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Re-examination of yushkinite: chemical composition, optical properties and interlayer charge transfer

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ABSTRACT

The hydroxy-sulphide yushkinite from the type deposit has been re-examined by electron probe microanalysis and reflectance measurement. The EPMA indicates minor Cu (up to 1.5 wt.%) and confirms an excess of V. Taking into account its composite structure (brucite-like hydroxide layer alternating with a berndtite-type sulphide layer) the proposed structural formula is, with the addition of minor intercalated Cu: $[(Mg_{0.71}Al_{0.36}V_{0.03})_{\Sigma 1.10}(OH)_{2.18}O_{0.02}]Cu_{0.02}\,[VS_2]$. At the crystal scale, some crystal edges give a variable excess of Si and Al (in the 1/1 ratio), indicating a late topotactic intergrowth with a layered alumino-silicate (or a composite silicate-sulphide). New specular reflectance data are given in air and oil from 400 to 800 nm, with the polarization plane parallel or perpendicular to the elongation. The refractive index n and absorption coefficient k are given; no absorption band exists in the perpendicular position, with constant n close to 1.9, and k to 0.3. In a parallel position, a pseudo-transparency window is centred around 500–520 nm (~2.4 eV). The main absorption band, centred around 730 nm (~1.7 eV), corresponds probably to a transition $t_{2g} \rightarrow e_g$ related to intra-layer V–V bonding. Charge transfer from the brucite-type layer to the VS_2 one, strictly controlled through H-bonding, induces a mean formal valency of V close to 3.6. Yushkinite is compared with other synthetic layered hydroxy-sulphides, as well as brucite-type intercalated compounds.

Keywords: yushkinite, hydroxy-sulphide, vanadium, electron microprobe data, specular reflectance data, charge transfer, hydrogen bonding.

Introduction

Yushkinite is a complex lamellar hydroxy-sulphide of V discovered by Makeev *et al.* (1984) in quartz-calcite hydrothermal veins near the Sylova-Yaha river (Pai-Hoi anticlinorium, Komi Autonomous Republic, in the former Soviet Union). To date, this is the only known occurrence of yushkinite, and it has not been synthetized. Makeev *et al.* (1984) revealed the hybrid, non-commensurate character of the crystal structure of yushkinite, and showed that it was related to those of valleriite and tochilinite. In yushkinite, a brucite-like hydroxide layer alternates with a V-containing octahedral sulphide layer. Makeev *et al.* (1984) gave the structural formula:

$$[V_{0.62}S]_{0.612}[(Mg_{0.67}Al_{0.33})_{\Sigma=0.99}(OH)_2].$$

Organova (1989) proposed a new crystal chemical formula on the basis of the ratio of the two intra-layer sub-cells: $[V_{1+x}S_2]\,1.1[(Mg_{0.67}Al_{0.33})(OH)_2]$. More recently, Makovicky and Hyde (1992), in a general study of the group of minerals with incommensurate sandwiched layered structure ('2D-misfit compounds'), highlighted the close relationship between the sulphide layer of yushkinite and the pseudo-hexagonal VS_2 layer of synthetic $(PbS)_{1.12}VS_2$, which is closely related to the layered structure of berndtite, SnS_2.

During the study of synthetic lanthanide-V sulphides of the misfit type (Cario, 1998), a new compound close to $(SmS)_{1.21}VS_2$ revealed optical properties (purple colour and reflectance data) very similar to those of yushkinite. This led to the current re-examination of yushkinite, in order to understand the relationship between its crystal chemistry, optical properties and interlayer charge transfer. For this study, a cm-sized sample of massive calcite with numerous yushkinite inclusions was kindly given to us in 1995 by N.P. Yushkin. This sample was broken into small pieces, and the one with the highest concentration of yushkinite lamellae was included in epoxy and polished for metallographic observation. The biggest lamella is ~300 μm long and 40 μm wide; it is characteristically strongly dichroic from bluish grey to light purple (Makeev *et al.*, 1984). Some very small pyrite crystals (<10 μm) are also present.

Chemical re-examination

Electron probe microanalysis (EPMA)

Wavelength-dispersive EPMA was performed on a CAMECA SX50 apparatus (Common Analysis Laboratory BRGM-CNRS-University, Orléans). First, a qualitative analysis showed major V, Mg, Al and O, with minor Cu, Fe and Si. Together with elements of higher Z number, quantitative analysis of oxygen was attempted but failed, due to the superposition of the main $L\alpha$ and $L\beta$ lines of V with the $K\alpha$ line of oxygen (with a PC1 crystal detector). Oxygen excluded, the final operating conditions were as follows: accelerating voltage 12 kV; beam current 20 nA; counting time for one spot analysis 10 s; standards (element, emission line): V metal (V-$K\alpha$), Si metal (Si-$K\alpha$), Cu metal (Cu-$K\alpha$), FeS_2 (Fe- and S-$K\alpha$), forsterite (Mg-$K\alpha$) and corundum (Al-$K\alpha$). The detection limits (wt.%) for minor metals (for one spot analysis) were: 0.02 (Si), 0.10 (Fe) and 0.25 (Cu). Natural sulvanite Cu_3VS_4 and synthetic V_5S_8 were used as secondary standards for a slight correction (~ −0.4 wt.%) of V content of yushkinite. For the direct correction of matrix effects, the cations Mg, Al, Fe and Si have been considered to be entirely within the brucite layer, and their mass concentration expressed as MeO_2 (independently of their formal valence). Hydrogen concentration was derived directly from that of oxygen.

Fifty eight spot analyses were collected. Even after adding H, the total weight percentages clearly show a deficit of at least 2 wt.%. Larger deficits sometimes result from cleavage planes, but in other cases larger deficits, up to 10 wt.%, are clearly related to a high Si content (SiO_2 up to 10 wt.%). This last group of Si-rich analyses will be considered separately. Ten analyses of 'pure' yushkinite (SiO_2 <0.4 wt.%) with a total weight >97.5% were selected for crystal chemical discussion (Table 1). The main difference from the first study of Makeev *et al.* (1984) is the presence of a significant amount of Cu, from ~0–1.5 wt.% (1.16 wt.% in Table 1*a*). Despite the variation of Cu content, there is no significant difference in the concentrations of major elements, which are remarkably stable. Except for Cu, the mean wt.% total of selected analyses is very close to analysis no. 2 of Makeev *et al.* (1984).

Cationic ratios on the basis of S = 2 atoms are given in Table 1*b*. They confirm the main conclusions of Makeev *et al.* (1984): i.e. (1) the Mg/Al ratio is very close to 2 (mean 1.969); (2) for two S atoms pfu, the V concentration is significantly >1 (mean 1.043); (3) the (Mg + Al + Fe) concentration (mean 1.074) is below the ideal value of 1.100 deduced from X-ray data (that is the ratio of subcell areas); and (4) the total concentration of all the cations, except Cu, is 2.125, in very good agreement with the theoretical total of 2.100 atoms.

Crystal chemical interpretation

Vanadium excess

In synthetic layer misfit compounds of the general formula $(MeS)_{1+x}VS_2$ (Me = lanthanides, or Pb: Wiegers and Meerschaut, 1992), the VS_2 layer is of the CdI_2 type, i.e. with V in octahedral coordination. Such a layer cannot accept excess V cations, and anionic vacancies in such misfit compounds are known only in the MeS layer (Cario, 1998). The same consideration applied to yushkinite means that the V excess relative to the sulphide layer is incorporated into the brucite layer, which would also explain the (Mg + Al) deficit. Without Cu, the structural formula then becomes:

$$(Mg_{0.714}Al_{0.360}Fe_{0.002}Si_{0.002}V_{0.022})_{\Sigma 1.10}(OH)_{2.20}V_{1.021}S_2$$

Note that this V excess in the brucite layer must be accounted for in the same way as other metals, by (OH) groups in the one-for-two ratio; it adds ~0.4 wt.% (OH) to the final mean total, which becomes close to 98.5 wt.%.

Location of copper

An increase of Cu content from 0.2 up to 1.2 wt.% induces no significant variation in the

TABLE 1. Electron microprobe analysis of yushkinite. (*a*) Wt.% tot. = total after adding H as OH group. Spot analyses ordered with decreasing Cu content. Mk2: analysis no. 2 of Makeev *et al.* (1982). (*b*) Cationic ratio on the basis of S = 2 at. Σox. = Total of cations in the brucite-type sub-layer (= Mg+Al+Fe−Si, see text); V_{bruc}: V in the brucite layer (= 1.10−Σox.); $v(V)_s$ = mean formal valency of V in the VS_2 sub-layer (= 4−Al+Si−$2V_{bruc}$).

a

Analysis no.	V	Cu	S	MgO_2	AlO_2	FeO_2	SiO_2	Sum	H	Tot.
1	28.15	1.15	34.20	21.75	11.45	0.30	0.08	96.8	1.15	98.3
2	28.00	0.75	34.15	21.60	11.55	0.45	0.06	96.1	1.14	97.7
3	28.60	0.70	34.55	21.50	11.20	–	0.09	96.4	1.13	97.9
4	28.60	0.70	34.25	21.40	11.30	0.20	0.07	96.2	1.13	97.7
5	28.65	0.60	34.55	21.60	11.40	–	0.25	96.8	1.14	98.3
6	28.20	0.40	34.85	21.75	11.35	0.25	0.18	96.7	1.14	98.2
7	28.95	0.40	34.60	21.50	11.45	–	0.09	96.7	1.14	98.2
8	29.05	0.35	34.75	21.90	11.65	–	0.17	97.6	1.16	99.1
9	28.85	0.35	34.45	21.35	11.45	–	0.35	96.6	1.13	98.1
10	28.65	0.25	34.40	21.80	11.45	–	0.06	96.3	1.15	97.8
Mean	28.57	0.57	34.47	21.61	11.43	0.12	0.14	96.6	1.14	98.1
	(34)	(28)	(23)	(18)	(12)	(12)	(10)	(4)	(1)	(4)
Mk2	29.08	n.d.	34.20	20.82	11.08	0.22	n.d.	95.39	1.11	96.50

b

Analysis no.	V	Cu	Mg	Al	Fe	Si	Σox.	Mg/Al	V_{bruc}	$v(V)_s$
1	1.037	0.034	0.724	0.364	0.007	0.002	1.093	1.99	0.007	3.62
2	1.031	0.023	0.720	0.367	0.009	0.002	1.095	1.96	0.005	3.62
3	1.041	0.021	0.708	0.353	–	0.003	1.060	2.01	0.040	3.57
4	1.052	0.021	0.712	0.359	0.004	0.002	1.073	1.98	0.027	3.59
5	1.045	0.018	0.713	0.359	–	0.008	1.065	1.99	0.035	3.58
6	1.019	0.012	0.711	0.354	0.005	0.006	1.065	2.01	0.035	3.58
7	1.054	0.011	0.708	0.361	–	0.003	1.067	1.96	0.033	3.58
8	1.052	0.010	0.718	0.365	–	0.005	1.080	1.97	0.020	3.60
9	1.053	0.010	0.705	0.362	–	0.011	1.058	1.95	0.042	3.57
10	1.048	0.007	0.722	0.362	–	0.002	1.085	1.99	0.015	3.61
Mean	1.043	0.017	0.714	0.360	0.003	0.004	1.074	1.98	0.026	3.59
	(11)	(8)	(7)	(5)	(3)	(3)	(14)	(2)	(14)	(2)
Mk2	1.070	–	0.693	0.352	0.005	–	1.050	1.97	0.050	3.55

content of major elements. The simplest way to explain this anomaly is to consider Cu as an intercalation element between the hydroxide and sulphide layers. For comparison, intercalation of alkali metals (Li, Na) between simple VS_2 layers is well known, while pure VS_2 is metastable (and known only from de-intercalation of Li from $Li_{1-x}VS_2$: Murphy *et al.*, 1977).

Thus, due to the great similarity of monovalent Li and Cu, one may envisage that Cu is intercalated at the monovalent state between the two layers of yushkinite, and substitutes for H (with a different, stronger bonding). The corrected structural formula then becomes:

$$[(Mg_{0.714}Al_{0.360}Fe_{0.002}Si_{0.002}V_{0.022})_{\Sigma 1.100}(OH)_{2.183}O_{0.017}]Cu_{0.017}[V_{1.021}S_2] \quad (1)$$

A final correction due to the Si content is given below.

(Si,Al)-rich EPM analyses

Many spot EPM analyses showed a variable, sometimes very high (up to 10 wt.%) content of Si, correlated with an increase of Al, while other major components have lower concentrations. Table 2 selects the spot analysis with the highest Si content, together with the mean of two groups of analyses with similar Si contents. If one

TABLE 2. Electron microprobe analysis of (Si,Al)-enriched areas in yushkinite crystals. (*a*) Wt % tot. = total after adding H as OH group. Analyses ordered with decreasing (Si,Al) content. A: one spot analysis; B and C: mean of four spot analyses; Pure = mean Si-free analysis of Table 1. (*b*) Cationic ratio on the basis of S = 2 at. Al_{cor} = Al excess relative to pure yushkinite (after subtraction of Al from yushkinite composition – last line)

a

Analysis no.	V	Cu	S	MgO_2	AlO_2	FeO_2	SiO_2	Sum	H	Tot.
A	19.50	0.45	24.05	15.50	18.00	–	10.65	87.8	1.50	89.7
B	24.39	0.39	30.23	18.77	14.68	0.20	5.55	93.8	1.34	95.5
	(37)	(25)	(35)	(17)	(27)	(8)	(14)	(1)	(1)	(1)
C	26.21	1.25	32.46	20.57	13.15	0.17	2.91	96.3	1.26	98.0
	(15)	(28)	(21)	(15)	(12)	(6)	(23)	(6)	(1)	(6)
Pure	28.48	0.58	34.51	21.61	11.43	0.12	0.14	96.6	1.14	98.1

b

Analysis no.	V	Cu	Mg	Al	Fe	Si	Al_{cor}
A	1.022	0.020	0.734	0.814	0.001	0.472	0.454
B	1.016	0.013	0.707	0.528	0.005	0.197	0.168
	(18)	(9)	(11)	(12)	(2)	(7)	
C	1.017	0.039	0.722	0.441	0.004	0.096	0.081
	(8)	(9)	(6)	(5)	(1)	(7)	
Pure	1.043	0.017	0.714	0.360	0.004	0.004	–

subtracts the Al content related to 'pure' yushkinite (that is half of the Mg content, in atomic proportions), it appears that the Al excess is very close to the Si content (in atomic proportions). This clearly indicates a very fine intergrowth with an alumino-silicate component. Electron microprobe scanning for Si on the biggest crystal shows increasing Si content at the margin or along visible cleavage planes (late crystallization), but the geometry of this intergrowth at the crystal scale is not known.

As the Mg content decreases and thus does not follow the increasing Si and Al, these two last cations both ought to be fixed in tetrahedral coordination with oxygen. The minor amount of Si in 'pure' yushkinite (Table 1) is probably due to such a silicate intergrowth at a very low concentration. Subtraction of Si and an equal proportion of Al in the brucite-type sub-layer of formula (1) will enhance its V content, to give the corrected formula:

$$[(Mg_{0.714}Al_{0.356}Fe_{0.004}V_{0.026})_{\Sigma 1.100}(OH)_{2.183}O_{0.017}]\ Cu_{0.017}\ [V_{1.017}S_2] \quad (2)$$

Finally, the following simplified formula is suggested:

$$[(Mg_{0.71}Al_{0.36}V_{0.03})_{\Sigma 1.10}(OH)_{2.18}O_{0.02}]Cu_{0.02}\ [VS_2]$$

In the Norilsk deposit (Russia), a chlorite-sulphide composite structure derived from the hydroxy-sulphide valleriite was described by Organova (1989), with the structural formula:

$$6(Cu,Fe)S_2.1.52[(Mg,Fe,Al)_3(Si,Al)_4O_{10}(OH)_2.(Mg,Fe,Al)_3(OH)_6]$$

Thus it is possible that a similar composite silicate-sulphide compound is present in topotactic association with yushkinite.

Reflectance data on yushkinite

Metallographic description

A very specific property of yushkinite is its strong dichroism in reflected light, with a strong purple colour in the direction of maximum reflectance R_o (ordinary vibration direction in the basal plane: Makeev *et al.*, 1984). This gives very strong polarization effects with crossed polars. Curiously, the same optical properties were encountered in a synthetic compound of the $(SmS)_{1+x}VS_2$ type. This 'purple phase' has a dimorph, which is grey, with low polarization

TABLE 3. Reflectance (%) in air of yushkinite (parallel ($R_{//}$) and perpendicular ($R_\perp$) to the elongation) from 400 to 800 nm. Polishing method: 600/1200 mesh carborundum (paper); 6, 3, 1 and ¼ diamond on cloth; final buffing with Cr_2O_3 on cloth. LEICA DMR microscope with objective FLUOTAR 20 × /0.50 POL. Microscope photometer: Leica MPV-SP, monochromator: Δλ 2 nm. Standard: SiC (NPL no. 50)

λ (nm)	$R_{//}$	$R_\perp$	λ (nm)	$R_{//}$	$R_\perp$	λ (nm)	$R_{//}$	$R_\perp$	λ (nm)	$R_{//}$	$R_\perp$
400	21.1	10.1	500	14.3	10.5	600	19.8	10.4	700	30.4	10.5
410	22.2	10.6	510	14.2	10.3	610	21.0	10.1	710	30.9	10.2
420	20.8	10.5	520	13.8	10.3	620	22.3	10.4	720	32.3	10.9
430	20.5	10.4	530	13.8	10.3	630	23.6	10.3	730	31.8	10.1
440	18.7	10.6	540	14.4	10.3	640	24.8	10.1	740	31.8	10.9
450	17.9	10.5	550	14.7	10.3	650	26.7	10.4	750	32.1	10.1
460	17.0	10.4	560	15.4	10.4	660	27.7	10.0	760	31.8	10.3
470	16.4	10.5	570	16.4	10.1	670	28.8	10.1	770	31.1	11.8
480	15.5	10.3	580	17.4	10.2	680	29.1	10.3	780	31.6	11.2
490	15.0	10.3	590	18.4	10.3	690	30.2	10.3	790	32.1	11.4
									800	29.6	10.2
470	16.4	10.5	546	14.6	10.3	589	18.4	10.3	650	26.7	10.4

properties (Cario, 1998). Further details about these dimorphs (chemical composition, optics, crystallography and chemical bonding) will be published separately (Moëlo *et al.*, in prep.). Only the reflectance data for yushkinite are reported here.

Method

Reflectance measurements were obtained using a Leitz system (DM RXP metallographic microscope coupled with a MPV spectrophotometer). The size of the rectangular diaphragm of measurement was adjusted to the elongated morphology of the studied crystals in order to obtain the best output. Polished sections were ground with diamond to the finest grain size of 1/10 μm. For each lamella, two measurements were obtained with the polarization vector parallel or perpendicular to the elongation ($R_{//}$ and $R_\perp$ respectively). Other operating conditions are given in the captions of Tables 3 and 4. Below

TABLE 4. Reflectance (%) in oil of yushkinite (parallel ($R_{//}$) and perpendicular ($R_\perp$) to the elongation) from 400 to 800 nm. LEICA DMR microscope with objective OEL 50 × /0.85. Microscope photometer: Leica MPV-SP, monochromator: Δλ 2 nm. Standard: SiC (NPL no. 50). Immersion oil Leitz (n_e^{23} = 1.518)

λ (nm)	$R_{//}$	$R_\perp$	λ (nm)	$R_{//}$	$R_\perp$	λ (nm)	$R_{//}$	$R_\perp$	λ (nm)	$R_{//}$	$R_\perp$
400	7.01	1.91	500	5.08	1.96	600	10.8	1.88	700	18.3	1.94
410	7.15	1.73	510	5.12	1.97	610	11.6	1.84	710	18.3	2.01
420	7.30	1.94	520	5.24	1.95	620	12.6	1.94	720	18.7	1.90
430	6.90	1.87	530	5.53	1.91	630	13.5	1.83	730	18.7	1.96
440	6.89	1.97	540	5.84	1.90	640	15.0	1.93	740	18.2	2.06
450	6.62	1.90	550	6.51	1.92	650	15.3	1.91	750	18.7	1.94
460	6.25	1.95	560	7.07	1.88	660	16.1	1.85	760	18.0	2.18
470	5.95	1.93	570	7.87	1.85	670	17.0	2.01	770	17.6	1.87
480	5.56	1.94	580	8.96	1.84	680	17.5	1.91	780	17.5	1.90
490	5.36	2.01	590	9.74	1.82	690	17.6	1.96	790	17.6	2.11
									800	16.9	1.88
470	5.95	1.93	546	6.24	1.91	589	9.66	1.82	650	15.3	1.91

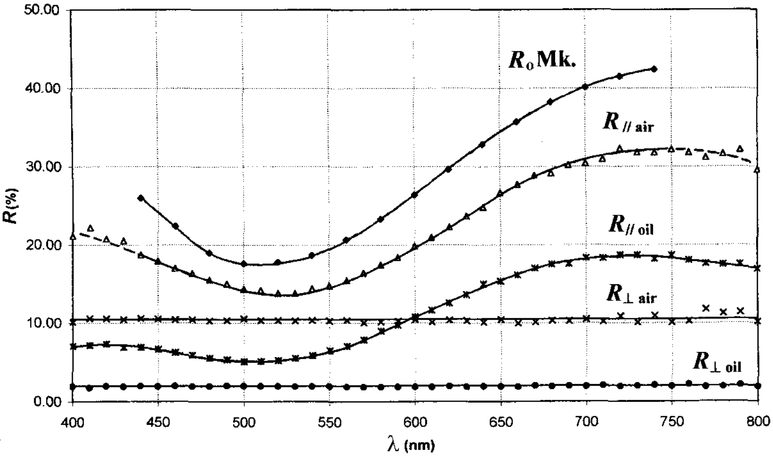

FIG. 1. Reflectance curves of yushkinite in air and oil from 400 to 800 nm, according to the data in Tables 3 and 4. R_o Mk.: maximum reflectance for ordinary vibration direction, from Makeev *et al.* (1984).

450 nm and above 700 nm, the sensitivity of the spectrophotometer decreases rapidly, and induces increasingly erratic fluctuations on reflectance measurement, e.g. Fig. 1.

Results

Table 3 gives selected reflectance data in air and oil from 400 to 800 nm. Figure 1 represents the corresponding reflectance curves. These data agree very well with those of Makeev *et al.* (1984); the only difference being the great uniformity of $R_\perp$ values (~10.3% in air, and 1.9% in oil), while these authors indicated a minimum around 550 nm. The $R_{//}$ curve gives a minimum around 500–520 nm, with values close to 13.8% (air) and 5.1% (oil). A maximum appears at 730–750 nm (32 and 18.7% respectively). This curve is intermediate between R_o and R'_o curves of Makeev *et al.* (1984), who indicated a minimum at the same position (514 nm).

These data were used to calculate the colour values according to the recommendations of the Commission on Ore Mineralogy of the IMA (Criddle and Stanley, 1993). With CIE illuminant C, these colours values are as follows: In air: for $R_{//}$: x = 0.334, y = 0.295, Y% = 16.6, λ_c = 554 nm; P_c% = 16; and for $R_\perp$: x = 0.308, y = 0.314, Y% = 10.3, λ_d = 482 nm; P_e% = 10. In oil: for $R_{//}$: x = 0.379, y = 0.315, Y% = 7.8, λ_c = 496 nm; P_e% = 14; and for $R_\perp$: x = 0.306, y = 0.315, Y% = 1.9, λ_d = 482 nm; P_e% = 11.

Refractive index n and absorption coefficient k for yushkninite

The flat curve obtained for $R_\perp$ of yushkinite in air indicates typically the absence of strong absorption (absorption coefficient k very low compared to the refractive index n), very much like graphite when the polarization vector is perpendicular to the basal plane (pseudo-transparency direction: Vaughan, 1990). Considering the absorption coefficient $k_\perp$ equal to 0 as a first approximation, one can calculate directly the refractive index $n_\perp$ according to the formula for transparent medium: $R = (n-1)^2/(n+1)^2$. For $R_\perp \approx 10\%$, $n_\perp \approx 1.92$. Taking into account the values obtained for $R_\perp$ in oil, the combination of these two sets of data makes it possible to calculate $n_\perp$ directly (Table 5) and $k_\perp$ (more accurately, $k^2_\perp$ (Table 6), because small measurement errors may easily result in aberrant negative values of $k^2_\perp$: Embrey and Criddle, 1978). Thus one obtains a very constant value of $n_\perp$ close to 1.9 (as with k nil), and $k^2_\perp$ close to 0.10, that is a value of ~0.3 for $k_\perp$ (Fig. 2).

For $R_{//}$, the two curves in air and oil show minima distinctly above the $R_\perp$ curves (Fig. 1). Thus, there is not a true transparency window at this position. Calculation of $n_{//}$ indicates erratic fluctuations below 440 and above 760 nm (Table 5), sometimes with negative values of $k^2_{//}$ (Table 6). Such high relative errors on n, together with aberrant values of $k^2_{//}$, are easily obtained when the (R_{oil}, R_{air}) measured pair plots onto the right side of the R_{oil}/R_{air} cigare diagram of

TABLE 5. Yushkinite: refractive indices parallel ($n_{//}$) and perpendicular ($n_{\perp}$) to the elongation

λ (nm)	$n_{//}$	$n_{\perp}$	λ (nm)	$n_{//}$	$n_{\perp}$	λ (nm)	$n_{//}$	$n_{\perp}$	λ (nm)	$n_{//}$	$n_{\perp}$
400	3.09	1.85	500	1.88	1.90	600	1.67	1.90	700	2.00	1.89
410	3.60	1.95	510	1.85	1.87	610	1.68	1.87	710	2.15	1.84
420	2.80	1.90	520	1.78	1.87	620	1.72	1.88	720	2.49	1.96
430	2.88	1.90	530	1.73	1.88	630	1.74	1.88	730	2.29	1.84
440	2.31	1.90	540	1.76	1.88	640	1.66	1.85	740	2.47	1.94
450	2.20	1.91	550	1.70	1.87	650	1.92	1.90	750	2.44	1.84
460	2.10	1.89	560	1.70	1.89	660	1.95	1.84	760	2.56	1.83
470	2.05	1.89	570	1.69	1.85	670	1.98	1.83	770	2.49	2.11
480	1.98	1.87	580	1.65	1.87	680	1.92	1.88	780	2.75	2.02
490	1.93	1.86	590	1.65	1.89	690	2.17	1.86	790	3.00	2.00
									800	2.21	1.86
470	2.1	1.9	546	1.7	1.9	589	1.7	1.9	650	1.9	1.9

Embrey and Criddle (1978). Omitting these values, $n_{//}$ decreases slightly from 2.3 (440 nm) to 1.65 (590 nm), then increases steadily up to 2.6 (560 nm) (Fig. 3). The corresponding change in $k^2_{//}$ is close to 0.5 up to 520 nm ($k_{//}$ = 0.7), then increases steadily up to 2.6 (730 nm, $k_{//}$ = 1.6). Above 730 nm, $k^2_{//}$ shows a slight decrease.

Interpretation of optical properties

In yushkinite, the brucite-type layer $(Mg,Al)(OH)_2$ (if minor amounts of V and possible Cu are neglected) acts optically as a transparent medium (optical gap over the visible range). Thus the absorption bands in the visible range are strictly related to the VS_2 layer. The strong anisotropy of this absorption can be compared to that described for MoS_2 (Vaughan, 1990), and is related to chemical bonding of metallic character between V atoms (partial filling of the lowest t_{2g} band). In MoS_2 the transition active in the visible range (but inactive with the polarization plane perpendicular to the layer) corresponds to the transition d_z^2 (= lowest t_{2g}) → σ*.

TABLE 6. Yushkinite: squared absorption coefficients parallel ($k^2_{//}$) and perpendicular ($k^2_{\perp}$) to the elongation

λ (nm)	$k^2_{//}$	$k^2_{\perp}$	λ (nm)	$k^2_{//}$	$k^2_{\perp}$	λ (nm)	$k^2_{//}$	$k^2_{\perp}$	λ (nm)	$k^2_{//}$	$k^2_{\perp}$
400	(−1.05)	0.11	500	0.48	0.08	600	1.20	0.07	700	2.49	0.09
410	(−2.67)	0.02	510	0.49	0.11	610	1.32	0.09	710	2.52	0.12
420	(−0.31)	0.08	520	0.53	0.10	620	1.46	0.09	720	2.53	0.04
430	(−0.55)	0.07	530	0.57	0.09	630	1.61	0.08	730	2.60	0.12
440	0.41	0.08	540	0.60	0.09	640	1.76	0.11	740	2.43	0.07
450	0.48	0.07	550	0.69	0.10	650	1.95	0.08	750	2.55	0.12
460	0.51	0.09	560	0.75	0.08	660	2.09	0.10	760	2.33	0.15
470	0.51	0.09	570	0.85	0.10	670	2.25	0.13	770	2.28	(−0.11)
480	0.50	0.10	580	0.97	0.09	680	2.31	0.09	780	2.02	(−0.01)
490	0.49	0.11	590	1.06	0.08	690	2.38	0.11	790	1.68	0.03
									800	2.25	0.10
470	0.51	0.09	546	0.65	0.10	589	1.09	0.08	650	1.95	0.08
	$k_{//}$	$k_{\perp}$		$k_{//}$	$k_{\perp}$		$k_{//}$	$k_{\perp}$		$k_{//}$	$k_{\perp}$
470	0.71	0.30	546	0.81	0.32	589	1.04	0.28	650	1.40	0.28

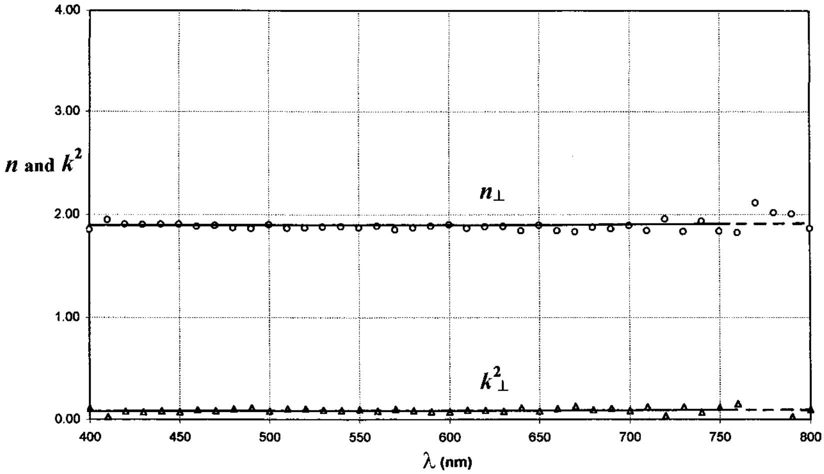

FIG. 2. Yushkinite: curves of refraction index $n_\perp$ and squared absorption coefficient $k^2_\perp$ perpendicular to the elongation (negative values omitted: see Tables 5 and 6).

In yushkinite, band structure calculations would be necessary to identify clearly the transition active in the visible/near-IR range. Nevertheless, one must point out that, in the ~$LaVS_3$ layered composite structure, where the LaS sub-layer also acts as a transparent medium, the only possible transition for an energy close to 1.7 eV (maximum of the refectance curve) is the transition $t_{2g} \rightarrow e_g$ in the VS_2 sub-layer, as proved by its band structure (Cario, 1998). Thus the same transition is highly probable for yushkinite.

Interlayer charge transfer in yushkinite

Vanadium valence state

In layered misfit compounds, the main factor stabilizing the association of two distinct layers is the chemical bonding through the donor effect of one layer towards the second one. This was first shown by Makovicky (1974) for cylindrite, where the substitution of $2Pb^{2+}$ by $2Sb^{3+}$ in the PbS-type layer induces an electron donation to the SnS_2-type layer, where one Sn^{4+} is replaced by one

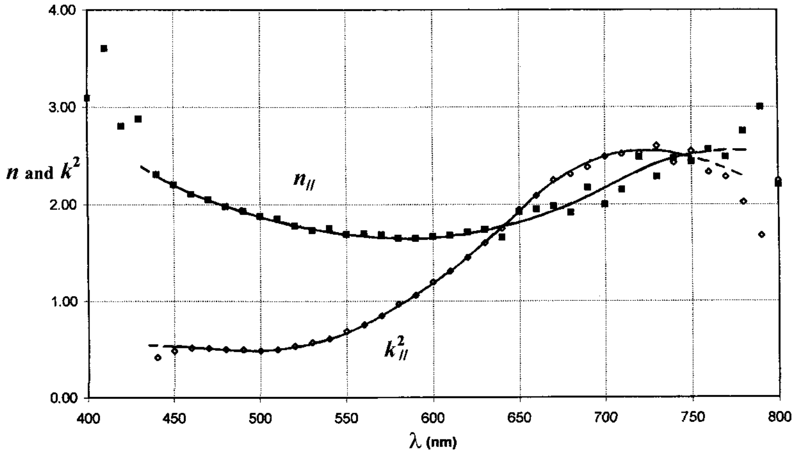

FIG. 3. Yushkinite: curves of refraction index $n_{//}$ and squared absorption coefficient $k^2_{//}$ parallel to the elongation (negative values omitted: see Tables 5 and 6).

Fe^{2+}. This rule has been generalized and extended to synthetic misfit compounds, through the example of $(Pb/Sn)S_{1+x}$ $(Nb/Ti)S_2$ compounds, where it has been demonstrated that Pb or Sn is partially substituted by minor Nb or Ti with a higher valence state (Moëlo *et al.*, 1995). There is a double cationic exchange (or change of the valence state), which must be localized (cationic coupling), and then controls the mutual modulation of the two sub-layers.

In yushkinite, Makeev *et al.* (1984) have considered V exclusively in the sulphide layer, at the trivalent state. This gave a negative charge of −0.28 for this layer, equilibrated by a positive one of the brucite-type layer. The new crystal chemical formula (2) proposed above, leads us to re-examine the valence state of V in the sulphide layer, together with chemical bonding and interlayer charge transfer.

In hydroxy-sulphides, the chemical bonding always implies H bonds. In the brucite layer of yushkinite, the substitution of Mg^{2+} mainly by Al^{3+} weakens the O−H bonds of the O atoms of the AlO_6 octahedra. Thus, electrons of these H atoms will be partially delocalized towards the nearest S atoms of the VS_2 layer, which will decrease the valence state of the V atoms bound to these S atoms. The electron donation from the hydroxide to the sulphide layer is assumed to take place through three types of (iono-)covalent bonds (= electronic delocalizations), according to the sequence: $Al \rightarrow O$, $O \rightarrow (H) \rightarrow S$ and finally $S \rightarrow V$.

The substitution of Mg by cations of higher valence state will give a positive charge to the brucite-type layer, equilibrated by a negative charge of the VS_2 layer, due to a shift of the mean valence state of V below 4+. The proposed formula (2) can be used to calculate this valence state. The valence state of Fe and V bound to oxygen in the brucite layer are uncertain. In hydrothermal conditions, Fe is generally divalent (cf. the ready formation of chlorite in hydrothermal alteration zones). More difficult is the choice of the valence state for V, which can be 3, 4 or 5. The intermediate 4+ state has been chosen arbitrarily. In formula (2), the excess of positive charges on the brucite layer is thus close to 0.41, and the mean valence state of V close to 3.59 (i.e. 4−0.41), is significantly below the theoretical maximum of the pure, metastable VS_2 compound.

Another way to approximate the charge transfer is to consider the H-bonding from a general point of view. One knows that such bonding is generally highly asymmetric between two anions, with an electronic exchange of ~0.8 e^- on one hand, and 0.2 e^- on the other. In yushkinite, if one assumes that the strongest electronic exchange is with oxygen (the most electro-negative anion), and that all H atoms are involved in H-bonding, the total electronic exchange of the brucite layer towards the V sulphide one (for 1 VS_2 unit) would be:

$$0.2 \times 2 \times 1.10 = 0.44\ e^-$$

Thus the mean formal valency of V would be 4−0.44 = 3.56, very close to that deduced from the microprobe analysis. One can conclude that H-bonding is the main chemical factor governing the charge transfer between the two sub-layers of yushkinite, and limiting its chemical substitutions inside the brucite-type sub-layer.

This problem of interlayer charge transfer through H-bonding in yushkinite is closely related to the general problem of the limit of intercalation in layered double hydroxides (LDH) of the brucite type (Trifirò and Vaccari, 1996). All of these compounds have the general formula $[M^{z+}_{1-x}M^{3+}_{x}(OH)_2]^{b+}[A^{n-}_{b/n}].m\ H_2O$ (with $b = x$ if $z = 2$, or $b = 2x$ if $z = 1$). Generally $z = 2$, and the charge $b+$ (=$x+$) varies between 0.10 and 0.50, with a mean of ~0.33. Here also, the more stable intercalation compounds seem to be governed by the same maximum charge transfer towards the intercalated anion A^{n-} through global H-bonding.

Comparison with other natural and synthetic composite hydroxy-sulphides

Due to the high volatility of H_2S, true H sulphides are not known in nature. Incorporation of H (bound with S) at low concentrations has been detected qualitatively in synthetic fülöppite by nuclear magnetic resonance (Mozgova *et al.*, 1987), and in sphalerites (Bokiy *et al.*, 1990). But in all sulphides or hydroxy-sulphides H−S bonds are probably very delicate, and stable only in epithermal conditions. This explains the rarity of hydroxy-sulphides in nature. They are mainly of the layered composite type (Makovicky and Hyde, 1992), with the same brucite-type sub-layer, bound with various sulphide ones: $Cu_{1-x}Fe_{1+x}S_2$ (in valleriite), $Fe_{1+x}Ni_{1-x}S_2$ (in haapalaite) and $Fe_{1-x}S$ (in tochilinite). Here too, H-bonding is the cohesive force which controls the substitution of divalent Mg by trivalent Al or Fe in the hydroxide layer.

In the field of solid chemistry, numerous hydroxy- or hydrated sulphides of the layered composite type are known (Subba Rao *et al.*, 1975; Danot *et al.*, 1994; Golub *et al.*, 1997). In all these cases, their conditions of synthesis correspond to low temperature conditions. For instance, the synthesis of a composite structure of iron hydroxide layers alternating with molybdenite layers, MoS_2, has been obtained by Danot *et al.* (1994) at ambient conditions. It has the formula: $[0.5(Fe^{2+}_{0.5}Fe^{3+}_{0.5})(OH)_2]^{0.25+}\ (MoS_2)^{0.25-}$, where trivalent Fe permits electron donation to the sulphide layer, as in yushkinite. More recently Co and Ni hydroxide isotypes were described (Golub *et al.*, 1997), corresponding to the general formula: $M_{0.5}(OH)_{1-x}(H_2O)_x\ MoS_2$, where the M cation (Co or Ni) is strictly divalent. Here the electron donation would be due to proton excess in the hydroxide layer. Golub *et al.* (1997) also propose the derivative with only divalent M cations: $M(II)_{0.5}(OH).MoS_2$, but such a formula, with a neutral hydroxide layer, cannot explain the stability of the composite structure through H-bonding. On the other hand, the M/Mo ratio evolves towards that of hydrated hydroxy-sulphides of the type described by Subba Rao *et al.* (1975) with Ta or Nb.

In these compounds with Fe, Co and Ni, the M/Mo ratio (0.5) corresponds to a stage-I commensurate intercalate from the parent disulphide (one incomplete $M(OH)_2$ layer for one MoS_2 layer). One might also envisage the stability of the yushkinite-type derivatives (that is, stage-I misfit intercalates with complete $M(OH)_2$ layer). Taking into account the basal a parameter of M hydroxides and MoS_2 ($a(Fe(OH)_2) = 3.24$ Å; $a(Co(OH)_2) = 3.18$ Å; $a(Ni(OH)_2) = 3.14$ Å; $a(MoS_2) = 3.16$ Å), the theoretical formulae of these misfit compounds would be: $0.951[Fe(OH)_2].MoS_2$, $0.987[Co(OH)_2].MoS_2$, and $1.013[Ni(OH)_2].MoS_2$ respectively. A mixture of Fe or Co with Ni could give a commensurate composite structure.

Conclusion

New electron probe microanalyses of yushkinite revealed its precise crystal chemistry, and minor amounts of Cu, probably intercalated between the two layers, by substitution with H. The small excess of V relative to an ideal VS_2 layer would correspond to its incorporation in the brucite layer. The electronic exchange from the hydroxide towards the sulphide layer through H-bonding gives a mean valence state close to 3.6 for V bound to S. Partial H-bonding with S atoms signifies that yushkinite is not strictly a hydroxy-sulphide, but, more exactly, a hydroxy-H sulphide.

The exact crystal structure of yushkinite is not known. Certainly it would help to confirm the positions of minor Cu and excess V in the structure. Correlation between the precise structure of the VS_2 sub-layer and band structure calculation would confirm the valence state(s) of V (in relation to inter-layer modulation) and, in addition, help in identifying the optical transition.

More generally, such a combined approach ought to be applied to the other natural composite layered hydroxy-sulphides, which have been poorly characterized, with respect to their structural complexity. In all these minerals (valleriite, tochilinite, yushkinite etc.: Organova, 1989; Makovicky and Hyde, 1992), the brucite-like layer contains trivalent anions (Al, Fe) which control the electron transfer to the sulphide layer, and it is very important to examine the distribution of these anions, with probable short-range ordering.

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