = 8$) is 7.63 g/cm^3. The VHN_{100} microhardness has an average value of 464 (range 420–514 for three indentations). These data agree with those given by Zhuravlev & Zhdanov (1956) for synthetic $CoSb_3$: $D_m= 7.2$ g/cm^3 (the measured density D_m is low, probably because of the porous nature of the material), $D_x= 7.68$ g/cm^3 and $VHN_{20}= 455$ (420–490). The polishing hardness of kieftite is higher than that of chalcopyrite and tetrahedrite, and is very close to that of gudmundite.

In reflected, plane-polarized light, kieftite is tin-white in air and in oil. The mineral is isotropic; internal reflections have not been observed. Reflectance measurements in air were made against a carborundum standard (Zeiss WC–6); average reflectance values for six grains (nm, %) are: 470, 59.0; 546, 58.7; 589, 58.7; 650, 58.7.

CRYSTAL-STRUCTURE ANALYSIS OF KIEFTITE

A crystal of kieftite with approximate dimensions $0.10 \times 0.15 \times 0.25$ mm was studied with an Enraf–Nonius CAD–4 diffractometer, using a graphite-monochromated Cu$K\alpha$ radiation [$\lambda = 1.5418$ Å]. Structure determination was done using the anisotropic full-matrix least-squares program (XTAL) of Hall & Stewart (1990). Twenty-three reflections in the 2θ range 81–95° gave a refined unit-cell para-

TABLE 2. FRACTIONAL COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS (Å^2) FOR KIEFTITE

	X	Y	Z	U_{eq}
Co	0.25	0.25	0.25	-0.034(1)
Sb	0.0	0.3352(1)	0.1575(1)	-0.0321(7)

TABLE 3. ANISOTROPIC THERMAL PARAMETERS (Å^2) FOR KIEFTITE

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	-0.035(1)	-0.035(1)	-0.035(1)	0.014(8)	0.0014(8)	0.014(8)
Sb	-0.0354(8)	0.0297(6)	-0.0321(8)	0.0	0	0.0010(3)

meter a of 9.0411(3) Å. The intensity of 915 reflections [ω-2θ scan, $(\sin \theta)/\lambda < 0.63$ Å^{-1}, ranges $0 \leq h \leq 11$, $-11 \leq k \leq 0$, $0 \leq l \leq 11$] was measured; of these, 431 reflections have an intensity exceeding the significance level $2.5\sigma(I)$, and 151 of these are unique. Data reduction included background, Lorentz, polarization and empirical absorption corrections (linear absorption coefficient: $\mu(\text{Cu}K\alpha) = 2108.7$ cm^{-1}, transmission factor range $\sim$ 0.10 to 1.76; Walker & Stuart 1983). Two reference reflections ($4\overline{2}0,0\overline{1}3$) were measured hourly and showed no significant variation throughout the 10 hours of the experiment. Structural refinement proceeded from the positional parameters of Schmidt *et al.* (1987) for synthetic $CoSb_3$ in space group $Im3$. The scattering factors of neutral atoms were taken from the International Tables for X-ray Crystallography (1974). The quantity $\Sigma w(\Delta F^2)$ was minimized according to w = $[\theta(F^{obs})]^{-1}$. The refinement in $Im3$ converged to an R of 0.045 ($R_w = 0.037$), $(\Delta/\sigma)_{max} = 0.03$, $\Delta\rho = -6.5$ eÅ^{-3} to 12.8 eÅ^{-3}. The final positional parameters for kieftite are presented in Tables 2 and 3.
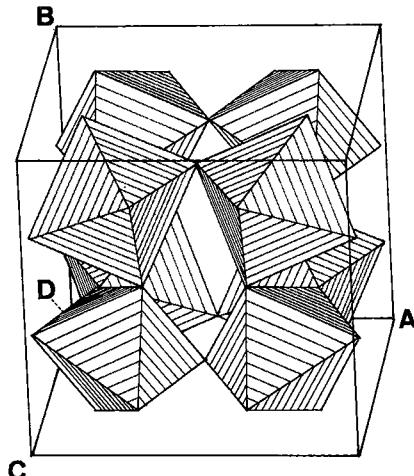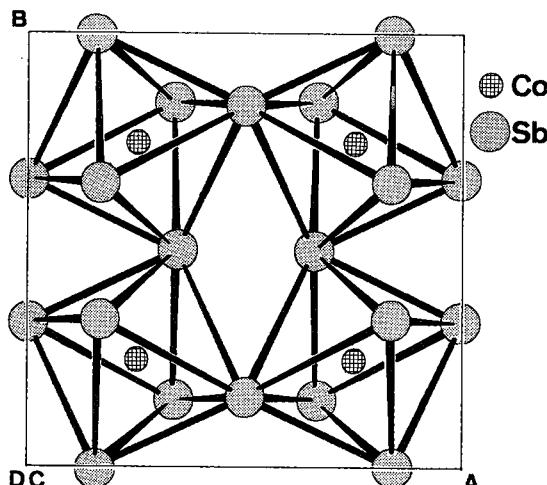

FIG. 3. Left: A c-axis projection of the crystal structure of kieftite showing coordination of ions. Right: Three-dimensional view of the crystal structure of kieftite showing linkage of octahedra.

TABLE 4. X-RAY POWDER DATA FOR KIEFTITE AND SYNTHETIC $CoSb_3$

KIEFTITE			SYNTHETIC $CoSb_3$ PDF 19-336		
d(meas)	I	d(calc)	hkl	d(meas)	I
		3.691	211	3.68	10
2.86	10	2.859	310	2.85	100
2.42	6	2.416	321	2.40	40
2.13	2	2.131	330	2.12	20
2.02	8	2.022	420	2.01	80
1.93	4	1.928	332	1.92	80
1.85	5	1.846	422	1.84	80
1.77	6	1.773	510	1.76	40
1.55	6	1.551	530	1.54	40
1.507	4	1.507	600	1.50	80
		1.467	611	1.46	10
		1.430	620	1.42	10
1.374	1	1.363	622	1.36	20
1.331	7	1.333	631	1.33	60
		1.305	444	1.30	10
1.281	4			1.27	20
		1.254	640	1.25	10
1.232	1	1.230	721	1.227	20
1.186	B6	1.187	730	1.185	80
1.142	2	1.148	651	1.147	80
1.097	2	1.096	820	1.095	20
1.079	4	1.081	653	1.079	20
1.064	5	1.066	660	1.064	60
1.052	6	1.051	750	1.050	60
0.998	B3	0.998	910	0.997	80
0.976	1	0.975	761	0.974	10
0.953	1	0.953	930	0.952	10
0.933	8	0.933	932	0.932	60
0.922	1	0.923	844	0.922	10
0.913	B6	0.913	770	0.913	80
		0.878	950	0.878	20
		0.870	10̄22	0.869	20
		0.862	10̄31	0.861	80
		0.847	8̄71	0.847	10
		0.839	10̄40	0.839	80
		0.832	9̄61	0.832	60
		0.825	10̄42	0.825	60
		0.819	11̄10	0.818	60
		0.805	10̄51	0.805	80
		0.793	9̄70	0.792	50
		0.787	882	0.786	60
		0.781	972	0.780	100
				0.735	80
a = 9.0411(3) Å (*)			a = 9.034 Å		

- 114.6-mm-diameter Gandolfi camera
- Fe-filtered $CoK\alpha$ radiation
- (*) refinement from diffractometer data
- B = broad line

Kieftite has a cubic primitive lattice (Fig. 3). The structure consists of trigonally distorted $CoSb_6$ octahedra [<Co–Sb> = 2.5302(5) Å]. The rectangular arrangement of the Sb atoms [<Sb–Sb> = 2.8478(15) and 2.9794(14) Å], is analogous to that in skutterudite $CoAs_3$ (Mandel & Donohue 1971), synthetic $CoSb_3$ (Zhuravlev 1956, Schmidt et al. 1987), and MY_3 synthetic compounds in general (M = Co, Rh, Ir; Y = P, As, Sb) (Zhuravlev & Zhdanov 1956, Kjekshus & Rakke 1974, Lutz & Kliche 1982).

The X-ray powder-diffraction pattern of kieftite from Tunaberg is presented in Table 4. It seems to be virtually identical to that of synthetic $CoSb_3$ (PDF 19–336).

REFERENCES

HALL, S.R. & STEWART, J.M., eds. (1990): XTAL3.0 User's Manual. Univ. of Western Australia, and Univ. of Maryland, College Park, Maryland.

INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY, VOL. IV (1974): The Kynoch Press, Birmingham, England.

KJEKSHUS, A. & RAKKE, T. (1974): Compounds with the skutterudite type crystal structure. III. Structural data for arsenides and antimonides. Acta Chem. Scand., Ser. A28, 99-103.

LUTZ, H.D. & KLICHE, G. (1982): Far-infrared reflection spectra, optical and dielectric constants, effective charges, and lattice dynamics of the skutterudites CoP_3, $CoAs_3$, and $CoSb_3$. Phys. Stat. Solidi B112, 549-557.

MANDEL, N. & DONOHUE, J. (1971): The refinement of the crystal structure of skutterudite, $CoAs_3$. Acta Crystallogr. B27, 2288-2289.

REED, S.J.B. (1993): Electron Microprobe Analysis. Cambridge University Press, London, U.K.

SCHMIDT, T., KLICHE, G. & LUTZ, H.D. (1987): Structure refinement of skutterudite-type cobalt triantimonide, $CoSb_3$. Acta Crystallogr. C43, 1678-1679.

WALKER, N. & STUART, D. (1983): An empirical method for correcting diffractometer data for absorption effects. Acta Crystallogr. A39, 158-166.

ZHURAVLEV, N.N. (1956): Microscope and X-ray structural study of cobalt – antimony alloys. Sov. Phys. Crystallogr. 1(5), 402-403.

—— & ZHDANOV, G.S. (1956): X-ray diffraction determination of the structure of $CoSb_3$, $RhSb_3$ and $IrSb_3$. Sov. Phys. Crystallogr. 1(5), 404-406.