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KUPČÍKITE, $Cu_{3.4}Fe_{0.6}Bi_5S_{10}$, A NEW Cu–Bi SULFOSALT FROM FELBERTAL, AUSTRIA, AND ITS CRYSTAL STRUCTURE

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Abstract

Kupčíkite, $Cu_{3.4}Fe_{0.6}Bi_5S_{10}$, a new mineral species, is found in the scheelite deposit of Felbertal, Austria, in a quartz gangue, in association with chalcopyrite, pyrrhotite, molybdenite, sphalerite and native bismuth, intergrown with makovickyite, cupromakovickyite, hodrushite, cuprobismutite and derivatives of the bismuthinite–aikinite series. The mineral is grey with metallic luster, brittle, and without cleavage. Mean micro-indentation hardness is 192 kg/mm^2 (Mohs hardness 3.3), and the calculated density is 6.42 g/cm^3. In reflected light, it is grayish white; the anisotropy is moderate in air and strong in oil, and it does not show internal reflections. Reflectance values (in %) in air are, for R_1 and R_2, 33.55, 40.56 at 470 nm, 33.92, 41.14 at 546 nm, 34.16, 41.35 at 589 nm, and 34.2, 41.32 at 650 nm. The average results of seven electron-microprobe analyses are: Cu 13.02, Fe 2.23, Ag 0.11, Cd 0.3, Bi 64.21, Sb 0.12, S 20.10, total 100.08 wt.%, corresponding to $Fe_{0.64}Cu_{3.29}Ag_{0.015}Cd_{0.045}Sb_{0.015}Bi_{4.94}S_{10.07}$ (basis: 19 atoms per formula unit). The simplified formula, in accordance with the crystal-structure analysis, is $Fe_{0.6}Cu_{3.4}Bi_5S_{10}$. The crystal structure was solved, to $R = 4.1\%$, from single-crystal data obtained on a four-circle diffractometer with an area detector. Kupčíkite has a monoclinic cell with a 17.512(2), b 3.9103(4), c 12.869(1) Å, β 108.56(1)°, V 835.4(1) Å^3, space group $C2/m$, with $Z = 2$. The strongest lines in the calculated powder-diffraction pattern [d in Å (I)(hkl)] are: 6.028(4)(201), 3.596(7)(401), 3.213(4)($\bar{2}04$), 3.128(10)(112), 3.071(7)($\bar{3}12$), and 2.683(5)(113). Its structure corresponds to the structure of synthetic $Cu_4Bi_5S_{10}$; the (Cu,Fe) position in the mineral is distinctly split. Kupčíkite is closely structurally related to cuprobismutite and hodrushite. It is the $N = 1$ member of the cuprobismutite series, whereas cuprobismutite is the $N = 2$ member. Hodrushite is composed of a regular 1:1 intergrowth of kupčíkite-like and cuprobismutite-like layers. In typical intergrowths with makovickyite or hodrushite, kupčíkite shows sharp straight boundaries with both of these phases, but where in contact with derivatives of the bismuthinite–aikinite series, the latter replace kupčíkite. In a rare occurrence of kupčíkite with cuprobismutite in the same aggregate, the cuprobismutite is replaced by kupčíkite.

Keywords: kupčíkite, single-crystal X-ray diffraction, electron-microprobe analyses, cuprobismutite homologous series, Felbertal deposit, Austria.

Sommaire

Nous avons découvert la kupčíkite, $Cu_{3.4}Fe_{0.6}Bi_5S_{10}$, nouvelle espèce minérale, dans le gisement de scheelite de Felbertal, en Autriche, dans une gangue de quartz, en association avec chalcopyrite, pyrrhotite, molybdénite, sphalérite et bismuth natif, en intercroissances avec la makovickyite, la cupromakovickyite, la hodrushite, la cuprobismutite et des dérivés de la série bismuthinite–aikinite. Il s'agit d'un minéral gris avec éclat métallique, cassant, et sans clivage. En moyenne, les micro-indentations indiquent un dureté de 192 kg/mm^2, équivalente à un dureté de Mohs de 3.3, et la densité calculée est 6.42 g/cm^3. En lumière réfléchie, la kupčíkite est blanc grisâtre; l'anisotropie est modérée dans l'air et forte dans l'huile. Elle ne montre aucune réflexion interne. Les valeurs de la réflectance R_1 et R_2 dans l'air sont 33.55, 40.56% à 470 nm, 33.92, 41.14% à 546 nm, 34.16, 41.35% à 589 nm, et 34.2, 41.32% à 650 nm. Sept analyses à la microsonde électronique ont donné, en moyenne, Cu 13.02, Fe 2.23, Ag 0.11, Cd 0.3, Bi 64.21, Sb 0.12, S 20.10, total 100.08% (en poids), ce qui correspond à $Fe_{0.64}Cu_{3.29}Ag_{0.015}Cd_{0.045}Sb_{0.015}Bi_{4.94}S_{10.07}$ sur une base de 19 atomes par unité formulaire. La formule simplifiée, en concordance avec les résultats de l'ébauche de la structure cristalline, est $Fe_{0.6}Cu_{3.4}Bi_5S_{10}$. Nous en avons résolu la structure jusqu'à un résidu R de 4.1% à partir de données

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obtenues sur monocristal avec un diffractomètre à quatre cercles et un détecteur de type CCD. La kupčíkite possède une maille monoclinique, *a* 17.512(2), *b* 3.9103(4), *c* 12.869(1) Å, β 108.56(1)°, *V* 835.4(1) $Å^3$, groupe spatial *C*2/*m*, avec *Z* = 2. Les six raies les plus intenses du spectre de diffraction calculé [*d* en Å (I)(*hkl*)] sont: 6.028(4)(201), 3.596(7)(401), 3.213(4)($\bar{2}$04), 3.128(10)(112), 3.071(7)($\bar{3}$12), et 2.683(5)(113). Sa structure correspond à celle du composé synthétique $Cu_4Bi_5S_{10}$; la position (Cu,Fe) du minéral, par contre, est distinctement scindée. La kupčíkite montre une relation structurale étroite avec la cuprobismutite et la hodrushite. Elle est l'homologue *N* = 1 de la série de la cuprobismutite, tandis que la cuprobismutite en est le membre ayant *N* égal à 2. La hodrushite est composée d'une intercroissance régulière 1:1 de couches de type kupčíkite et cuprobismutite. Dans les intercroissances typiques avec la makovickyite ou la hodrushite, la kupčíkite fait preuve d'interfaces rectilignes et franches avec ces deux phases, mais en contact avec les dérivés de la série de la bismuthinite–aikinite, ces derniers la remplacent. Dans un rare exemple de kupčíkite avec cuprobismutite dans le même aggrégat, la cuprobismutite se voit remplacée par la kupčíkite.

(Traduit par la Rédaction)

Mots-clés: kupčíkite, diffraction X sur monocristal, analyses à la microsonde électronique, série d'homologues de la cuprobismutite, gisement de Felbertal, Autriche.

INTRODUCTION

Copper and bismuth together form a series of complex sulfides that have various stoichiometries and distinct structures; in many instances, minor amounts of other elements seem essential for their formation, especially under natural conditions. At the Cu-rich end, this series starts with wittichenite, Cu_3BiS_3, whose crystal structure was determined by Matzat (1972) and Kocman & Nuffield (1973). It continues with emplectite, $CuBiS_2$ (structure by Portheine & Nowacki 1975), hodrushite [Kupčík & Makovicky (1968), Koděra *et al.* (1970); the chemical composition was given as $Cu_{8.1}Fe_{0.3}Bi_{11.5}S_{22}$, with Pb attributed an uncertain role by Makovicky & MacLean (1972)] and cuprobismutite [Nuffield (1952), Taylor *et al.* (1973); $Cu_{10.4}Bi_{12.6}S_{24}$ for the synthetic, Ag-free analogue; structure by Ozawa & Nowacki (1975)] and ends with the Cu–Bi-based homologues of pavonite: *N* = 4, makovickyite (Mumme 1990, Žák *et al.* 1994) and *N* = 8, mummeite (Karup-Møller & Makovicky 1992, Mumme 1990). The *N* = 4 homologue of pavonite, with a chemical formula $Cu_{3.21}Bi_{4.79}S_9$, and an *N* = 3 homologue, $Cu_{1.57}Bi_{4.57}S_8$, have also been described as pure synthetic Cu–Bi compounds (Tomeoka *et al.* 1980).

Kupčíkite, the new natural Cu–Bi sulfosalt discovered at Felbertal, Austria, corresponds structurally to the synthetic phase $Cu_4Bi_5S_{10}$ (Mariolacos *et al.* 1975); its discovery enriches further the spectrum of natural Cu–Bi sulfosalts, reveals the first natural occurrence of this member of the cuprobismutite homologous series (Makovicky 1989), and contributes to an understanding of the role of minor elements in Cu–Bi sulfosalts.

Kupčíkite has been named after Professor Vladimir Kupčík (1934–1990), who was active at the University of Bratislava and the University of Göttingen, in acknowledgment of his outstanding contributions to the crystal chemistry of sulfosalts in general, and his understanding of the principles determining the structures of Cu–Bi sulfosalts in particular. The pronunciation of the name in English is k-ou-p-tch-ee-kite, the diacritical signs respectively indicating a consonant tch and a long vowel. The new mineral and its name have been approved prior to publication by the IMA Commission on New Minerals and Mineral Names (IMA 2001–017). The holotype material is deposited at the Geological Institute and Geological Museum, University of Copenhagen, Denmark, and a cotype is in the reference collection of the Mineralogical Institute, University of Salzburg, Austria (catalogue no. 14933).

APPEARANCE AND PHYSICAL PROPERTIES

Rare elongate aggregates that are intergrowths of kupčíkite with makovickyite or bismuthinite derivatives in the range krupkaite–aikinite, as well as the less common parallel intergrowths of kupčíkite with hodrushite, do not exceed 0.5 mm in size. Kupčíkite is grey, opaque with a metallic luster. It is brittle, with an uneven fracture. No cleavage or parting was observed, as in the related hodrushite (Koděra *et al.* 1970). The bulk of material is a fine-grained quartz gangue with parallel strings of sulfides, especially chalcopyrite, pyrrhotite, molybdenite, occasional sphalerite and native bismuth.

The micro-indentation hardness was measured with six indentations on two grains, using a VHN load of 50 g. The mean value obtained is 192 kg/mm^2, range 179–210 kg/mm^2, yielding a calculated Mohs hardness of 3.2–3.4. These values are comparable to the values obtained on hodrushite from Banská Hodruša, Slovakia: mean value 200 kg/mm^2 (range 187–213), *i.e.*, 3.7 on the Mohs scale (Koděra *et al.* 1970); a 20-g load was used in the latter investigation.

In reflected light, kupčíkite is grayish white; internal reflections are absent. The anisotropy is moderate in air and strong in oil; the bireflectance is perceptible in air, and moderate in oil. The pleochroism of kupčíkite is weak in air, white with bluish tints, and enhanced in oil. The rotation tints between polars are dark bluish gray to yellowish brown for the most anisotropic grains.

Quantitative data on reflectance were obtained in air; we used a WTiC standard and Leitz MPV–SP microscope photometer (Table 1, Fig. 1). The measured values of R_{max} (in air) coincide with those of hodrushite and cuprobismutite from Felbertal (D. Topa, unpubl. data), whereas the R_{min} values (in air) are on average 2.5% lower than those of cuprobismutite and almost 2% lower than those of hodrushite. Both kupčíkite curves display only a very flat maximum of ~1% at about 625 nm, in agreement with the white color of the mineral.

CHEMICAL DATA

Quantitative chemical data for kupčíkite and the associated sulfosalts were obtained with an electron microprobe (JEOL Superprobe JXA–8600, controlled by LINK–*eXL* system, operated at 25 kV, 30 nA, 20 s counting time for peaks and 7 s for background). The following natural (n) and synthetic (s) standards and X-ray lines were used: n-$CuFeS_2$ (Cu$K\alpha$), s-Bi_2S_3 (Bi$L\alpha$, S$K\alpha$), n-PbS (Pb$L\alpha$), s-CdTe (Cd$L\beta$, Te$L\alpha$), n-Sb_2S_3 (Sb$L\alpha$) and pure metal for Ag$L\alpha$. The raw data were corrected with the on-line ZAF–4 procedure. Standard deviations of concentrations of the elements sought (error in wt.%) for the cuprobismutite series from Felbertal deposit are: Bi 0.17, Pb, Cd and S 0.06, Cu 0.04, Ag 0.03, Sb 0.02 and Fe 0.01. The only minor elements detected in kupčíkite are Cd, Ag, Pb and Sb.

Results of three to five point analyses obtained from a homogeneous grain or an individual phase in an aggregate were averaged. These mean compositions are compiled in Tables 2a, 2b and 2c. Empirical formula of kupčíkite, normalized to 19 atoms per formula unit (*apfu*), which is the content of the two asymmetric units as determined by the structure analysis, is:

$$Cu_{3.29}Ag_{0.02}Fe_{0.64}Cd_{0.04}(Bi_{4.94}Sb_{0.02})_{\Sigma 4.96}S_{10.06}$$

or

$$(Cu_{3.29}Fe_{0.64})_{\Sigma 3.93}(Bi_{4.94}Sb_{0.02}Ag_{0.02}Cd_{0.04})_{\Sigma 5.02}S_{10.06}$$

The empirical formula was matched by the model composition $Cu_{3.4}Fe_{0.6}Bi_5S_{10}$ obtained in the crystal-structure refinement under the conditions specified below. The simplified formula of kupčíkite is $Cu^{+}_{3.4}Fe^{3+}_{0.6}Bi_5S_{10}$.

TABLE 1. REFLECTANCE DATA (IN AIR) FOR KUPČÍKITE

λ (nm)	R1	R2	λ (nm)	R1	R2
400	33.50	40.66	560	34.05	41.34
420	33.47	40.21	580	34.15	41.28
440	33.48	40.27	**589**	**34.16**	**41.35**
460	33.48	40.29	600	34.18	41.28
470	**33.55**	**40.56**	620	34.32	41.27
480	33.50	40.60	640	34.26	41.42
500	33.48	40.79	**650**	**34.20**	**41.32**
520	33.68	40.96	660	34.11	41.10
540	33.90	41.06	680	34.02	40.92
546	**33.92**	**41.14**	700	34.00	40.94

X-RAY-DIFFRACTION DATA

The limited amount of material, commonly intergrown with other sulfosalts, and the small size of the crystals extracted, limited the X-ray studies to the use of a single-crystal diffractometer with an area-detector system (Table 3). Kupčíkite is monoclinic, space group *C*2/*m*, with two of its unit-cell parameters, *a* and *b*, very close to those of cuprobismutite and hodrushite; they also coincide with those of two synthetic compounds (Table 4). The table of structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada. As powder data could not be obtained because of insufficient material, a theoretical powder pattern was calculated with PowderCell 2.3 software (Kraus & Nolze 1999) for Debye–Scherrer geometry and Cu$K\alpha$ radiation (λ 1.540598 Å), without the anomalous dispersion correction (Table 5). Cell parameters, space group, atom positions, site occupancies and isotropic displacement factors were taken from the results of the single-crystal refinement of the structure.

CRYSTAL-STRUCTURE ANALYSIS

The crystal structure was solved by direct methods. Among the 13 highest maxima in the E-Fourier map, ten were shown to be the real atom-positions. The assignment of positions was based on typical interatomic distances [Bi–S in the range 2.6–3.5 Å, Cu(Fe)–S in the range 2.3–2.9 Å]. The assignments were confirmed by

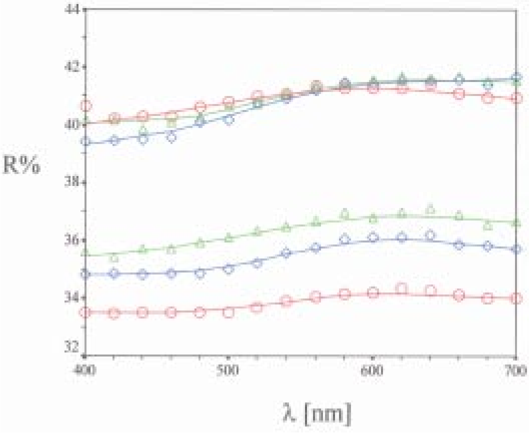

FIG. 1. Reflectance data for kupčíkite (○), hodrushite (◇) and cuprobismutite (△) from Felbertal.

TABLE 2a. AVERAGE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF THE CUPROBISMUTITE SERIES FROM FELBERTAL

No.	Phase	Sample	Fig.	Cu	Ag	Fe	Pb	Cd	Bi	Sb	S	Total	N_{chem}	Σ_{met}	cb
1	kupčíkite	FE-89/9-sg29-d	5a	13.02	0.11	2.23	0.00	0.30	64.21	0.12	20.10	100.08	1.05	8.93	0.07
2	kupčíkite	FE-89/9-1-71-d	5b	13.17	0.00	2.02	0.00	0.29	64.81	0.13	19.82	100.23	1.08	9.00	0.59
3	kupčíkite	FE-89/10-F-d	5c	13.41	0.12	2.09	0.22	0.24	64.75	0.00	20.27	101.09	1.03	8.94	-0.14
4	kupčíkite	FE-89/9-1-2-d	5d	13.45	0.00	1.95	0.00	0.00	65.10	0.10	19.80	100.40	1.03	9.02	0.59
5	kupčíkite	FE-86/k7-2-2-d	5e	13.11	0.00	2.12	0.32	0.00	64.35	0.13	19.82	99.86	1.04	8.99	0.45
6	kupčíkite	FE-86/k7-6-52-d	5f	13.17	0.00	2.13	0.00	0.00	64.62	0.00	19.86	99.77	1.02	8.98	0.33
7	hodrushite	FE-89/9-sg29-d'	5a	13.21	1.06	0.57	0.32	0.19	65.63	0.00	19.25	100.24	1.50	19.99	-0.14
8	hodrushite	FE-86/k7-2-2-d'	5e	13.19	1.09	0.60	0.16	0.19	66.01	0.00	19.23	100.48	1.51	20.03	0.10
9	hodrushite	FE-86/k7-6-52-d'	5f	13.25	1.12	0.54	0.27	0.20	65.99	0.00	19.19	100.56	1.52	20.06	0.15
10	cuprobismutite	FE-89/10-F-m	5c	12.50	2.54	0.00	0.75	0.22	65.48	0.00	18.74	100.23	1.98	11.04	0.12
11	cuprobismutite	FE-89/9-1-2-m	5d	12.39	2.50	0.00	0.81	0.27	65.06	0.00	18.70	99.72	1.99	11.02	-0.06

No.	Chemical formulae	Average simplified formulae
1	$(Cu_{3.29}Fe_{0.64})_{\Sigma 3.93}(Bi_{4.94}Ag_{0.01}Pb_{0.00}Sb_{0.01}Cd_{0.04})_{\Sigma 5.00}S_{10.07}$	kupčíkite
2	$(Cu_{3.35}Fe_{0.59})_{\Sigma 3.94}(Bi_{5.01}Ag_{0.00}Pb_{0.00}Sb_{0.01}Cd_{0.04})_{\Sigma 5.06}S_{10.00}$	$(Cu_{3.4}Fe_{0.6})_{\Sigma 4}Bi_5S_{10}$
3	$(Cu_{3.36}Fe_{0.60})_{\Sigma 3.96}(Bi_{4.92}Ag_{0.01}Pb_{0.02}Sb_{0.00}Cd_{0.03})_{\Sigma 4.98}S_{10.06}$	
4	$(Cu_{3.42}Fe_{0.57})_{\Sigma 3.99}(Bi_{5.02}Ag_{0.00}Pb_{0.00}Sb_{0.01}Cd_{0.00})_{\Sigma 5.03}S_{9.98}$	
5	$(Cu_{3.34}Fe_{0.62})_{\Sigma 3.96}(Bi_{4.99}Ag_{0.00}Pb_{0.02}Sb_{0.02}Cd_{0.00})_{\Sigma 5.03}S_{10.01}$	
6	$(Cu_{3.36}Fe_{0.62})_{\Sigma 3.98}(Bi_{5.00}Ag_{0.00}Pb_{0.00}Sb_{0.00}Cd_{0.00})_{\Sigma 5.00}S_{10.02}$	
7	$(Cu_{7.62}Fe_{0.37})_{\Sigma 8.00}(Bi_{11.51}Ag_{0.36}Pb_{0.06}Sb_{0.00}Cd_{0.06})_{\Sigma 11.99}S_{22.01}$	hodrushite
8	$(Cu_{7.60}Fe_{0.39})_{\Sigma 8.00}(Bi_{11.57}Ag_{0.37}Pb_{0.03}Sb_{0.00}Cd_{0.06})_{\Sigma 12.03}S_{21.97}$	$(Cu_{7.6}Fe_{0.4})_{\Sigma 8}(Bi_{11.6}Ag_{0.4})_{\Sigma 12}S_{22}$
9	$(Cu_{7.64}Fe_{0.35})_{\Sigma 7.99}(Bi_{11.57}Ag_{0.38}Pb_{0.05}Sb_{0.00}Cd_{0.07})_{\Sigma 12.07}S_{21.94}$	
10	$(Cu_{4.03}Fe_{0.00})_{\Sigma 4.03}(Bi_{6.42}Ag_{0.48}Pb_{0.07}Sb_{0.00}Cd_{0.04})_{\Sigma 7.01}S_{11.96}$	cuprobismutite
11	$(Cu_{4.01}Fe_{0.00})_{\Sigma 4.01}(Bi_{6.40}Ag_{0.48}Pb_{0.08}Sb_{0.00}Cd_{0.04})_{\Sigma 7.00}S_{11.99}$	$Cu_4(Bi_{6.4}Ag_{0.5}Pb_{0.1})_{\Sigma 7}S_{12}$

N_{chem}: number of homologue, Σ_{met}: sum of cations, cb: charge balance. The raw data are quoted in wt.%.

TABLE 2b. AVERAGE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF THE BISMUTHINITE DERIVATIVES FROM FELBERTAL

No.	Sample	Fig.	Cu	Fe	Pb	Bi	Sb	S	Total	n_{aik}	n_k	Δn_{aik}	cb	ev	Pb/Cu
1	FE-89/9-sg29-b	5a	6.35	0.00	21.13	54.95	0.00	17.55	99.97	55.5	89.0	0.6	-0.04	-0.17	1.02
2	FE-89/9-1-71-b	5b	5.56	0.32	20.99	54.67	0.12	17.53	99.19	52.0	96.0	0.6	-0.09	-0.37	1.02
3	FE-89/10-F-b	5c	10.48	0.00	34.48	38.88	0.00	16.84	100.68	94.2	11.6	0.4	0.13	0.54	1.01
4	FE-89/9-1-2-b1	5d	8.81	0.00	29.13	45.08	0.00	16.83	99.85	78.6	42.8	0.6	0.39	1.65	1.01
5	FE-89/9-1-2-b2	5d	10.14	0.00	33.53	39.76	0.00	16.76	100.19	91.6	16.8	0.6	0.20	0.84	1.01
6	FE-86/k7-2-2-b	5e	6.40	0.00	21.14	54.61	0.00	17.64	99.80	55.9	88.2	0.4	-0.26	-1.07	1.01
7	FE-86/k7-6-52-b	5f	6.71	0.08	22.07	54.31	0.00	17.79	100.95	57.7	84.6	-0.5	-0.18	-0.74	0.98

No.	Formula	No.	Formula
1	$Cu_{2.20}Pb_{2.24}Bi_{5.78}S_{12.03}$	5	$Cu_{3.64}Pb_{3..69}Bi_{4.34}S_{11.91}$
2	$Cu_{2.06}Pb_{2.11}Bi_{5.92}S_{12.06}$	6	$Cu_{2.22}Pb_{2.25}Bi_{5.76}S_{12.14}$
3	$Cu_{3.75}Pb_{3.79}Bi_{4.23}S_{11.95}$	7	$Cu_{2.33}Pb_{2.29}Bi_{5.69}S_{12.08}$
4	$Cu_{3.12}Pb_{3.17}Bi_{4.86}S_{11.82}$		

n_{aik}: hypothetical percentage of the aikinite end-member, n_k: hypothetical percentage of krupkaite, Δn_{aik}: accuracy of the analytical data, cb: charge balance, ev: error relative to the total of valences. The raw data are quoted in wt.%.

subsequent least-squares refinements, and 3 Bi, 2Cu(Fe) and 5 S positions were confirmed. The scattering factors for neutral atoms were used for all elements. One of the Cu(Fe) positions appeared split in a difference-Fourier map and was further refined as two distinct Cu positions with independent occupancies and isotropic displacement factors. All other positions were refined anisotropically, and with full occupancies (except for the Cu1 position, with a free occupancy). The three Cu positions refined to occupancies 0.96 (Cu1), 0.69 (Cu2), and 0.25 (Cu3). Thereafter, a mixed (Cu,Fe) occupancy was defined for Cu2 and Cu3 sites with a constraint of full occupancy for Cu2 + Cu3 combined. Furthermore, the coordinates and the atom-displacement parameters for Cu and Fe in the same position were constrained to have identical values. The occupancy of Fe in Cu3 refined to null, and the iron was therefore excluded from this position in the last cycles and confined to the Cu2

TABLE 2c. AVERAGE RESULTS OF ELECTRON-MICROPROBE ANALYSES OF THE MAKOVICKYITE AND CUPROMAKOVICKYITE

No.	Sample	Fig.	Cu	Ag	Pb	Cd	Bi	Te	S	Total
1	FE-89/9-sg29-mb	5a	4.59	6.24	3.30	0.56	66.82	0.08	18.15	99.74
2	FE-89/9-sg29-md	5a	7.32	5.47	8.84	0.38	59.84	0.00	17.91	99.76
3	Fe-89/9-1-71-m	5b	4.45	5.40	2.22	0.49	69.55	0.11	18.06	100.29
4	FE-86/k7-2-2-ex.b	5e	4.39	5.53	2.10	0.91	68.35	0.04	18.34	99.67
5	FE-86/k7-2-2-ex.d	5e	7.21	4.20	7.59	0.79	61.38	0.00	18.12	99.29
6	Fe-86/k7-6-52-ex.b	5f	4.41	5.25	2.14	0.77	68.89	0.00	18.27	99.78
7	Fe-86/k7-6-52-ex.d	5f	7.89	4.10	8.85	0.76	60.35	0.10	18.39	100.43

1 $Cu_{1.15}Ag_{0.92}(Pb_{0.25}Cd_{0.08})_{\Sigma 0.33}Bi_{5.08}S_9$
2 $Cu_{1.85}Ag_{0.82}(Pb_{0.69}Cd_{0.06})_{\Sigma 0.75}Bi_{4.61}S_9$
3 $Cu_{1.12}Ag_{0.80}(Pb_{0.17}Cd_{0.07})_{\Sigma 0.24}Bi_{5.31}S_9$
4 $Cu_{1.09}Ag_{0.81}(Pb_{0.16}Cd_{0.13})_{\Sigma 0.29}Bi_{5.14}S_9$
5 $Cu_{1.81}Ag_{0.62}(Pb_{0.58}Cd_{0.12})_{\Sigma 0.70}Bi_{4.68}S_9$
6 $Cu_{1.10}Ag_{0.77}(Pb_{0.18}Cd_{0.11})_{\Sigma 0.29}Bi_{5.21}S_9$
7 $Cu_{1.94}Ag_{0.60}(Pb_{0.67}Cd_{0.11})_{\Sigma 0.78}Bi_{4.53}S_9$

The raw data are quoted in wt.%.

TABLE 3. X-RAY-DIFFRACTION INVESTIGATION (SINGLE CRYSTAL) OF KUPČÍKITE: EXPERIMENTAL DETAILS

Crystal data			
Chemical formula	$Cu_{3.4}Fe_{0.6}Bi_5S_{10}$	Formula weight	1615.12
Cell setting	Monoclinic	Space group	*C*2/*m*
a (Å)	17.512(2)	*b*(Å)	3.9103(4)
c (Å)	12.869(1)	β (°)	108.56(1)
V (Å³)	835.4(1)	*Z* 2	
D_x (g/cm³)	6.42	Radiation type	Mo*K*α
Wavelength (Å)	0.71073		
No. of reflections for cell parameters	2576	Temperature (K)	297(1)
		μ (mm⁻¹)	58.427
Crystal form	irregular	Crystal size (mm)	0.04 × 0.05 × 0.09
Crystal color	black		
Data collection			
Absorption correction: empirical (ellipsoidal function)			
T_{min}	0.0040	T_{max}	0.0258
No. of measured reflections	4393	No. of independent reflections	1422
No. of observed reflections	1275	Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	5.19%	θ_{max} (°)	30.58
Range of *h*	$-24 \le h \le 24$	Range of *k*	$-5 \le k \le 5$
Range of *l*	$-18 \le l \le 17$		
Refinement			
Refinement on	F_o^2	$R\,[F_o^2 > 2\sigma(F_o^2)]$	4.10%
$wR(F_o^2)$	10.74%	*S* (*GooF*)	1.055
No. of reflections used in refinement	1422	No. of parameters refined	63
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0732P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$		
$(\Delta/\sigma)_{max}$	0.003	$\Delta\rho_{max}$ (*e*/Å³)	2.647
$\Delta\rho_{min}$ (*e*/Å³)	–3.351	Extinction method	none
Source of atomic scattering factors: *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)			
Computer programs			
Structure solution:	*SHELXS97* (Sheldrick 1990)		
Structure refinement:	*SHELXL97* (Sheldrick 1997)		

position. An additional attempt was made to introduce Fe at the Cu1 site, and to refine the coordinates of Fe and Cu at both sites independently (the displacement factors were constrained to equal values per site). The improvement in *R* values was marginal (R_1 from 4.1% to 4.0%, wR_2 from 10.74% to 10.36%), whereas the summary occupancy of Fe per asymmetric unit increased to 0.53 (1.06 per formula unit) compared to 0.29 (0.58) for the former. Because the differences in *R* values are negligible, and the Fe occupancy obtained is unrealistic, the model with iron at two copper sites was discarded. After the final cycle of refinement, the largest matrix-correlations were between the *x* coordinates of (Cu,Fe)2 and Cu3 sites (in the direction of splitting), their occupancies and displacement factors (all between 0.85 and 0.6 absolute). All others correlations were below 0.6. The final atom-parameters are listed in Table 6; atom positions are illustrated in Figure 2.

DESCRIPTION OF THE STRUCTURE

The structure of kupčíkite (Fig. 3) is almost identical to that of the synthetic iron-free $Cu_4Bi_5S_{10}$ (Mariolacos *et al.* 1975). The only difference concerns the splitting of the one Cu position into two closely separated positions.

The structure is composed of two alternating types of slabs (001), each about ½ unit cell wide. One type of slab consists of double columns of square coordination

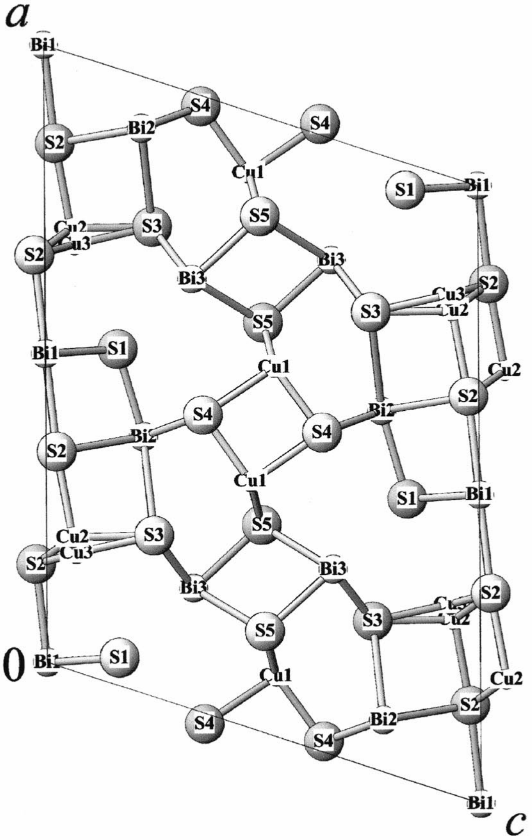

FIG. 2. Atom positions in kupčíkite. Length and orientation of unit-cell axes is indicated.

pyramids of Bi3, interconnected *via* common horizontal and inclined edges. These columns alternate with pairs of Cu1 tetrahedra. The latter can also be interpreted as portions of paired trigonal coordination bipyramids with Cu1 displaced toward the center of one pyramid and having a distorted tetrahedral coordination; the other pyramid is empty. As already noted by Mariolacos *et al.* (1975), these slabs correspond fully to those found in cuprobismutite and hodrushite.

The alternating layers can be described as thin (331) layers of the PbS archetype. They are composed of regular Bi1 octahedra flanked on two sides by square coordination pyramids of Bi2. The coordination of Bi2 is completed by S3 atoms from the first type of slab to give split octahedra or, alternatively, monocapped trigonal prisms. The cation positions between the [010] columns of Bi2–Bi1–Bi2 coordination polyhedra are split into Cu2, Cu3 sites. The full Cu2, Cu3 coordination polyhedron is a trigonal bipyramid. The cation position in the bipyramid is split into a trigonal-planar site (Cu3), and a distorted tetrahedral site (Cu2), situated inside the volume of one of the pyramids.

COORDINATION POLYHEDRA

Whereas Bi1 occupies the center of an almost perfect octahedron of S atoms, the other two Bi atoms have sevenfold coordination in the form of a monocapped trigonal prism, with the Bi atom situated close to the prism face facing the capping atom of sulfur. The latter coordination is therefore transitional between a capped trigonal prism and a "split" octahedron, in which one of the vertices is substituted by two vertices, converting half of the coordination octahedron into a trigonal prism. The central cation remains in the square face below the cap (Makovicky & Balić-Žunić 1998). As can be seen from Figure 2 and from the coordination parameters (Table 7), the Bi2 site is closer to the latter type, because the central atom lies closer to the plane of four S atoms, and the coordination polyhedron has a lower volume-distortion parameter than that of Bi3 (a characteristic of the "split" octahedron when compared to the monocapped trigonal prism: Makovicky & Balić-Žunić 1998).

Cu1 and Cu2 positions are tetrahedraly coordinated, with the central atom displaced toward one of the faces, as is characteristic for Cu^+ in sulfides. The positions have practically equal average distances to the coordinated S atoms, and the spheres circumscribed to the tetrahedra have practically equal radii. The tetrahedron around Cu2 is, however, more regular and thus has a slightly larger volume. The Cu3 position is in a trigonal planar coordination, occupying one of the faces of the Cu2 coordination tetrahedron. The Cu2 and Cu3 positions are very close to each other (0.46 Å), with partial occupancies summing to a full one. As mentioned earlier, the full coordination of this cation site in the structure is trigonal bipyramidal if the more distant S1 atoms also are included in the coordination polyhedron. The same is true for the Cu1 position if the more distant S3 atoms are included. The refinement of the (Cu,Fe) occupancies in the three distinct positions suggests a preference of Fe for the Cu2 site.

Bond distances, angles and the characteristic parameters of the polyhedra for Bi and Cu(Fe) coordinations are represented in Table 7.

THE ROLE OF FE IN THE STRUCTURE

As can be concluded from the chemical and structural analysis, Fe substitutes for part of the Cu in the structure. The refinement of element occupancies in the Cu1, Cu2, and Cu3 sites suggests a preference of Fe for the Cu2 site, and an avoidance of the Cu3 site. We note, however, that the sensitivity of the refinement based on the available X-ray-diffraction data is probably not sufficient for a definite conclusion about the occupancy preferences. Bond-valence calculations based on the approach of Brown & Altermatt (1985) and Brese & O'Keeffe (1991), with Fe variously distributed between the Cu2 and Cu3 positions, did not help in either supporting or refuting the inference derived from the structure refinement. The valence of the S atoms refined to similar values in all models. The only positive information is that the valence sum for each of the (Cu,Fe) sites suggests a valence close to 1 for Cu, and between 2 and 3 for Fe.

If we assume Cu^+ and Fe^{2+} in the formula obtained by the chemical analysis, a valence deficit is obtained for cations, and we should assume that some of them are in the higher valence-state. In this case, Fe^{3+} is assumed to be present, on the basis of an analogy with chalcopyrite $Cu^+Fe^{3+}S_2$ (Greenwood & Whitfield 1968), bornite $Cu^+{}_5Fe^{3+}S_4$ (Vaughan & Burns 1972), and a low-iron synthetic tetrahedrite $Cu^+{}_{11}Fe^{3+}Sb_4S_{13}$ (Makovicky *et al.* 1990), all of which were examined by Mössbauer spectroscopy. If all the Cu in kupčíkite is assumed to be monovalent, the valence of iron in the formula obtained by chemical analysis calculates to 2.95, and its idealized formula is $Cu^+{}_{3.5}Fe^{3+}{}_{0.5}Bi_5S_{10}$.

TABLE 4. UNIT-CELL PARAMETER OF KUPČÍKITE AND RELATED COMPOUNDS

Phase	$Cu_4Bi_5S_{10}$	Z = "$Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$"	Kupčíkite
Formula	$Cu_4Bi_5S_{10}$	$Cu_{3.8}Fe_{0.55}Bi_{4.9}S_{10}$	$Cu_{3.4}Fe_{0.6}Bi_5S_{10}$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C2/m*	*C2/m*	*C2/m*
a (Å)	17.539	17.483	17.512
b (Å)	3.931	3.902	3.910
c (Å)	12.847	12.869	12.869
β (°)	108.00	108.11	108.57
Z (f.u./unit cell)	2	2	2
ρ_c (g/cm^3)	6.39	6.82	6.42
R_1 factor (%)	8.1	-	4.1
References	Mariolacos *et al.* (1975)	Sugaki *et al.* (1981)	this study

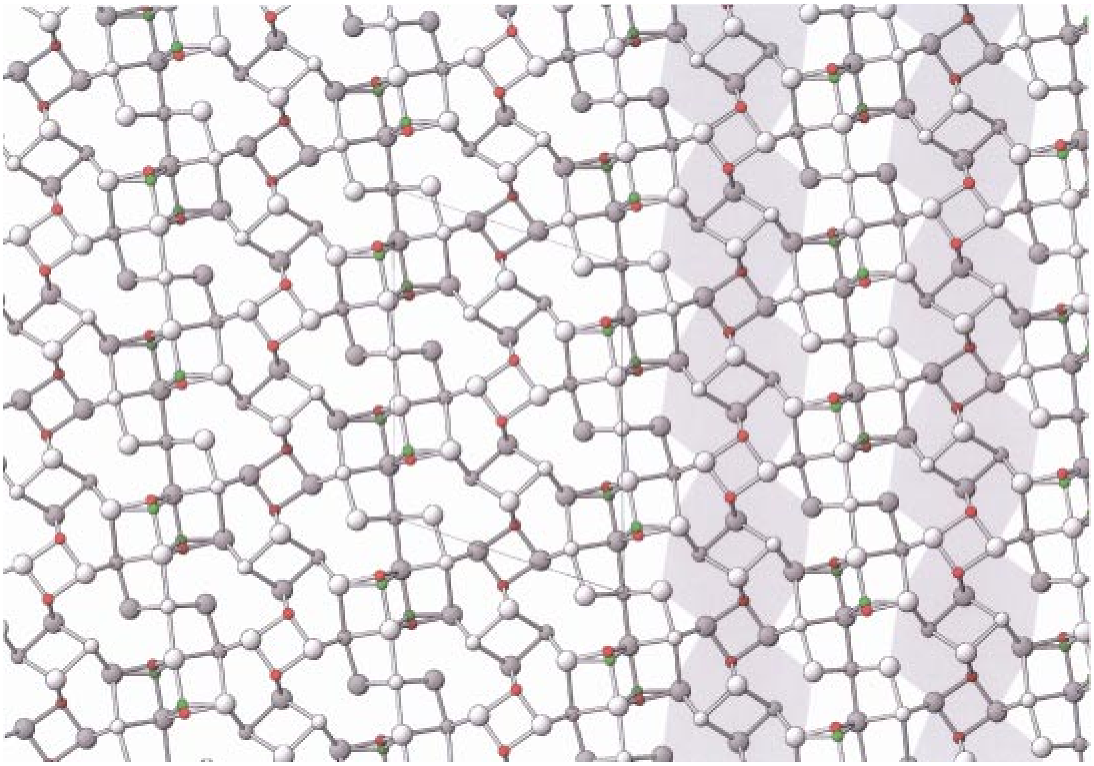

FIG. 3. The crystal structure of kupčíkite projected along [010]. In order of decreasing size the circles indicate S, Bi and Cu. Two atomic levels, 2 Å apart, are indicated by shaded and empty circles, respectively. Cu2 (green) represents a mixed (Cu,Fe) position. Two layers, combining paired coordination pyramids of Bi with Cu tetrahedra (shaded), and one $(331)_{PbS}$ layer, are indicated.

The splitting of the (Cu2,Cu3) position in the ratio 0.74:0.26 is probably not caused by the presence of Fe in the structure. Although the amount of the Cu3 site recalculated as a pure Fe site gives approximately the same amount of Fe as found by chemical analysis, the refinement suggests Fe to be completely excluded from this site; moreover, a very similar split in the Cu coordination is observed in the structures of $Cu_4Bi_4S_9$ (Bente & Kupčík 1984) and $Cu_4Bi_4Se_9$ (Makovicky *et al.* 2002), where no Fe is present. In the latter two structures, all the Cu is in a monovalent state (the structures contain a disulfide and a diselenide group, respectively, and the valences of cations and anions sum to 16 valence units per formula unit), so that the splitting cannot be attributed to the various valence states of Cu either. The same kind of splitting was not reported for the synthetic $Cu_4Bi_5S_{10}$ (Mariolacos *et al.* 1975), in which both Cu sites have been refined as one and fully occupied. To satisfy the stoichiometry, one-quarter of the Cu should be in a divalent state, amounting to one-half of a structural site. The Cu2 site of Mariolacos *et al.* (1975) corresponds to the present Cu1 site, in terms of both its position in the structure and its coordination. Their Cu1 is in a position equivalent to that of the present (Cu2, Cu3). Interestingly, it has coordination characteristics intermediate between the two. It is difficult to make a definite conclusion about this difference, but we believe that a split of this Cu site in $Cu_4Bi_5S_{10}$, also indicated by its augmented displacement-factor, could have been overlooked owing to the lower resolution of the data (the *R* factor obtained in that study was 12.2%).

RELATED SPECIES

Kupčíkite is the N = 1 member of a cuprobismutite homologous series (Makovicky 1989). The N = 2 member is cuprobismutite, which differs from kupčíkite by a greater thickness of the PbS-like portions of the structure, or, in terms of a polyhedron-based description, by the attachment of two coordination pyramids of Bi to a side of the central Bi octahedron instead of only one pyramid, as in kupčíkite. Remarkably, the first struc-

TABLE 5. POWDER-DIFFRACTION DATA FOR KUPČÍKITE AND PHASE Z

Kupčíkite						Phase Z	
h	*k*	*l*	*d*(calc.)	*I*(calc.)	*I*(obs.)	*d*	*I*
$\bar{2}$	0	1	18.1799	7		8.16	10
0	0	2	6.0996	4		6.11	15
2	0	1	6.0278	42		6.05	30
$\bar{2}$	0	2	5.8910	4		5.870	6
$\bar{4}$	0	1	4.3769	24	29	4.370	30
2	0	2	4.3046	11		4.327	18
4	0	0	4.1503	2	2		
$\bar{4}$	0	2	4.0900	19	23		
0	0	3	4.0664	12	15	4.075	12
1	1	0	3.8061	1	1		
$\bar{1}$	1	1	3.7112	16	17	3.703	20
4	0	1	3.5955	68	62	3.606	70
1	1	1	3.5603	29	31	3.557	35
$\bar{4}$	0	3	3.5180	32	35	3.506	30
$\bar{1}$	1	2	3.3404	5	7	3.350	9
2	0	3	3.2642	21	24	3.278	19
$\bar{3}$	1	1	3.2386	34	38	3.232	45
$\bar{2}$	0	4	3.2129	44	42	3.212	40
3	1	0	3.1935	1		3.190	1
1	1	2	3.1281	100	100	3.130	100
$\bar{3}$	1	2	3.0705	70	74	3.061	75
0	0	4	3.0498	12	13		
4	0	2	3.0139	1	2	3.029	3
3	1	1	2.9590	1			
$\bar{4}$	0	4	2.9455	7	9	2.936	16
$\bar{6}$	0	1	2.9052	11	13	2.903	15
$\bar{6}$	0	2	2.8895	8	10	2.882	30
$\bar{1}$	1	3	2.8859	9	12		
$\bar{3}$	1	3	2.7710	23	27	2.763	45
$\bar{6}$	0	3	2.7266	29	31	2.717	60
1	1	3	2.6828	48	56	2.685	50
$\bar{5}$	1	2	2.5688	16	20	2.5620	30
						2.5419	14
5	1	0	2.5309	34	36	2.5359	50
6	0	1	2.5301	2	3	2.5300	2
4	0	3	2.5297	5	6		
$\bar{3}$	1	4	2.4409	1	1	2.4463	7
0	0	5	2.4399	2	2	2.4353	3
$\bar{5}$	1	3	2.4295	11	14	2.4227	25
3	1	3	2.3135	5	6	2.3180	12
1	1	4	2.2995	2	2	2.3034	4
6	0	2	2.2632	12	14	2.2715	16
$\bar{6}$	0	5	2.2125	2	2	2.2047	4
$\bar{8}$	0	2	2.1885	10	12	2.1857	13
$\bar{8}$	0	1	2.1627	4	4	2.1714	35
2	0	5	2.1620	22	22	2.1637	25
5	1	2	2.1595	13	16		
$\bar{8}$	0	3	2.1455	4	4		
$\bar{2}$	0	6	2.1384	1			
$\bar{3}$	1	5	2.1375	22	24	2.1350	45
$\bar{1}$	1	5	2.1258	10	13	2.1268	14
$\bar{7}$	1	2	2.1033	3	4	2.0986	11
$\bar{7}$	1	1	2.0947	13	16	2.0928	14
8	0	0	2.0751	2	2	2.0777	3
$\bar{8}$	0	4	2.0450	2	2	2.0383	10
0	0	6	2.0332	3	4	2.0334	17
7	1	0	2.0278	4	5		
3	1	4	2.0274	9	11	2.0284	10
$\bar{5}$	1	5	2.0183	13	16	2.0126	25
6	0	3	2.0093	3	4		
1	1	5	1.9891	3	5	1.9934	7
$\bar{6}$	0	6	1.9637	8	9		
0	2	0	1.9552	30	24	1.9574	30
$\bar{7}$	1	4	1.9512	16	18	1.9518	70
5	1	3	1.9472	13	15	1.9450	30
7	1	1	1.9177	9	11	1.9196	13
$\bar{8}$	0	5	1.9089	5	5	1.9016	11
$\bar{3}$	1	6	1.8786	1	2		
2	2	1	1.8598	3	4	1.8575	14
$\bar{1}$	1	6	1.8504	11	12	1.8514	17
$\bar{2}$	0	7	1.8265	3	3	1.8286	12
$\bar{7}$	1	5	1.8223	4	5	1.8159	6
$\bar{5}$	1	6	1.8146	5	7	1.8102	9
3	1	5	1.7868	3	4	1.7931	14
6	0	4	1.7857	3	4	1.7884	7
$\bar{4}$	2	1	1.7851	3	4	1.7843	4
7	1	2	1.7843	4	5	1.7810	8
2	2	2	1.7801	2	2		
$\bar{4}$	2	2	1.7640	3	4	1.7597	14
0	2	3	1.7621	2	2		
5	1	4	1.7501	1			
$\bar{6}$	0	7	1.7465	6	7	1.7466	12
$\overline{10}$	0	3	1.7434	1			
0	0	7	1.7428	3	4	1.7414	12
$\bar{9}$	1	2	1.7419	3	4		
1	1	6	1.7413	2	3	1.7387	10
$\bar{9}$	1	3	1.7280	3	4	1.7231	9
$\bar{9}$	1	1	1.7207	13	16	1.7197	17
4	2	1	1.7176	12	14	1.7163	19
$\bar{4}$	2	3	1.7090	6	7	1.7045	12
$\bar{7}$	1	6	1.6830	5	6	1.6830	5
2	2	3	1.6773	5	5	1.6773	12
$\bar{2}$	2	4	1.6702	10	12	1.6677	25
9	1	0	1.6683	2	3	1.6621	10
$\bar{3}$	1	7	1.6637	1	2		
10	0	0	1.6601	5	5		
8	0	3	1.6481	1	2		
0	2	4	1.6460	3	3		
7	1	3	1.6447	1			
$\overline{10}$	0	5	1.6360	1	1		
$\bar{5}$	1	7	1.6323	2	2		
4	0	6	1.6321	2	3		
$\bar{1}$	1	7	1.6302	3	4		
$\bar{4}$	2	4	1.6290	2	2		
$\bar{6}$	2	1	1.6220	3	4		
$\bar{6}$	2	2	1.6193	2	2		
$\bar{8}$	0	7	1.6108	1			
$\bar{9}$	1	5	1.6100	1	1		
$\bar{4}$	0	8	1.6065	5	5		
$\bar{2}$	0	8	1.5926	2	2		
9	1	1	1.5925	6	6		
$\bar{6}$	2	3	1.5889	8	9		
3	1	6	1.5880	4	5		
10	0	1	1.5791	1			
5	1	5	1.5758	1	1		
$\overline{10}$	0	6	1.5502	2	2		
6	2	1	1.5471	1			
4	2	3	1.5470	1	2		
$\bar{7}$	1	7	1.5460	1	1		
1	1	7	1.5425	1	1		

The data for kupčíkite are calculated *d* values, followed by I(calc.) based on the crystal-structure parameters and I(obs.) recalculated from the measured single-crystal diffraction intensities. The data for phase Z are from Sugaki *et al.* (1981).

ture of the series to be determined was that of hodrushite (Kupčík & Makovicky 1968), which is a regular 1:1 intergrowth of *N* = 1 and *N* = 2 layers, *i.e.*, it has kupčíkite-like and cuprobismutite-like modules in regular alternation. It lacks the fractionally occupied (Cu,Bi) sites observed in synthetic, pure end-member cuprobismutite (Ozawa & Nowacki 1975), with the problems of charge balance apparently taken care of by incorporation of minor cations. The same way of charge balancing has been observed by us for natural kupčíkite, cuprobismutite and hodrushite from Felbertal (Topa *et al.*, in prep.). The composition of the hodrushite structure from two regularly alternating layers, one with a cuprobismutite-like cell and the other without an analogue at the time of publication, was clearly suggested by Kodĕra *et al.* (1970), who likened the situation to that in the sartorite homologous series, already known.

The synthetic compound $Cu_4Bi_5S_{10}$, fully analogous to kupčíkite, and structurally analyzed by Mariolacos *et al.* (1975), was synthesized at 340°C. As stated above, the charge-balance problems in it must be compensated for by the presence of a certain amount of divalent copper. Mariolacos *et al.* (1975) also gave a more detailed discussion of the structural relations between $Cu_4Bi_5S_{10}$, cuprobismutite and hodrushite, along the lines already suggested by Kupčík & Makovicky (1968) and Koděra *et al.* (1970).

The closest analogue to natural kupčíkite is the synthetic phase Z, prepared by Sugaki *et al.* (1981) at 300 and 420°C. It was given with a formula $Cu_{8.4}Fe_{1.2}Bi_{10.8}S_{22}$, analogous to hodrushite, although its unit-cell parameters (Table 4) are practically identical to those of $Cu_4Bi_5S_{10}$ (*i.e.*, of only the kupčíkite-like component of the hodrushite structure; the recalculated formula is $Cu_{3.8}Fe_{0.5}Bi_{4.9}S_{10}$). Characteristically, this phase can coexist with synthetic cuprobismutite and has in some cases smaller amounts of iron than kupčíkite. The above formula is almost identical to that of kupčíkite and as-

TABLE 6. ATOMIC PARAMETERS FOR KUPČÍKITE

Atom	x	y	z	sof	U_{11}	U_{22}	U_{33}	U_{13}	U_{eq}
Bi1	0.5	0	0.00000	1	0.0389(4)	0.0275(3)	0.0345(3)	0.0108(3)	0.0339(2)
Bi2	0.41619(3)	0.5	0.22470(4)	1	0.0364(3)	0.0335(2)	0.0358(2)	0.0130(2)	0.0349(2)
Bi3	0.19776(3)	0.5	0.33891(4)	1	0.0330(3)	0.0329(2)	0.0345(2)	0.0088(2)	0.0339(2)
Cu1	0.4007(1)	0	0.4719(2)	1	0.0431(9)	0.0374(9)	0.065(1)	0.0258(9)	0.0464(4)
Cu2	0.2158(3)	0	0.0602(2)	0.45(3)	0.0365(9)				
Fe2	0.2158(3)	0	0.0602(2)	0.29(4)	0.0365(9)				
Cu3	0.1925(9)	0	0.0688(6)	0.26(2)	0.034(3)				
S1	0.5454(2)	0.5	0.1669(2)	1	0.034(1)	0.029(1)	0.031(1)	0.010(1)	0.0313(6)
S2	0.3465(2)	0	0.0243(2)	1	0.035(1)	0.028(1)	0.034(1)	0.011(1)	0.0323(6)
S3	0.2614(2)	0	0.2482(2)	1	0.032(1)	0.028(1)	0.031(1)	0.011(1)	0.0303(5)
S4	0.4827(2)	0	0.3626(2)	1	0.034(1)	0.031(1)	0.031(1)	0.009(1)	0.0324(6)
S5	0.3353(2)	0.5	0.4970(2)	1	0.027(1)	0.026(1)	0.029(1)	0.009(1)	0.0273(5)

sof: site-occupancy factor; for all atoms $U_{12} = U_{23} = 0$ by symmetry.

TABLE 7. INTERATOMIC DISTANCES, BOND ANGLES AND POLYHEDRON CHARACTERISTICS FOR KUPČÍKITE

Bi1	S2	S2	S1	S1	S1	S1
S2	**2.803(4)**	180.0(1)	92.1(1)	92.1(1)	87.9(1)	87.9(1)
S2	5.605(5)	**2.803(4)**	87.9(1)	87.9(1)	92.1(1)	92.1(1)
S1	4.053(5)	3.904(4)	**2.825(2)**	87.6(1)	180.0(1)	92.4(1)
S1	4.053(5)	3.904(4)	3.910(0)	**2.825(2)**	92.4(1)	180.0(1)
S1	3.904(4)	4.053(5)	5.650(2)	4.078(3)	**2.825(2)**	87.6(1)
S1	3.904(4)	4.053(5)	4.078(3)	5.650(2)	3.910(0)	**2.825(2)**

$\Delta = 0$, $r_S = 2.82$, $V_S = 93.69$, $\sigma = 0.996$, $V_P = 29.75$, $\upsilon = 0.002$.

Bi2	S1	S4	S4	S2	S2	S3	S3
S1	**2.596(4)**	87.4(1)	87.4(1)	84.9(1)	84.9(1)	144.1(1)	144.1(1)
S4	3.623(4)	**2.648(2)**	95.2(1)	168.0(1)	93.6(1)	123.6(1)	73.2(1)
S4	3.623(4)	3.910(0)	**2.648(2)**	93.6(1)	168.0(1)	73.2(1)	123.6(1)
S2	3.904(4)	5.772(3)	4.246(4)	**3.156(3)**	76.6(1)	67.0(1)	108.3(1)
S2	3.904(4)	4.246(4)	5.772(3)	3.910(0)	**3.156(3)**	108.3(1)	67.0(1)
S3	5.740(5)	5.370(3)	3.681(4)	3.641(5)	5.343(4)	**3.432(3)**	69.5(1)
S3	5.740(5)	3.681(4)	5.370(3)	5.343(4)	3.641(5)	3.910(0)	**3.432(3)**

$\Delta = 0.196$, $r_S = 3.00$, $V_S = 112.99$, $\sigma = 0.983$, $V_P = 38.08$, $\upsilon = 0.109$

Bi3	S5	S3	S3	S5	S5	S1	S1
S5	**2.611(2)**	86.1(1)	86.1(1)	78.0(1)	78.0(1)	145.8(1)	145.8(1)
S3	3.621(3)	**2.694(2)**	93.1(1)	91.8(1)	163.0(1)	69.9(1)	118.2(1)
S3	3.621(3)	3.910(0)	**2.694(2)**	163.0(1)	91.8(1)	118.2(1)	69.9(1)
S5	3.592(4)	4.142(4)	5.696(3)	**3.065(2)**	79.3(1)	78.7(1)	121.5(1)
S5	3.592(4)	5.696(3)	4.142(4)	3.910(0)	**3.065(2)**	121.5(1)	78.7(1)
S1	5.824(3)	3.591(5)	5.309(3)	4.162(3)	5.711(2)	**3.476(2)**	68.5(1)
S1	5.824(3)	5.309(3)	3.591(5)	5.711(2)	4.162(3)	3.910(0)	**3.476(2)**

$\Delta = 0.198$, $r_S = 3.04$, $V_S = 117.66$, $\sigma = 0.981$, $V_P = 38.22$, $\upsilon = 0.142$

Cu1	S4	S5	S5	S4	S3
S4	**2.308(4)**	120.7(1)	120.7(1)	91.3(1)	83.9(1)
S5	4.040(4)	**2.340(2)**	113.4(1)	101.0(1)	81.6(1)
S5	4.040(4)	3.910(0)	**2.340(2)**	101.0(1)	81.6(1)
S4	3.392(4)	3.685(3)	3.685(3)	**2.437(3)**	175.1(1)
S3	3.681(4)	3.621(3)	3.621(3)	5.556(3)	**3.125(3)**

$\Delta = 0.140$, $r_S = 2.50$, $V_S = 65.25$, $\sigma = 0.897$, $V_P = 12.77$, $\upsilon = 0.053$ (trigonal bipyramid); $\Delta = 0.042$, $r_S = 2.34$, $V_S = 53.90$, $\sigma = 1$, $V_P = 6.29$, $\upsilon = 0.048$ (tetrahedron)

(Cu,Fe)2	S3	S2	S2	S2	S1
S3	**2.294(3)**	116.5(2)	116.5(2)	99.5(2)	69.9(1)
S2	3.934(4)	**2.333(2)**	113.9(2)	103.7(2)	81.9(1)
S2	3.934(4)	3.910(0)	**2.333(2)**	103.7(2)	81.9(1)
S2	3.641(5)	3.782(4)	3.782(4)	**2.476(7)**	169.4(2)
S1	3.591(5)	4.053(5)	4.053(5)	6.112(5)	**3.661(6)**

$\Delta = 0.235$, $r_S = 2.59$, $V_S = 72.63$, $\sigma = 0.830$, $V_P = 13.57$, $\upsilon = 0.096$ (trigonal bipyramid); $\Delta = 0.055$, $r_S = 2.35$, $V_S = 54.35$, $\sigma = 1$, $V_P = 6.60$, $\upsilon = 0.010$ (tetrahedron)

Cu3	S3	S2	S2	S2	S1
S3	**2.239(8)**	121.0(5)	121.0(5)	88.5(3)	80.3(3)
S2	3.934(4)	**2.281(4)**	118.0(5)	92.2(3)	93.5(3)
S2	3.934(4)	3.910(0)	**2.281(4)**	92.2(3)	93.5(3)
S2	3.641(5)	3.782(4)	3.782(4)	**2.929(16)**	168.8(4)
S1	3.591(5)	4.053(5)	4.053(5)	6.112(5)	**3.212(16)**

$\Delta = 0.066$, $r_S = 2.59$, $V_S = 72.63$, $\sigma = 0.830$, $V_P = 13.57$, $\upsilon = 0.096$ (trigonal bipyramid); $\Delta = 0.021$, $r_S = 2.27$, $V_S = 48.78$ (trigonal planar coordination).

The values in diagonals (bold) are the central atom-ligand distances, in the upper-right triangle, the bond angles and in the lower left the ligand–ligand distances are given. Δ: eccentricity (Å), r_S: radius of sphere fitted to ligands (Å), V_S: sphere volume (Å^3), σ: sphericity, V_P: volume of coordination polyhedron (Å^3), υ: volume distortion. For explanations, see Balič-Žunič & Makovicky (1996) and Makovicky & Balič-Žunič (1998).

sumes Fe^{3+}. The iron content (in wt.%) in the three cuprobismutite homologues that coexist in the Felbertal deposit can be seen in Figure 4, reflecting the fact that Fe can be accommodated only in the kupčíkite-like module. The content of silver in these homologues is inversely proportional to that of iron. A discussion of the role and place of Ag in these structures will be a topic of an upcoming contribution.

MINERAL ASSOCIATIONS

Kupčíkite was found in two distinct orebodies, K7 and K8, respectively, of the Felbertal scheelite deposit, situated in the Tauern Window of the Austrian Alps. These orebodies, most distal in respect to the rest of the deposit, lie in diverse types of amphibolite with lenses of leucocratic gneisses and, in the case of the K8 orebody, also quartz masses. For a concise summary of the geology and mineralogy of the deposit, the reader is referred to Topa *et al*. (2002). The ore association is considered a product of polyphase Variscan magmatic events; it was subsequently reworked during a prograde episode of Alpine metamorphism, followed by retrograde metamorphism.

In both orebodies, kupčíkite nearly invariably occurs in a typical mineral association kupčíkite – makovickyite (the pavonite homologue ^4P, either as a low-Cu variety or with exsolution lamellae of cupromakovickyite) – bismuthinite derivatives (bd) (Fig. 5). The composition of the latter is $50 < n_{aik} < 62$, and only rarely higher. In our short-hand notation, we write in what follows the content of the aikinite component as a subscript to bd. Only rarely can a replacement product with low n_{aik} be observed at the margins of the aggregate, or between the bismuthinite derivative and other sulfosalts. Occasionally, homogeneous cupromakovickyite [$^4P_{(Cu,Pb)}$] is present in parallel growth with makovickyite (Table 2b, Fig. 5a). Kupčíkite was found in several instances also in association with hodrushite (as parallel intergrowths), associated mostly with $bd_{\sim 55}$, only exceptionally with $bd_{\sim 88}$.

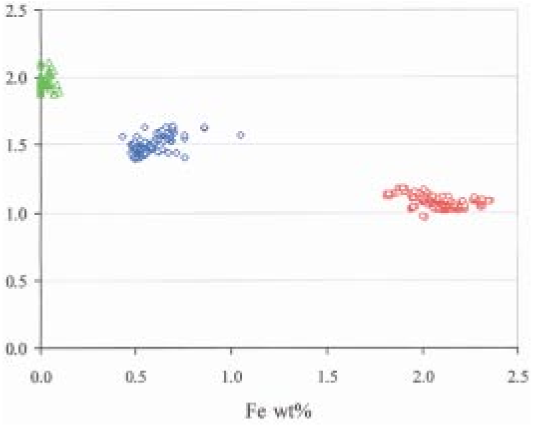

FIG. 4. Iron content (wt.%) in the minerals of the cuprobismutite series from Felbertal *versus* homologue number. Symbols: kupčíkite (○), hodrushite (◇) and cuprobismutite (△).

In the kupčíkite – hodrushite intergrowths from the Felbertal deposit, these phases, commonly multiply intergrown, retain their compositional integrity, resulting in sharp straight boundaries without transitional compositions (Figs. 5a, c). Contacts of kupčíkite with makovickyite (^4P) display straight crystal faces as well (Fig. 5b), whereas in all intergrowths with interpretable textures, the bismuthinite derivative ($bd_{50–96}$, less commonly also the late-formed bismuthinite derivative with $n_{aik} \leq 50$) replaces kupčíkite (Figs. 5b–d). It replaces makovickyite as well. Most of these intergrowths of three to four sulfosalt phases come from thin quartz layers in the metamorphic rock and were slightly replaced from the margins by quartz or sulfides (Figs. 5c, e).

The rare occurrence of kupčíkite and cuprobismutite in one aggregate is characterized by the replacement of the latter by the former. This replacement is associated with, or followed by, a replacement of both phases by $bd_{92–94}$ (Figs. 5c, d). In one instance, the bismuthinite derivative that formed after partly replaced kupčíkite has a value of $n_{aik} = 79$, and was followed by a phase with $n_{aik} = 92$.

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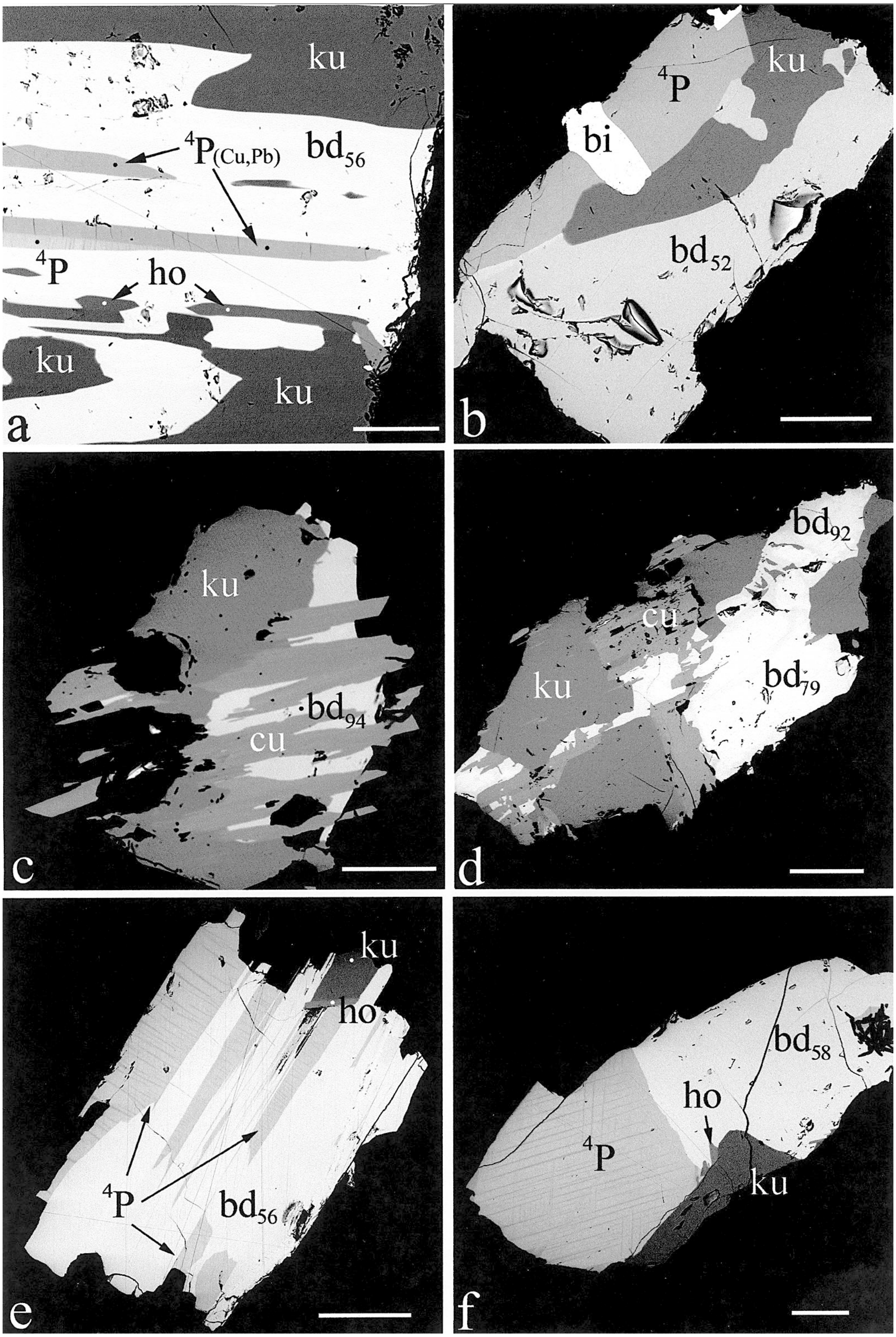
FIG. 5. Sulfosalt associations of kupčíkite in Felbertal. BSE photographs, bar indicates 100 μm. (a) Kupčíkite (ku) and hodrushite (ho) partly replaced by bismuthinite derivative ($n_{aik} = 56$) with relict lamellae of low-Cu (^4P) and cupromakovickyite [$^4P_{(Cu,Pb)}$]. (b) Kupčíkite and makovickyite; the former is replaced by bd_{52}, the latter by native bismuth (bi). (c, d) Kupčíkite replacing cuprobismutite (cu); both phases are in turn replaced by $bd_{79–92}$. Quartz gangue and sulfides partly replace sulfosalts from periphery. (e, f) Three-phase aggregates of makovickyite (with exsolution lamellae of cupromakovickyite) – $bd_{56–58}$ – kupčíkite. In both cases, minor hodrushite is present. Selective replacement, especially of makovickyite, from the aggregate's periphery is observed, primarily in (e).


ku
⁴P(Cu,Pb)
bd56
⁴P
ho
ku
ku
a
ku
⁴P
bi
bd52
b
ku
bd94
cu
c
bd92
cu
ku
bd79
d
ku
ho
⁴P
bd56
e
bd58
ho
⁴P
ku
f

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