Structural study of tochilinite.

II. Acicular variety: Unusual diffraction patterns

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(Submitted July 3, 1972; resubmitted October 30, 1972)
Kristallografiya, 18, 966-972 (September-October 1973)

Powder patterns and acicular textures have been recorded with x rays for the acicular variety of tochilinite, and electron-diffraction studies have been made on microcrystals in the electron microscope. The material is found to consist of a set of two regularly oriented phases, one of which has a structure analogous to that of the isometric tochilinite I, while the second (tochilinite II) differs from the I variety in having a different distribution of the vacancies in the sulfide component; the sulfide and brucite components of type II are described in different sublattices: the sulfide has P1, a = 8.34; b = 8.54; c = 10.74 Å, α = 87° 20', β = 94°30', γ = 92° and the brucite has C1, a = 5.42; b = 15.65; c = 10.74 Å, $\alpha = \gamma$ = 90°, β = 95°. The chemical formula is $6Fe_{0.8}S \cdot 5[Mg_{0.7}Fe_{0.3}(OH)_2]$. The isometric and acicular varieties have been examined by microdiffraction in the electron microscope, and some unusual diffraction patterns have been observed, which are ascribed to features of the structure.

It has been shown[1,2] that the recently discovered mineral tochilinite (isometric variety) consists of an alternation of layers of iron sulfide and brucite; the sulfide layers have an iron deficiency and contain an ordered disposition of the vacancies, while the brucite layers contain not only magnesium but also iron. The adjacent layers of the same type are displaced one relative to another by $a/6$. The crystallographic characteristics of the isometric variety are space group C1, a = 5.37; b = 15.60; c = 10.70 Å, $\alpha = \gamma$ = 90°, β = 95°; chemical formula $6Fe_{0.9}S \cdot 5[Mg_{0.7} \cdot Fe_{0.3}(OH)_2]$.

The isometric and acicular morphologic varieties of the mineral have similar powder patterns and similar compositions, so their structures must be similar or identical.[1,2] However, the acicular variety has been found to contain macroscopic needles, whose x-ray patterns show that they consist of an acicular texture. The basal ($00l$) reflections on the zero layer line for rotation patterns have been used to show that tochilinite is a hybrid structure, from which the z coordinates of the atoms have been deduced.[1,2] The hk0 point electron-diffraction patterns for the two varieties indicate that the acicular one consists of two phases; there is a set of peaks with cmm symmetry, and also reflections arranged in accordance with a pseudosquare pattern. We find that a_{sq} = 8.34, b_{sq} = 8.54 Å, γ = 92°, with the angle between the x^*_{sq} and y^*_0 axes being 21°. Figure 1 shows an idealized scheme for the hk0 diffraction pattern of the acicular variety; the orthorhombic variety in this pattern is represented by a pattern analogous to that of the isometric variety. In what follows we call the structure responsible for the latter system of reflections tochilinite I. The additional pseudosquare network of reflections indicates that the variety I is accompanied by a second component with a regular orientation with respect to the first. We have examined numerous electron-diffraction patterns and found that the geometrical relationship between the two parts of the pattern is the same in every case, as is the intensity ratio between the two sets of reflections, but with individual intensities varying from one pattern to another, which indicates variation in the quantitative relationships between the two phases.

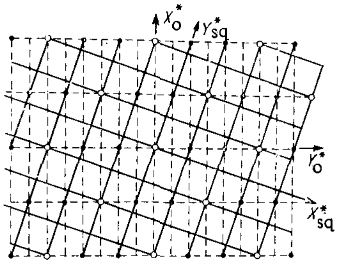

Fig. 1. An idealized scheme for the point electron-diffraction pattern of the acicular variety of tochilinite.

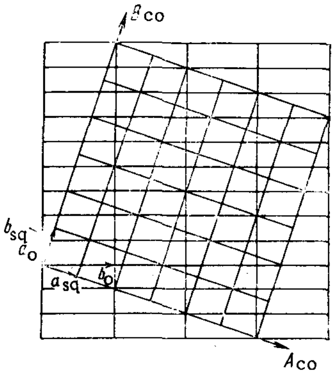

Fig. 2. An idealized relation between the orthorhombic and pseudosquare unit cells.

The reflections from the orthorhombic and pseudosquare components coincide in part (Fig. 1), which enables us to describe the entire set of reflections within a single unit cell; Fig. 2 shows the idealized relationship between the corresponding unit cells in ordinary space. The relation between the coordinate axes can be found in vector form from Fig. 2: $a_o + b_o = 2a_{sq}$, $9a_o + b_o = 6b_{sq}$; for the common unit cell $A_{co} = 6a_{sq}$, $B_{co} = 6b_{sq}$.

The structure responsible for the pseudosquare pattern was interpreted by measuring the intensities; in all we measured 166 independent reflections for the pseudosquare system, of which 39 coincided with the orthorhombic pattern. The maximum $\sin\vartheta/\lambda$ = 0.66, while the measurements were made by the method of ref. 2. We converted from the intensities to the structure amplitudes via the equation $\Phi \sim \sqrt{I}$.

TABLE 1. Atomic Coordinates for a Sulfide Layer in Tochilinite II

Atom	x	y	z	Atom	x	y	z
Fe_1	0.29	0.092	0	S_2	0.790	0.107	—0.129
Fe_2	0.582	0.206	0	S_3	0.093	0.201	0.129
Fe_3	0.906	0.287	0	S_4	0.386	0.307	—0.129
Fe_4	0.226	0.411	0	S_5	0.692	0.387	0.129
Fe_5	0.774	0.589	0	S_6	0	0.5	—0.129
Fe_6	0.418	0.794	0	S_7	0.210	0.893	—0.129
Fe_7	0.094	0.713	0	S_8	0.907	0.799	0.129
Fe_8	0.774	0.589	0	S_9	0.614	0.693	—0.129
S_1	0.5	0	0.129	S_{10}	0.308	0.611	0.129

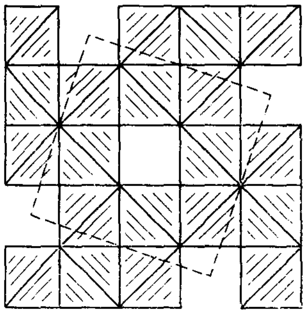

Fig. 3. Idealized model of a sulfide layer in the second phase in the acicular variety of tochilinite.

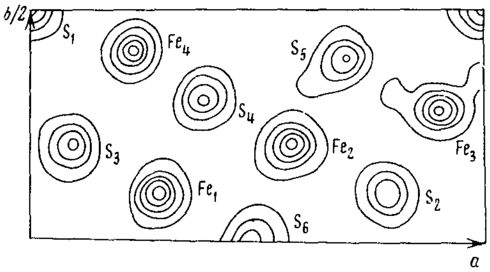

Fig. 4. Final potential synthesis for the sulfide part of tochilinite II.

The Patterson synthesis constructed with all the measured intensities had the peaks lying on slightly distorted squares, with their heights corresponding in magnitude and geometry to the makinawite sulfide pattern (as in the layered iron sulfide makinawite[3] FeS), each layer containing Fe tetrahedra with a four-fold environment. The intensities were distributed in the pseudosquare pattern in such a way that as a rule reflections with hk0 indices for which h + k = 2n were usually stronger than those with h + k = 2n + 1, which indicates pseudocentering of the cell. This indicates a possible form for the structure as shown idealized in Fig. 3. We used the ideal model with the planar symmetry group p2 to calculate the R for various degrees of population of the tetrahedra shown empty in Fig. 3. The agreement was best (R = 40%) when the empty tetrahedra were not populated at all. The atomic coordinates could not be revised via potential syntheses because some of the reflections for the two systems coincided, but least-squares refinement with the intensities for the pseudosquare set gave R = 29.9% when we assumed that the coincident reflections had zero intensity. We derived the theoretical structure amplitudes from the coordinates found after refinement, which showed that the strongest structure amplitudes are ones corresponding to the reflections in common with the orthorhombic pattern, which agreed with experiment. We replaced the coincident reflections by the theoretical intensities, which improved R to 21.6%; the corresponding potential synthesis showed small displacements of the atoms. A further application of least squares with zero intensities for the coincident reflections gave R = 25%. The complete set of intensities with theoretical values for the superimposed ones gave a final R of 18.4%.

Table 1 gives the coordinates of the atoms in the sulfide layer of the second phase for the acicular variety; as in the case of the isometric variety, the symmetry of the projection is higher than that of the structure as a whole, the center of symmetry being lost in passing to the three-dimensional coordinates.

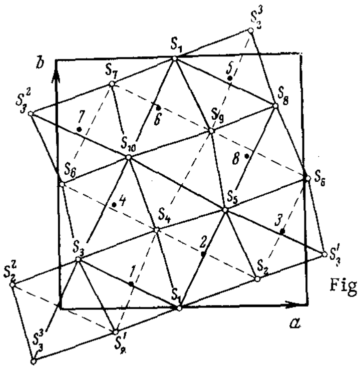

Fig. 5. Normal projection of a sulfide layer in tochilinite II.

Figure 4 gives the final potential synthesis, while Fig. 5 gives the normal projection of the sulfide layer from the second phase in the acicular variety.

The mean Fe−S interatomic distance was 2.34 Å (as against 2.32 Å for the isometric variety), with a range from 2.10 to 2.54 Å. The unshared edges had lengths from 3.68 to 3.94 Å with a mean of 3.78 Å, while the shared edges had from 3.67 to 4.10 Å with a mean of 3.84 Å. The mean interatomic distances in the sulfide layer of the second phase in the acicular variety are somewhat larger than those in the isometric variety. The mode of distortion of the sulfur tetrahedra is similar to that in the isometric variety.[2]

We used the equations of ref. 4 to estimate the level of error in the atomic coordinates, which gave Δx = Δy = 0.022 Å for the iron and Δx = Δy = 0.035 Å for the sulfur with b = 0.2; the error in determining the interatomic distances was at least 0.05 Å.

These sulfide layers are responsible for the pseudosquare reflection pattern in electron diffraction, and they are intercolated with brucite layers, as in the isometric variety; this was deduced as follows. First of all, if the specimen contained only the sulfide phase, it would be unlikely that the dimensions of the unit cell would be an exact multiple of the thickness of a tochilinite layer. If the agreement were not exact, the even order of the basal reflections would be split into pairs, since the thickness of a makinawite layer is 5.046 Å, and the strongest reflection in the powder pattern of makinawite itself has a (001) index and the corresponding reflection would always be present on the zero layer line in the rotation pattern. Besides, a satisfactory value of the R factor, equal to 9.4% according to the x-ray data, resulting from the calculation of the z coordinates of the atoms in the acicular variety, likewise implies a coherent intercalation of sulfide layers with a pseudosquare structure and brucite layers. The vacancies in the sulfide layer require compensation of the negative charge, which is provided as in the isometric variety, i.e., via the positive charge on the brucite layers. This part of the brucite layers has a periodicity coincident with that for variety I, so the scattering from this produces precisely the reflections found for variety I.

The acicular variety thus consists of two phases: The first phase has a structure analogous to that for tochilinite I, while the second phase has a hybrid structure also,[5] with alternation of sulfide and brucite layers, which we call tochilinite II. The second phase differs from the first in having a different distribution of the vacancies in the sulfide layer, which alters the size of the unit cell for the sulfide component of variety II in the plane of the layer and implies also a separate crystallographic description for each of the two components. A similar division of a single crystal into two sublattices for two distinct components occurs also in two other minerals with hybrid structures: the mineral kenenite[6] with the formula $(Na, Mg)Cl_2 \cdot 1.78[Mg, Al(OH)_2]$ and the mineral valleriite[5] with the formula $2(Cu, Fe)S \cdot 1.524[Mg, Al(OH)_2]$. However, these structures have only the basal $00l$ reflections common in reciprocal space, whereas tochilinite II has some of the reflections of general hkl type in coincidence, which indicates that the structure of tochilinite II can be described within a single large unit cell. However, it is clear that the structural investigation is considerably facilitated by separate consideration of the nonoverlapping reflections.

If we assume that adjacent sulfide layers in variety II have a mutual disposition analogous to that in variety I, we can determine all the dimensions of the sulfide sublattice: a = 8.34; b = 8.54; c = 10.74 Å, α = 87°20', β = 94.5°, γ = 92° with space group P1. Calculation of the theoretical structural formula for tochilinite II gives the relationship between the number of sulfide and brucite molecules found for tochilinite I, but with a different value for the coefficient of the iron atom in the sulfide layer: $6Fe_{0.8}S \cdot 5[Mg_{0.7}Fe_{0.3}(OH)_2]$.

When we come to describe and interpret the unusual diffraction patterns of the two varieties of the mineral, one should begin with the explanation of the distribution of the hk0 reflections of high intensity on the electron-diffraction point patterns; some of these fit a pseudosquare net, while the others form a pseudohexagonal pattern, whose distribution is close to that of the reflections for a brucite structure. We calculated the theoretical intensities for the isometric variety separately for the sulfide and brucite parts, which showed that the strongest reflections were determined mainly either by the sulfide component or by the brucite one. For instance, the main contribution to the strong (350) and (0.10.0) reflections comes from the brucite layers, and the same applies to the weaker (200) and (150) reflections. Conversely, the (260) and (0.12.0) reflections, and also (400), arise mainly from the sulfide layers. Figure 6 shows the hk0 reciprocal lattice plane for the isometric variety; the circles denote the brucite reflections, and the triangles the sulfide ones. The first set of reciprocal-lattice points corresponds to a_h = 3.13 Å (a = 3.12 for brucite), while the second has a_{sq} = 1.87 Å, which is the makinawite subcell of the sulfide layer, which corresponds to projection of the Fe–S distance in the sulfur tetrahedron.

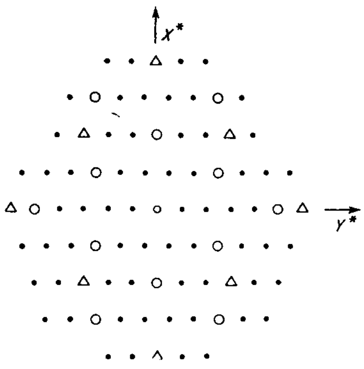

Fig. 6. Cross section in kh0 for the reciprocal lattice of isometric tochilinite.

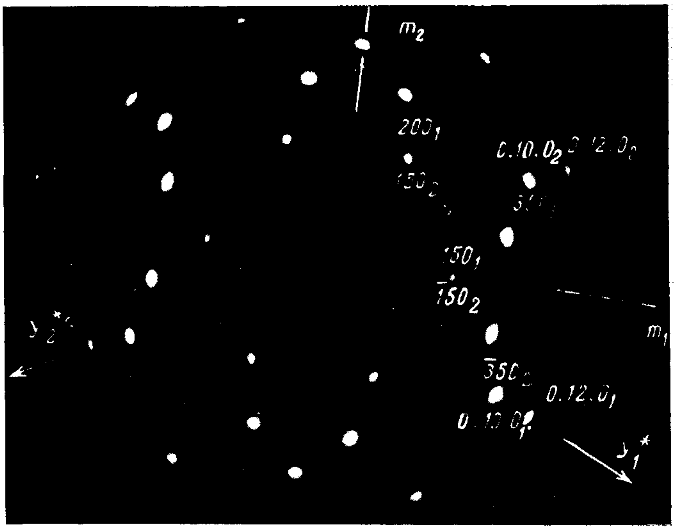

Fig. 7. Electron-diffraction pattern of a twinned microcrystal of tochilinite (m_1 and m_2 are symmetry planes).

The electron microscope revealed unusual diffraction patterns of four types for both varieties; each of these could be explained in terms of the above features in the distribution of the hk0 reflection intensities.

Type 1. Figure 7 shows the electron-diffraction spot pattern from the isometric variety, and similar patterns were observed for the other variety; the reflections

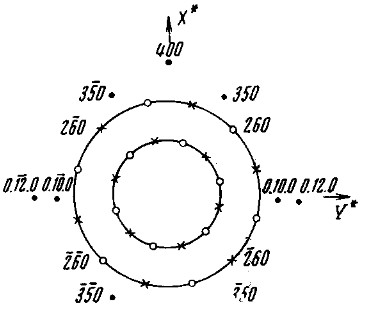

Fig. 8. Scheme for the electron-diffraction pattern of isometric tochilinite containing a valeriite component.

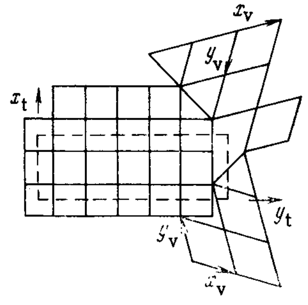

Fig. 9. Likely mutual disposition of the tochilinite and valeriite-type structures within a sulfide layer.

seen on the plate constitute an ensemble of two tochilinite patterns, one turned relative to the other through 120°. Figure 7 shows the Y_1^* and Y_2^* axes of the reciprocal lattice for each of the components. The diffraction pattern has two mutually perpendicular symmetry planes, which are absent in each of the components, i.e., the diffracting volume is a twin. This twin is formed by error in superposition of adjacent sulfide layers; the pseudotrigonal symmetry of a brucite layer causes one part of the scattering volume to be turned relative to the other through 120°. The volumes turned one relative to the other are approximately equal, so the point electron-diffraction pattern contains additional symmetry elements (Fig. 7 shows the indices for some of the reflections, among which are also the brucite ones).

Type 2. This occurs in both varieties. The tochilinite pattern is accompanied by a series of additional reflections, among which one can distinguish ones derived from the strongest reflections of tochilinite, namely (260) and ($2\bar{6}0$). The geometry and intensity of the pattern shown in Fig. 8 indicate that there are 12 reflections at identical distances from the primary electron beam, half of which are related via a six-fold axis to the (260) reflection, while the other half are related to the ($2\bar{6}0$) reflection of tochilinite. A similar system lies on a circle at a distance less by a factor $\sqrt{3}$ (Fig. 8). The intensities and the distances from the primary beam enable one to assign these reflections to the sulfide component of the valleriite-type structure.[5] The essential difference between the structures of tochilinite and valleriite lies in the disposition of the atoms in the sulfide layer; in tochilinite, the sulfide layer $Fe_{1-x}S$ consists of tetrahedra lying on the side edges, while in valleriite the sulfide layer $Cu_{2-x}Fe_xS_2$ is constructed from tetrahedra standing on their bases and has a three-fold symmetry axis. Figure 9 shows a scheme for the most probable mode of coexistence of parts with tochilinite and valleriite atomic dispositions within a single sulfide layer, the latter having two equally probable orientations. The elementary squares shown in the figure are tochilinite tetrahedra,[1,2] while the rhombs are unit cells of the sulfide part with the valleriite type of structure.[5] The disposition of the reflections on the point electron-diffraction pattern agrees with this mutual disposition of the squares and rhombs, in which the diagonals of the squares coincide with the small diagonals of the rhombs. This gives us two orientations of the valleriite atomic ray in the sulfide layer.

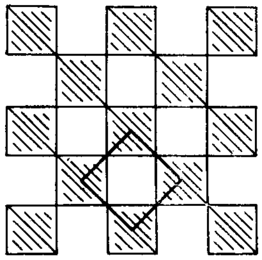

Fig. 10. Vacancy redistribution in a sulfide layer in tochilinite, type 3.

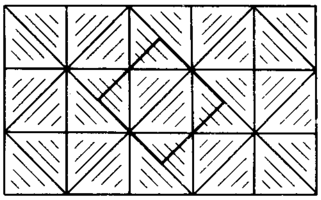

Fig. 11. Vacancy redistribution in a sulfide layer in tochilinite, type 4.

Types 3 and 4. When specimens were made from an aqeuous suspension in which isometric tochilinite particles had been left for a month, there was a considerable redistribution of the intensities in the corresponding point electron-diffraction patterns; this concerned mainly reflections arranged in the square pattern, which indicates a change in the sulfide part of the structure. One of these unusual patterns had high-intensity reflections corresponding to a square subcell in reciprocal space of side $\sqrt{5.37^2 + (15.65/3)^2}/2 = 3.74$ Å, while a second corresponded to $a = 5.37/2 = 2.68$ Å, $b = 15.65/6 = 2.6$ Å; the most probable explanation of this observed intensity redistribution is a change in the vacancy distribution in the sulfide layer of tochilinite I, where the vacancies are distributed in a centered rhombic pattern.[1,2] The treatment in aqueous suspension provides for a more equilibrium location of most of the vacancies with respect to the squares; Fig. 10 shows the vacancy distribution in a sulfide layer corresponding to one type of these diffraction patterns, while Fig. 11 does the same for the other type. In the first case, the vacancies are arranged in a chessboard pattern, while in the second they are uniformly distributed over all tetrahedra.

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