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**On the crystal structure of leucophanite.** By E. CANNILLO, G. GIUSEPPETTI and V. TAZZOLI, *Centro di Cristallografia del C.N.R., Sez. VI, Istituto di Mineralogia dell'Università di Pavia, Italy*

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The space group and the structure parameters of leucophanite given in a previous paper are confirmed.

In a previous paper (Cannillo, Giuseppetti & Tazzoli, 1967) the space group  $P2_12_12_1$  was assumed for the determination of the crystal structure of leucophanite. Some features of the measured intensities led to the conclusion that the true space group would have been  $P1$ .

In order to resolve the question, the collection of the intensities has been repeated and extended to one half of the reciprocal sphere for Cu  $K\alpha$  radiation. The refinement with the least-squares method has been continued in the space group  $P1$ .

However, the atomic shifts from orthorhombic symmetry were not significant and the variations in the thermal parameters did not suggest another kind of order for the calcium and sodium atoms.

At this stage the suspicion arose that some double reflexion effects were responsible for the 'anomalies' in the

measured intensities. Precession pictures taken with Mo  $K\alpha$  radiation did not show the previously observed 'anomalies', thus confirming the suspicion; in particular, the three reflexions  $h00$  ( $h$  odd), inconsistent with the orthorhombic space group, did not appear and the sensible differences between some intensities which would be equivalent in the orthorhombic space group, were not now observed.

Thus the space group of leucophanite is, without any doubt,  $P2_12_12_1$ , and the structure parameters published in the cited paper are substantially confirmed.

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**A comment on the synthesis and lattice constants of transition metal thionibates with berthierite ( $\text{FeSb}_2\text{S}_4$ ) structure.** By B. VAN LAAR, *Reactor Centrum Nederland, Petten, The Netherlands* and D.J.W. IJDO, *Laboratory of Inorganic Chemistry, University of Leiden, The Netherlands*

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Transition metal thionibates ( $M\text{Nb}_2\text{S}_4$  where  $M = \text{Mn, Fe, Co, Ni}$  or  $\text{Cu}$ ) have been indexed on the basis of a hexagonal unit cell. The results are much more satisfactory than those from earlier indexing on the basis of an orthorhombic unit cell.

Eibschütz, Hermon & Shtrikman (1967) describe the preparation and X-ray patterns of the compounds  $M\text{Nb}_2\text{S}_4$  ( $M = \text{Mn, Fe, Co, Ni, and Cu}$ ). The X-ray powder photographs of these compounds were indexed on the basis of an orthorhombic unit cell having about the same lattice constants as those published for berthierite ( $\text{FeSb}_2\text{S}_4$ ) by Buerger & Hahn (1955). Eibschütz *et al.* consider this as evidence that the compounds  $M\text{Nb}_2\text{S}_4$  are isostructural with  $\text{FeSb}_2\text{S}_4$ .

These conclusions do not seem to be completely justified. If  $M\text{Nb}_2\text{S}_4$  is isostructural with  $\text{FeSb}_2\text{S}_4$ , it would be expected that their X-ray patterns should be very similar, because the scattering powers of Nb and Sb differ by only twenty per cent. Comparing the data of Eibschütz *et al.* with the diagram of  $\text{FeSb}_2\text{S}_4$  published by Buerger (1936), it is easily seen that this is not at all the case.

This discrepancy can be resolved by indexing the published data on the basis of hexagonal unit cells. The lattice

Table 1. Indexing of powder diffraction data of  $M_x\text{NbS}_2$ 

hkl	Mn			Fe			Co			Ni			Cu		
	$d_{\text{obs}}$	$d'_{\text{calc}}$	$I_0$	$d_{\text{obs}}$	$d'_{\text{calc}}$	$I_0$	$d_{\text{obs}}$	$d'_{\text{calc}}$	$I_0$	$d_{\text{obs}}$	$d'_{\text{calc}}$	$I_0$	$d_{\text{obs}}$	$d'_{\text{calc}}$	$I_0$
002	6.25	6.22	s	6.11	6.10	s	5.85	5.83	s	5.77	5.84	s	6.40	6.36	s
004	3.156	3.155	m	3.062	3.069	m	2.950	2.949	m	2.939	2.947	m	2.870	2.859	m
100	2.872	2.867	m	2.870	2.875	m	2.870	2.863	m	2.853	2.860	m	2.811	2.793	m
101	2.803	2.797	m	2.800	2.800	m	2.780	2.783	m	2.765	2.780	m	2.601	2.619	ms
102	2.592	2.614	ms	2.604	2.605	ms	2.581	2.579	ms	2.567	2.575	ms	2.376	2.390	m
103	2.370	2.376	m	2.351	2.356	m	2.318	2.320	m	2.300	2.317	m	2.148	2.152	vs
104	2.133	2.131	vs	2.100	2.102	vs	2.060	2.062	vs	2.050	2.058	vs			
105	1.899	1.905	w	2.049	2.051	m	1.829	1.829	w	1.822	1.826	w	1.930	1.930	w
106	1.706	1.707	m	1.873	1.872	w	1.630	1.630	m	1.630	1.627	m	1.690	1.662	m
110	1.666	1.665	ms	1.673	1.672	m	1.662	1.661	m	1.669	1.658	m	1.610	1.611	w
112	1.610	1.611	m	1.605	1.607	w	1.600	1.600	s	1.597	1.597	s	1.631	1.631	w
008	1.589	1.589	m	1.539	1.540	m	1.495	1.485	w	1.490	1.482	w	1.480	1.482	m
107	1.536	1.537	m	1.495	1.503	w	1.464	1.461	w	1.462	1.459	w			
114	1.464	1.477	m	1.440	1.440	w	1.440	1.440	w	1.439	1.437	w	1.440	1.441	vw
200	1.445	1.444	vw	1.405	1.405	w	1.400	1.400	w	1.397	1.397	w	1.416	1.421	vw
202	1.409	1.408	w	1.361	1.359	m	1.322	1.321	m	1.318	1.318	m			
108	1.394	1.393	m												

constants of these can then be determined by means of a least-squares computer program that minimizes the quantity

$$\Sigma [(h^2 + hk + k^2) \frac{4}{3a^2} + \frac{l^2}{c^2} - \frac{4}{\lambda^2} \sin^2 (\theta_{\text{obs}} - \theta_0)]^2$$

with respect to the lattice constants  $a$  and  $c$  and to  $\theta_0$ , the zero point of the  $\theta_{\text{obs}}$ -scale. The values of  $\theta_{\text{obs}}$  were deduced from the published values for  $d_{\text{obs}}$  by means of:  $\theta_{\text{obs}} = \arcsin (\lambda/2d_{\text{obs}})$ .

In Table 1 the resulting indexing is given for the reflexions with  $d_{\text{obs}} > \approx 1.3 \text{ \AA}$  together with values for  $d'_{\text{calc}}$ , calculated according to

$$d'_{\text{calc}} = \lambda/[2 \sin (\theta_{\text{calc}} - \theta_0)],$$

where  $\theta_{\text{calc}}$  is deduced from the lattice constants in the usual way.

Table 2. Lattice constants of  $M_x\text{NbS}_2$ 

M	$a$ (Å)	$c$ (Å)	$\theta_0$ (°)
Mn	$3.350 \pm 0.001$	$12.786 \pm 0.007$	$+0.22 \pm 0.02$
Fe	$3.340 \pm 0.002$	$12.356 \pm 0.008$	$+0.11 \pm 0.03$
Co	$3.342 \pm 0.002$	$11.931 \pm 0.008$	$+0.20 \pm 0.03$
Ni	$3.331 \pm 0.003$	$11.895 \pm 0.015$	$+0.16 \pm 0.05$
Cu	$3.347 \pm 0.009$	$13.137 \pm 0.035$	$+0.26 \pm 0.10$

The lattice constants and the values for  $\theta_0$  are given in Table 2. A refinement of the lattice constants proposed by Eibschütz *et al.* (1967) by means of our computer program resulted in standard deviations for these constants that are from four to ten times higher than the standard deviations given in Table 2. This suggests that the indexing on the basis of a hexagonal cell is the correct one.

An interesting feature is that the constants calculated by us for the copper compound are exactly the same as those reported by Koerts (1963) for  $\text{Cu}_{0.65}\text{NbS}_2$ .

We did not succeed in preparing ordered compounds of composition  $M_{0.5}\text{NbS}_2$  for  $M = \text{V}, \text{Mn}, \text{Fe}, \text{Co}$ , and  $\text{Ni}$ . In all cases the resulting phase was  $M_{0.33}\text{NbS}_2$  with a structure which can be described as a  $2s\text{-NbS}_2$  lattice with  $M$ -atoms ordered in octahedral holes, leading to a superstructure with an  $a$  axis that is about  $\sqrt{3}$  times as long as the  $a$  axis in  $2s\text{-NbS}_2$ . More detailed information on the structure of, and magnetic ordering in, these compounds, based on neutron diffraction data, will be published elsewhere.

Because of the information given above, together with the fact that the lattice constants in Table 2 correlate well with the constants of  $2s\text{-NbS}_2$  (Jellinek, 1960), it is possible that the compounds described by Eibschütz *et al.* are disordered phases. The corresponding ordered phases are  $M_x\text{NbS}_2$  with  $x \approx 0.33$  for  $M = \text{Mn}, \text{Fe}, \text{Co}$ , and  $\text{Ni}$  and with  $x \approx 0.65$  for  $M = \text{Cu}$ . The latter compound has a  $\text{MoS}_2$ -type structure, as was determined by Koerts (1963).

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