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KOLARITE $PbTeCl_2$ AND RADHAKRISHNAITE $PbTe_3(Cl,S)_2$, NEW MINERAL SPECIES FROM THE KOLAR GOLD DEPOSIT, INDIA

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Abstract

Kolarite $PbTeCl_2$ and radhakrishnaite $PbTe_3(Cl,S)_2$ are new mineral species found in gold–quartz ores of the Kolar deposit (India) at a depth of 1500 m. The minerals occur mostly intergrown as 20–40 μm aggregates that replace altaite inclusions in galena. Under reflected light the kolarite is grey with no visible anisotropism; radhakrisnaite is rose-brown with distinct anisotropism, in grains of 0.5 to 1 μm under magnification. Reflectance in air at 580 nm: kolarite 29.2%, radhakrishnaite 32.4%. Kolarite is orthorhombic, *a* 5.93(5), *b* 3.25(5), *c* 3.89(5) Å. The strongest seven diffraction-lines [*d* in Å(I)(*hkl*)] are: 3.91(4)(001), 3.27(10)(101,010), 2.35(5)(201), 2.00(4)(300), 1.79(3)(301), 1.50(3)(021,400), 1.35(3)(410,221). The calculated density is 9.14 g/cm³ for the mean composition, with $Z=1$. Radhakrishnaite is tetragonal, *a* 5.71(5), *c* 3.77(5) Å. The strongest seven diffraction-lines are: 3.78(6)(001), 3.16(10)(011), 2.73(4)(111), 2.29(4)(021), 1.92(5)(030), 1.78(5)(012,221), 1.59(4)(230). The calculated density is 8.89 g/cm³ for the mean composition, with $Z=1$.

Keywords: kolarite, radhakrishnaite, new mineral species, lead, tellurium, chlorine, sulfur, gold ores, Kolar, India.

Sommaire

Kolarite $PbTeCl_2$ et radhakrishnaïte $PbTe_3(Cl,S)_2$ sont de nouvelles espèces minérales, découvertes dans le minerai quartz–or du gisement de Kolar (Inde), à 1500 m de profondeur. En général, elles se présentent en intercroissances formant des agrégats de 20 à 40 μm qui remplacent des inclusions d'altaïte dans la galène. En lumière réfléchie, la kolarite est grise sans anisotropie nette; la radhakrishnaïte est rose-brun, avec anisotropie distincte en grains de 0.5 à 1 μm. Le pouvoir réflecteur dans l'air (580 nm) est de 29.2% pour la kolarite et de 32.4% pour la radhakrishnaïte. La kolarite est orthorhombique: *a* 5.93(5), *b* 3.25(5), *c* 3.89(5) Å. Les sept raies de diffraction les plus intenses [*d* en Å(I)(*hkl*)] sont: 3.91(4)(001), 3.27(10)(101,010), 2.35(5)(201), 2.00(4)(300), 1.79(3)(301), 1.50(3)(021,400), 1.35(3)(410,221). D(calc.) = 9.14 pour la composition moyenne et $Z=1$. La radhakrishnaïte est tétragonale: *a* 5.71(5), *c* 3.77(5) Å. Les sept raies de diffraction les plus intenses sont: 3.78(6)(001), 3.16(10)(011), 2.73(4)(111), 2.29(4)(021), 1.92(5)(030), 1.78(5)(012,221), 1.59(4)(230). D(calc.) 8.89 pour la composition moyenne et $Z=1$.

Mots-clés: kolarite, radhakrishnaïte, nouvelles espèces minérales, plomb, tellure, soufre, minerai d'or, Kolar, Inde.

Introduction

Two new mineral species, a chlorine-bearing telluride and a chlorine-bearing sulfotelluride of lead, have been discovered in quartz veins from the Kolar gold deposit in India. One of the minerals, $PbTeCl_2$, was named *kolarite* after the deposit, and the other, $PbTe_3(Cl,S)_2$, was named *radhakrishnaite* in honor of the well-known Indian geologist B.P. Radhakrishna. The new minerals and names were approved by the International Commission on New Minerals and Mineral Names, I.M.A.

A number of chlorine-containing ore minerals, which testify to the participation of chlorine in ore-forming processes, have been found recently. In these minerals, represented by sulfides of potassium (djerfisherite), sodium (bartonite), thallium (thalfenissite), by sulfosalts of lead (ardaite, dadsonite), by the minerals of mercury (keljanite, pojarkovite) and palladium and bismuth, the chlorine contents range from 0.4 to 6.4 wt.%. In the new minerals described here, the chlorine content reaches 16%. Attempts to synthesize the new minerals under dry and hydrothermal conditions have been unsuccessful.

Occurrence

The sample containing kolarite and radhakrishnaite was taken from a system of gold–quartz veins known as the Champion reef lode, at a depth 1500 m. The veins consist of fine-grained banded quartz or coarse-grained massive quartz with not more than 1% sulfides. The quartz veins of the Champion reef are traceable down-dip to depths exceeding 3200 m.

The main sulfide minerals in the sample studied are pyrrhotite and galena, which form small accumulations with sulfides that cement quartz grains. In addition to the two new minerals associated with pyrrhotite and galena, several others new to the Kolar deposit were identified: volynskite, hessite, altaite, ullmannite, hawleyite, cadmian tetrahedrite (6.1% Cd), sphalerite exceptionally rich in cadmium (>12%), and a lead sulfantimonide of the semseyite type (Genkin *et al.* 1981, 1983). The composition of all minerals was determined with a Cameca MS-46 microprobe.

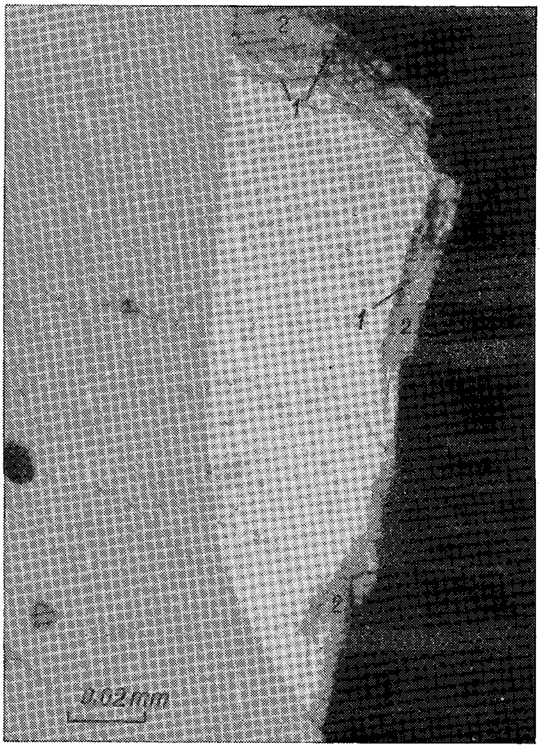

FIG. 1. Kolarite (1) and radhakrishnaite (2), replacing altaite (white) in galena (light grey).

The altaite that contains the grains of kolarite and radhakrishnaite occurs in galena as numerous inclusions of different sizes and forms, from irregular, oval, rounded to disk-like. Kolarite and radhakrishnaite evolved by veinlet and rim replacement of altaite grains (Fig. 1). Kolarite and radhakrishnaite are usually mutually intergrown. Radhakrishnaite occurs in these intergrowths as rims and irregular aggregates, up to 20×40 μm, at the periphery of altaite grains, whereas kolarite forms flame-like and veinlet-like aggregates up to 20 μm across in the inner parts of altaite grains. Small grains of altaite apparently fully replaced by the intergrowths of kolarite and radhakrishnaite, or by one of them, have been observed, but are rare. Also associated with kolarite and radhakrishnaite at the interface between galena and altaite are a few veinlet-like aggregates of cotunnite $PbCl_2$.

The very small grain-size of these minerals, which only rarely exceeds 20 μm, greatly complicated their study. The following sequence was adopted. After optical investigation, several of the mineral grains were analyzed by microprobe. Then the two largest aggregates (up to 40 μm), with different proportions of kolarite and radhakrishnaite, were extracted for electron-diffraction investigation. The particles from which electron-diffraction patterns were obtained were first checked by means of an energy-dispersion spectrometer, and the results were compared with the compositional data obtained by microprobe analysis.

OPTICAL PROPERTIES

Kolarite intergrown with altaite and radhakrishnaite is grey, visibly darker than radhakrishnaite. Anisotropism is not visible. Radhakrishnaite, in contrast to kolarite, possesses a distinct rose-brown tint. Under low magnifications, radhakrishnaite appears to be isotropic, but under magnifications of 500 to 800×, it shows distinct anisotropism in grains 0.5 to 1 μm across. The bireflectance of these grains is evident in oil immersion.

The reflectance spectra of kolarite and radhakrishnaite were studied on the "P1OR", MSF-10 and spectrophotometer MRM-01 ("Opton", FRG) using Si, SiC and (W, Ti)C as standards. The *R* values of minerals measured in the same conditions are presented in Table 1. The reflectance spectra are shown in Figure 2, from which it can be seen that *R* values of kolarite in the red part of the spectrum are 3–4% lower than the values of radhakrishnaite. At wavelengths of 400–440 nm the reverse is observed, and the spectral curves of the two minerals intersect at 450–460 nm. The coefficient of relative dispersion (R_{440}–R_{480}) for kolarite is 3%, much less than 7.5% for radhakrishnaite. Radkakrishnaite is characterized by a broad maximum at 660–680 nm, and by a linear increase of *R* values in the interval

TABLE 1. REFLECTANCE DATA FOR KOLARITE AND RADHAKRISHNAITE

nm	Kolarite 1	Kolarite 2	Radhakrishnaite 1	Radhakrishnaite 2
400	26.1	25.0	24.3	23.7
420	26.2	25.3	25.2	24.7
440	26.5	25.6	26.1	25.6
460	27.0	25.9	27.1	26.6
480	27.5	26.5	28.2	27.6
500	27.9	27.0	29.2	28.6
520	28.3	27.4	30.1	29.6
540	28.6	27.7	31.0	30.3
560	29.0	28.1	31.8	31.1
580	29.2	28.3	32.4	31.8
600	29.4	28.5	32.9	32.4
620	29.6	28.6	33.3	32.7
640	29.6	28.6	33.5	33.0
660	29.5	28.6	33.6	33.2
680	29.5	28.6	23.6	33.2
700	29.5	28.6	33.6	33.2
720	29.5	28.5	33.5	33.1
740	29.4	28.4	33.2	32.9

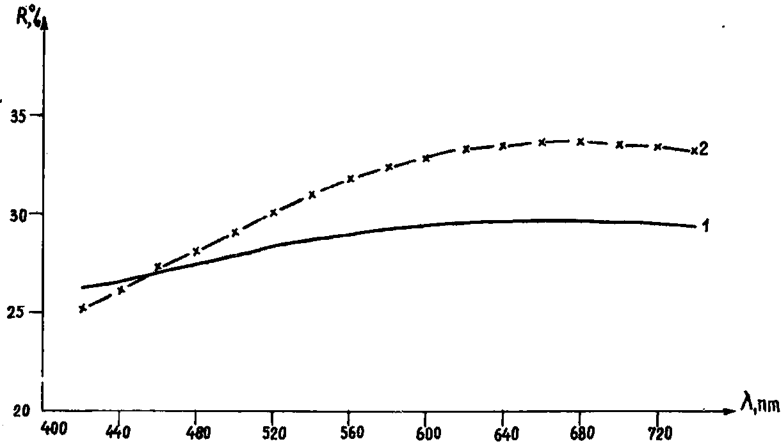

FIG. 2. Reflectance spectra of kolarite (1) and radhakrishnaite (2).

from 400 to 540 nm. Because of the fine grain-size of the radhakrishnaite, only the integral value of the reflectance coefficient was measured.

CHEMICAL COMPOSITION

The chemical composition of kolarite and radhakrishnaite was determined with a Cameca MS-46 microprobe operated with an accelerating voltage of 20 kV. Synthetic PbS, Te and $PbCl_2$ were used as standards. The following X-ray lines were used: $K\alpha$ for Cl and S, $L\alpha$ for Pb and Te. Corrections were made for dead time of the registration system, atomic number, absorption, and characteristic fluorescence. The corrections were calculated with the program PUMA (Boronikhin & Tsepin 1980). The results of the analyses are presented in Table 2.

The distribution of lead, tellurium and chlorine in the intergrowths of kolarite and radhakrishnaite, which replace altaite, is shown using scanning images (Fig. 3). The presence of chlorine is also visible in the fissure in galena near the grain of altaite replaced by the new minerals.

The analyses of kolarite grains revealed insignificant variations in lead, tellurium and chlorine contents (Table 2). The analytical formula (average value) is $Pb_{1.006}Te_{1.080}Cl_{1.913}$. The ideal formula of kolarite, based on a total of 4 atoms, is $PbTeCl_2$.

The analytical data on four grains of radhakrishnaite (Table 2) show relatively small variations in lead and tellurium contents and much greater variations in chlorine and sulfur contents. That the variation is not attributable to contamination is evident from the occurrence of kolarite and radhakrashnaite grains in altaite PbTe, which contains neither chlorine nor sulfur. Chlorine and sulfur show an inverse correlation (coefficient -0.953). Based on a total of 6 atoms, the ideal formula of radhakrishnaite is $PbTe_3(Cl,S)_2$. Substitution involving chlrorine and sulfur is implied, but direct evidence of it is lacking. The question of Cl–S substitution was considered recently by Breskovska *et al.* (1981), who proposed that in chlorine-bearing sulfosalts, limited substitu-

TABLE 2. CHEMICAL COMPOSITION OF KOLARITE AND RADHAKRISHNAITE*

	Pb	Te	Cl	S	Σ	Formula
			Kolarite			
1.	50.05	32.87	16.88	—	99.60	$Pb_{1.00}Te_{1.06}Cl_{1.94}$
2.	50.30	33.12	15.90	—	99.32	$Pb_{1.02}Te_{1.09}Cl_{1.89}$
3.	49.60	33.45	16.17	—	99.22	$Pb_{1.00}Te_{1.09}Cl_{1.91}$
			Radhakrishnaite			
1.	29.17	59.80	9.90	0.77	99.64	$Pb_{0.94}Te_{3.06}(Cl_{1.84}S_{0.16})_2$
2.	30.81	61.30	9.75	0.46	102.32	$Pb_{0.97}Te_{3.15}(Cl_{1.80}S_{0.09})_{1.88}$
3.	28.97	58.23	7.91	3.53	98.64	$Pb_{0.90}Te_{2.95}(Cl_{1.44}S_{0.71})_{2.15}$
4.	31.39	58.23	7.18	3.09	99.89	$Pb_{1.00}Te_{3.08}(Cl_{1.34}S_{0.64})_{1.98}$

* based on electron-microprobe data.

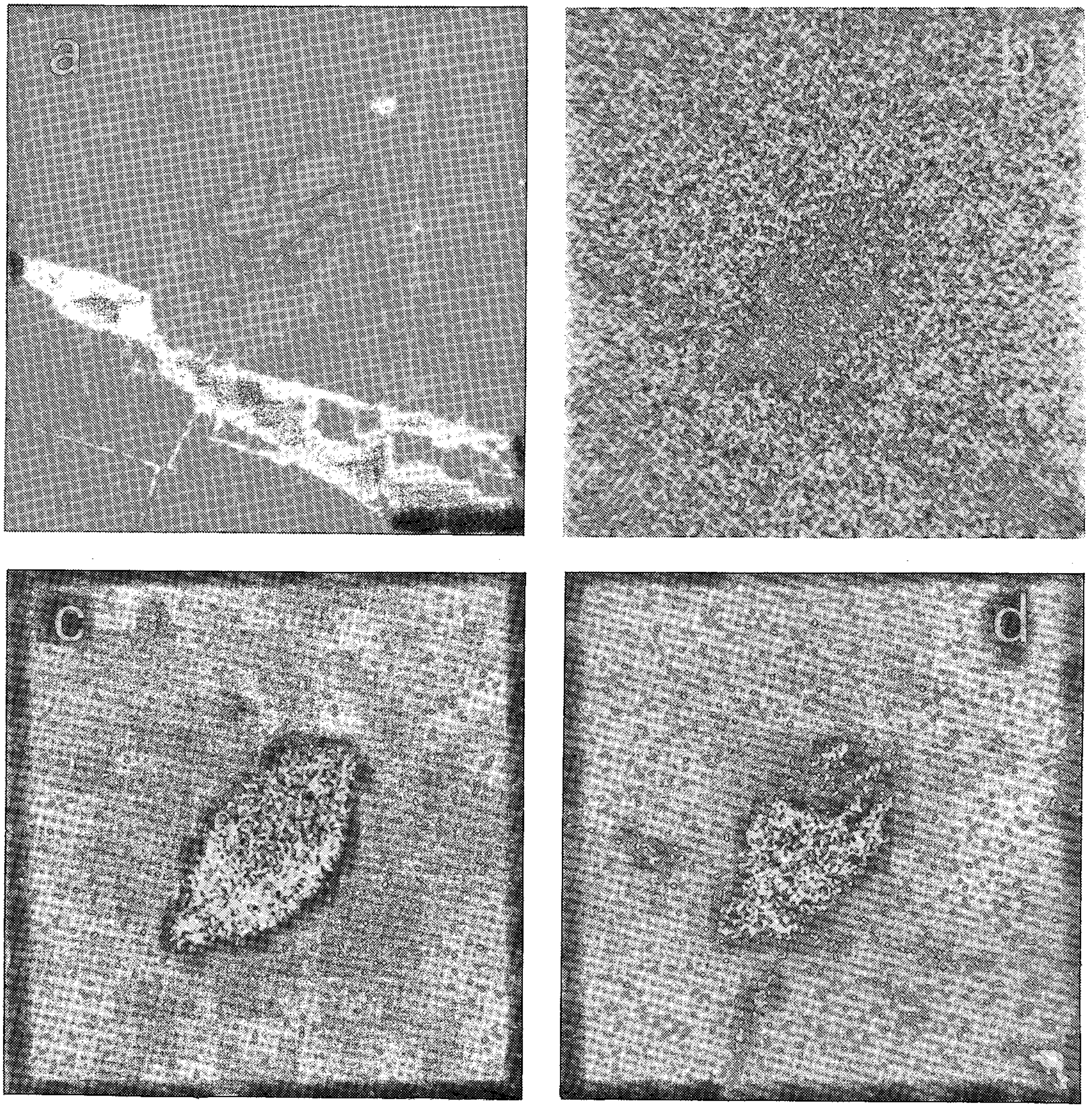

FIG. 3. Intergrowth of kolarite and radhakrishnaite in altaite in reflected light (a) and characteristic X radiation Pb$L\alpha$ (b), Te$L\alpha$ (c), and Cl$K\alpha$ (d). Scanning area 100 × 100 μm.

tion of sulfur by chlorine can occur on an atom-for-atom basis, or chlorine can occupy vacancies. To support this model, the authors cited the reported statistical filling of chlorine and sulfur positions in the compound $Bi_4Cl_2S_5$ (Kramer 1979).

STRUCTURE

The structural characteristics of kolarite $PbTeCl_2$ and radhakrishnaite $PbTe_3(Cl,S_2)$ were obtained by means of a JEM-100C transmission electron-microscope with a goniometer capable of ±60° tilts and 180° azimuthal rotation. The material for structural investigations was extracted from the analyzed grains of the minerals from the polished sections, and the composition of the extracted particles was checked by means of a semiconductor Kevex 5100 detector. The calculation of the kolarite and radhakrishnaite electron-diffraction patterns was performed with the use of the programs GRAFD, RD and LSM, written in BASIC for the Cannon CX-1 computer.

The study shows that kolarite consists of submicrometre-scale particles whose electron-diffraction pattern (Fig. 4) consists of ring reflections corresponding to the *d* values in Table 3. One particle gives a rectangular diffraction-net in which the largest *d* value (5.91 Å) is not evident on the ring patterns. Calculations indicate that the rectangular net represents the (010) plane and that kolarite is orthorhombic, with *a* 5.93(5), *b* 3.25(5), *c* 3.89(5) Å, and possible space-groups *Pmmm, Pmm*2 or *P*222. The *R* factor (identity factor) calculated from *d* values is equal to 0.812%. The calculated density is 9.14 g/cm^3 for the mean analytical data, with $Z = 1$.

An electron-microscope study of radhakrishnaite shows that it consists of aggregates of small (submicrometre-scale) particles. Electron-diffraction patterns for the majority of the particles of radhakrishnaite contain ring reflections. The set of interplanar spacings calculated from electron-diffraction patterns is represented in Table 4. From one of the particles (with rectangular set of reflections; see Fig. 5), an electron-diffraction pattern reflecting the reciprocal-lattice plane assumed to be (010) is obtained. The weak reflection 100 with $d = 5.74$ Å nearest to the centre of diffraction pattern is not visible on ring patterns because of its low intensity.

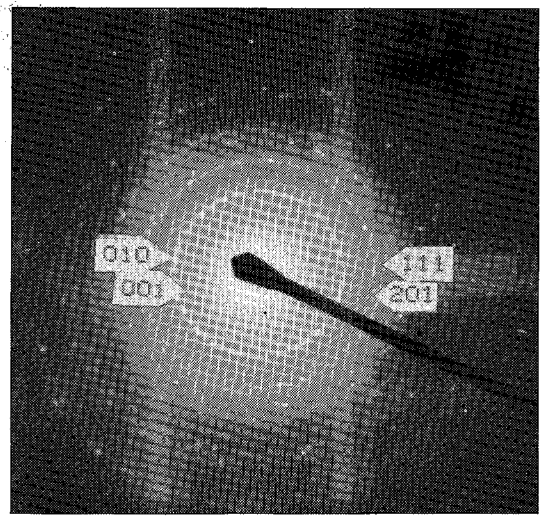

FIG. 4. Electron-diffraction pattern of kolarite aggregate.

The results of indexing of diffraction patterns are represented in Table 4. Radhakrishnaite has a fixed primitive tetragonal cell with the parameters $a = b$ 5.71(5), *c* 3.77(5) Å. The possible space-groups are

TABLE 3. RESULTS OF CALCULATION AND INDEXING OF ELECTRON-DIFFRACTION PATTERNS OF KOLARITE

I	d_{meas}	d_{calc}	h	k	l	difference
0.5	5.91	5.933	1	0	0	−0.023
4	3.91	3.892	0	0	1	+0.018
10	3.27	3.254	1	0	1	+0.016
		3.253	0	1	0	+0.017
5	2.35	2.359	2	0	1	−0.009
2	2.27	2.301	1	1	1	−0.031
2	2.15	2.192	2	1	0	−0.042
4	2.00	1.978	3	0	0	+0.022
3	1.86	1.849	1	0	2	+0.011
3	1.79	1.763	3	0	1	+0.027
2	1.63	1.627	2	0	2	+0.003
		1.627	0	2	0	+0.003

I	d_{meas}	d_{calc}	h	k	l	difference
3	1.50	1.501	0	2	1	−0.001
		1.483	4	0	0	+0.017
2	1.46	1.455	2	1	2	+0.005
		1.455	1	2	1	+0.005
2	1.41	1.426	2	2	0	−0.016
3	1.35	1.350	4	1	0	+0.000
		1.339	2	2	1	+0.011
2	1.23	1.221	1	2	2	+0.009
2	1.18	1.189	2	0	3	−0.009
		1.181	1	1	3	−0.001
		1.180	4	0	2	+0.000

TABLE 4. RESULTS OF CALCULATION AND INDEXING OF ELECTRON-DIFFRACTION PATTERNS OF RADHAKRISHNAITE

I	d_{meas}	d_{calc}	h	k	l	difference
6	3.78	3.772	0	0	1	+0.008
10	3.16	3.147	0	1	1	+0.013
2	2.87	2.855	0	2	0	+0.015
4	2.73	2.756	1	1	1	−0.026
4	2.29	2.276	0	2	1	+0.014
2	2.16	2.114	1	2	1	+0.046
3	2.04	2.018	2	2	0	+0.022
5	1.92	1.903	0	3	0	+0.017
5	1.78	1.791	0	1	2	−0.011
		1.780	2	2	1	+0.000

I	d_{meas}	d_{calc}	h	k	l	difference
3	1.71	1.709	1	1	2	+0.001
		1.699	0	3	1	+0.011
4	1.59	1.583	2	3	0	+0.007
3	1.43	1.427	0	4	0	+0.003
3	1.34	1.346	3	3	0	−0.006
		1.340	0	3	2	+0.000
		1.335	0	4	1	+0.

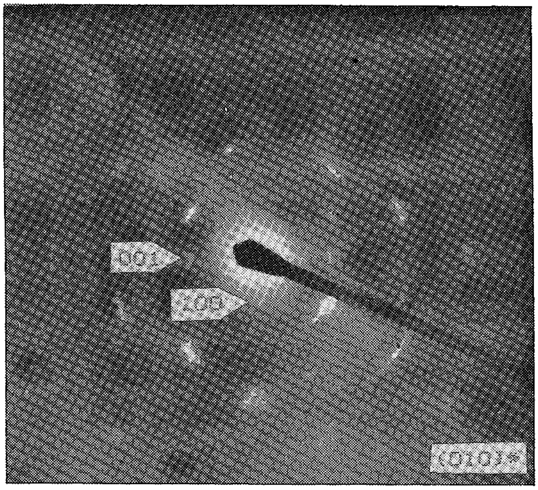

FIG. 5. Electron-diffraction pattern of individual particle of radhakrishnaite.

P4/m, *P4*, *P$\bar{4}$*, *P422*, *P4mm*, *P$\bar{4}$2m* or *P$\bar{4}$m2* and *P4/mmm*. The *R* factor is 0.68%. The calculated density is 8.89 g/cm^3 for the mean analytical data, with $Z = 1$.

CONCLUSIONS

The discovery of kolarite and radhakrishnaite, chlorine-bearing telluride and chlorosulfotelluride of lead, respectively, at considerable depth (1500 m) and the absence of secondary alteration in the associated main ore-forming sulfides galena, pyrrhotite and chalcopyrite testify to the hypogene origin of the new minerals. For cotunnite, which rarely occurs in nature, the hypogene origin was confirmed only after its discovery in the products of emanations from volcanoes, in particular at Vesuvius (Chukhrov & Bonstedt-Kupletskaya 1963).

The new mineral species belong to the latest assemblage of ore minerals, formed after the sphalerite–galena assemblage that includes tellurides and other rare minerals, and that bears the significant part of the ore-grade gold mineralization. The participation of chlorine in the process of ore formation at the Kolar deposit is established also for earlier stages of mineralization by the study of fluid inclusions in quartz. In quartz from the Champion reef lode from 2800–3000 m in depth, multiphase inclusions containing as daughter minerals halite and sylvite have been found (Safonov *et al.* 1980). The occurrence of kolarite, radhakrishnaite and cotunnite in microfissures in altaite and galena testify to the activity of unusual chlorine-rich emanations also in the latest stages of ore formation.

Polished sections containing kolarite and radhakrishnaite are preserved in the Mineralogical Museum of Academy of Sciences of the USSR and in the Mineragraphy Laboratory of IGEM, Academy of Sciences of the USSR, both in Moscow.

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