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Synthesis and Structure of Tochilinite: A Layered Metal Hydroxide/Sulfide Composite

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Hydrothermal treatment of mixtures of Fe(II) sulfide gels with Mg/Al hydroxide gels at 200°C, under reducing conditions, results in the formation of a molecular composite material with a composition range around $2Fe_{1-x}S \cdot 1.7|(Mg_{0.7}Al_{0.3})(OH)_2|$. The material comprises positively charged layers of $Fe_{1-x}S$ alternating with incommensurable, negatively charged hydrotalcite layers. Four distinct structural modifications were identified by TEM and electron diffraction, all with approximately the same composition: (i) A plate-like, (pseudo)hexagonal phase, the hydroxide layers of which have $a_H \approx 3.0$ Å and the sulfide layers $a_S \approx 3.7$ Å, indistinguishable from synthetic valleriite. (ii) A second plate-like phase comprising (pseudo) hexagonal hydroxide layers with $a_H \approx 3.1$ Å and (pseudo-)tetragonal sulfide layers with $a_S \approx 5.3$ Å, corresponding to the reported plate-like form of natural tochilinite. (iii) A uniquely disordered, nanotubular crystalline phase, probably derived from the (ii) form, and corresponding to the reported tubular form of natural tochilinite. (iv) a modification of the plate-like form (ii) in which the two layers are rotationally "disordered" or multiply twinned.

1. INTRODUCTION

Tochilinites (1, 2) are iron sulfide-containing members of a relatively widespread but little-known group of composite, double-layer metal sulfide–magnesium hydroxide minerals. Other examples include valleriite (3, 4), a mixed copper–iron sulfide-layer species and the related but somewhat less-common yushkinite (5), a vanadium sulfide-layer species, and haapalite (6), a nickel–iron sulfide-layer variant. As well as these minerals of terrestrial provenance, very closely related minerals have meteoric origin in the carbonaceous chondrites, such as the Murchison, Mighei and others. Barber *et al.* (7) obtained transmission electron microscope (TEM) lattice images and electron diffraction patterns from the "poorly characterized phases" (PCP's) in the Murchison and other meteorites and by electron energy-loss spectroscopy (EELS) determined this material to be hitherto unknown Fe–S–Ni–O compounds. Electron microscopy methods have also been employed by Organova *et al.* (8), Tomeoka and Buseck (9) and Mackinnon and Zolensky (10) who subsequently proposed structures for these PCP's which essentially categorise them as iron-rich, Fe–Ni–Mg tochilinites.

These minerals fall into the general category of "incommensurate" layered materials (11), because the unit-cell parameters of the two component layers, the sulfide and hydroxide, are unequal or irrational. However, whereas all the valleriites are rather similar (3) (with the possibility of small differences in the layer-stacking), a rather wide variety of modifications have been described for tochilinite, with plate-like and acicular (and/or tubular) forms known. Organova *et al.* (1, 12) have used both X-ray and electron diffraction methods to determine the crystal structures of the terrestrial tochilinite plate-like and acicular forms in detail. An electron microscopy study by Zolensky and Mackinnon (2) has shown that natural fibrous Fe–Mg–Al tochilinite from Pennsylvania and Brazil, consisting of individual needles or fibers up to 10 mm in length but often only 10 ~ 30 μm in diameter, possess cylindrical morphology. The innermost parts of these cylinders are composed of relatively flat "laths" of material, which are arranged to give a polygonal tube. Although the observed true curvature of the inner layers or laths was less than 10^{-2} rad, the outer parts of the cylinders are composed of truly rolled-up material, in a manner akin to the sulfosalt cylindrite and to some extent, serpentine as well. These authors suggested that the weak interlayer bonding is responsible for controlling the maximum curvature of the outer layers.

The various tochilinite and valleriite minerals are reviewed by Makovicky and Hyde (11). Both minerals comprise alternating, quasi-independent layers of two types: MS layers of edge-shared MS_4 tetrahedra and brucite-like $M'(OH)_2$ layers of edge-shared $M'(OH)_6$ octahedra. In both minerals the hydroxide layers M' are (Mg, Al, Fe). In the tochilinites, these layers alternate with macki-

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TABLE 1
Reported Compositions of Some Tochilinite Minerals

Location	Composition
Mamonovo, former USSR (13)	$6[Fe_{0.9}S] \cdot 5[Mg_{0.7}Fe_{0.3}(OH)_2]$
Cyprus (14)	$2[FeS] \cdot 1.58[Mg_{0.53}Fe_{0.47}(OH)_2]$
Amos Quebec (15)	$[Fe_{1.88}S_2] \cdot 1.82[Mg_{0.73}Fe_{0.27}(OH)_2]$
Pennsylvania, U.S.A. (15)	$[Fe_{1.62}S_2] \cdot 1.97[Mg_{0.79}Al_{0.21}(OH)_2]$
Kamaishi mine, Japan (16)	$2[Fe_{0.77-0.78}S] \cdot 1.81 \sim 1.85[Mg_{0.79}Al_{0.2}Ca_{0.01}(OH)_2]$ and $2[Fe_{0.77-0.68}Cu_{0.15-0.24}S] \cdot 1.65 \sim 1.71[Mg_{0.78}Al_{0.20-0.21}Ca_{0.01-0.21}(OH)_2]$
USSR (17)	$2[Fe_{1-x}S] \cdot n[(Mg, Fe, Al)(OH)_2]$ $x = 0.08 \sim 0.28$ and $n = 1.58 \sim 1.75$
Ransko, Czechoslovakia (18)	$[Fe_{1.921}Cu_{0.079}S_2] \cdot 7.324[Fe_{0.691}Mg_{0.080}Cr_{0.124}Mn_{0.034}Al_{0.053}Cr_{0.013}Ti_{0.005}(OH)_2]$

nawite-like tetragonal MS layers, {100} slices of antifluorite XM_2 with M = (Fe, □). The corresponding layer in valleriite is trigonal, {111} slices of antifluorite, with M = (Fe, Cu). Both minerals have *cp* layers of sulfur atoms. The various tochilinite modifications differ principally in the arrangement (ordering) of the Fe vacancies in the sulfide layer (12). Tochilinites occur in many localities, some of which are listed in Table 1 with their reported compositions. In contrast to the valleriites, the tochilinite layers are semicommensurate, and thus Organova *et al.* (8) were able to describe a common unit cell for their tochilinite I, comprising one layer-pair and of dimensions $a = 5.37$ Å, $b = 15.6$ Å, $c = 10.72$ Å, $\alpha = \gamma = 90°$, $\beta = 95°$, space group $C1$. This cell results from the interlayer semicommensurate subcell matching of $5b'_{\text{hydroxide}} = 6b'_{\text{sulfide}}$, the subcell a and c parameters of both layers being equal.

As part of our continuing study of "nanocomposite" materials, it was of interest to us to attempt the previously unreported synthesis of tochilinite. We describe elsewhere (4) the results of our parallel synthetic and structural study of valleriite.

2. EXPERIMENTAL

2.1. Preparation of Tochilinite

Tochilinite was prepared by a hydrothermal technique. Thus, 2 mmole of $Fe(ClO_4)_2 \cdot 6H_2O$ was dissolved in 5 ml of deionised, distilled water. To this stirred solution was added 2 mmol of $(NH_4)_2S$ (10% w/w, aqueous solution) to produce a black suspension. A separate Mg/Al hydroxide gel was prepared by adding an aqueous solution of NH_3 (25% w/w) drop-wise to 5 ml of an aqueous mixture containing 1.12 mmole of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.48 mmole of $Al(NO_3)_3 \cdot 9H_2O$, until the pH was in the range 8.5–9.5. This hydroxide gel was then stirred into the sulfide suspension and the pH of the mixture was then adjusted up to 8.5 by adding extra drops of 25% NH_3 (aq). An autoclave (Parr model 4740, 316 stainless steel, 71 ml capacity) was charged with this mixture plus a Teflon-coated stirring bead, flushed three times with hydrogen to 3 MPa, sealed at an initial partial pressure of hydrogen of 2.5 MPa at STP and then heated for 2 days at 200°C in a block heater positioned on a magnetic stirrer.

2.2. Analysis

The solid products were qualitatively assessed by powder X-ray diffraction (XRD) with a Siemens D-500 diffractometer using Ni-filtered Cu$K\alpha$ radiation. Transmission electron microscopy (TEM), together with energy-dispersive X-ray analysis (EDX), was performed using a Philips CM30 300 kV scanning transmission electron microscope. TEM samples were dispersed ultrasonically in ethanol and a drop of this suspension placed on a holey-carbon coated nickel grid. EDX analyses used an EDAX ultra-thin window detector and EDAX software for thin-film quantitative analysis. Samples of natural chalcopyrite, $Cu_{0.97}Fe_{0.93}S_2$ and olivine, $Mg_{1.89}Fe_{0.175}SiO_4$ kindly supplied by the South Australian Museum were used to standardize the EDX analyses. EDX analyses were performed using the scanning mode of the CM30, usually at magnifications of $\sim 10^5$ times and spot sizes of below 100 nm. In addition, transmission electron diffraction patterns and high-resolution images were obtained from selected samples.

3. RESULTS AND DISCUSSION

The synthetic mixture used in this work employed a similar composition to that found in the (Mg, Al) tochilinites from Pennsylvania and Jacupiranga reported by Jambor (15) and Zolensky and Mackinnon (2). Our hydrothermal synthesis required an iron/sulfide ratio of close to 1, although EDX analyses showed a ratio of 0.7–0.8 in the final product (vide infra). A deficiency of sulfide in the starting reaction mixture resulted in the formation of iron oxide, whereas the use of excess sulfide resulted in the formation of pyrite. The Mg/Al ratio of 2.3 in the product did not change from that used in the starting reaction mixture. The use of a hydrogen atmosphere during the reaction was essential to prevent the formation of haematite (Fe_2O_3).

No XRD patterns for these natural (Mg, Al) tochilinites appear to have been published, although Zolensky and Mackinnon gave lattice spacings from their TEM work which classify their tochilinite as the single-layer, ~11-Å material. XRD patterns from our synthetic material, in addition to traces of pyrrhotite, gave strong peaks corresponding to d spacings of 10.4 and 5.2 Å, which we attri-

bute to $d(001)$ and $d(002)$ of tochilinite. However, the XRD patterns from our synthetic material were not of sufficient quality to enable determination of the unit cells of the two component layers. Further analysis was therefore confined to TEM studies.

EDX analyses of individual tochilinite crystals showed little variation of Fe, Mg, Al, and S levels. Analysis of oxygen was not included in the quantification calculation due to its low X-ray energy and reduced accuracy of determination. Figure 1 shows a TEM image which shows the typical appearance of the product: the small crystallites are of two distinct forms, plate-like and acicular, although neither form exceeds linear dimensions of a few micrometers. Higher magnification reveals the acicular form to be tubular, with those parts of the tube wall parallel to the beam exhibiting dark fringes (Fig. 2). By selecting tubes which were fortuitously oriented parallel with one of the microscope goniometer axes, we could confirm that they were complete cylinders, rather than scrolls, by rotating them up to ±45°, and the tube ends also appear to confirm the circular cross section of these tubes. The insides of the great majority of the tubes appeared to be empty or possibly filled with material of much lower density than the tube walls, although it is clearly impossible to confirm whether they are truly hollow by observations in projections such as these. At still higher magnifications (Fig. 3) the layering in the tube walls may be seen to be quite heavily distorted, although a layer repeat distance of about 10.4 Å is evident. Plate-like crystals viewed edge-on also showed this layer-pair spacing. Although the plate-like crystals seemed to be usually flat, we occasionally observed plates with "scrolled" edges (arrows in Fig. 1). Selected-area diffraction patterns were obtained from the larger plate-like and tubular crystallites. Figure 4 shows the variety of patterns which we observed, although it should be noted that many, and perhaps the majority of crystallites, even those which appear (in images) to be quite well formed, are in fact seen to be highly disordered when their diffraction patterns are examined. This is an ubiquitous problem when examining soft, layered and especially nanocrystalline materials such as these in the TEM. We have therefore only presented selected patterns where the relevant reflections are clearly resolved.

The most common pattern (Fig. 4a), from the plate-like material, was that of a double hexagonal-layer (or pseudohexagonal) type, isomorphous with patterns that we obtained from good-quality synthetic valleriite (4). Indeed, patterns from the two kinds of material can be superimposed perfectly. This pattern suggests individual (hexagonal) cell parameters of a_S = 3.7 Å and a_H = 3.0 Å for the sulfide and hydroxide layers respectively. It was necessary to search assiduously in order to find a crystallite which gave the previously reported tochilinite system of cells with a (pseudo)tetragonal sulfide layer (Fig. 4b). Here the cell parameters for the two layers are (tetragonal system, centered cell) a_S = 5.25 Å and (pseudo)hexagonal a_H = 3.1 Å, $b_S = b_H$ = 5.4 Å. These values agree with published data for tochilinite. There is no clear evidence (satellite reflections) in the pattern to indicate a semicommensurate (3 : 5) match of the two layer types in the **a** direction as found in the natural material.

From the tubular crystals we obtained patterns which showed the interlayer spacing to be approximately 10.4 Å (Fig. 4c), again in general accord with the published information for the two-layer form of tochilinite. This pattern also shows the streaking of the $hk0$ reflections indicative of a tubular crystal. Thus, we can confirm the synthesis of at least small quantities of this material, in intimate mixture with material of similar composition but having a structure isomorphous with valleriite. The fourth variety of diffraction pattern found is shown in Fig. 4d: this sort was quite common, and so far as we were able to determine, both the plate-like (from which this particular pattern was taken) and the tubular crystallites, as shown in Fig. 4e, generate similar reflections from their $\{hk0\}$ net planes. In Fig. 4d, the angle between adjacent S or H reflections on each ring is exactly 15°, with 24 spots in each ring. By inspection of Fig. 4b, which shows a pattern consistent with the previously reported tochilinite system of cells, it can be seen that the a_S^* and a_H^* vectors are separated by approximately 15° (for a tochilinite composed of perfect hexagonal H and tetragonal S layers the value is ideally 15°, the angle between octahedra and tetrahedra edges in projection). Hence, rather than a variant of the double-hexagonal valleriite-like Fig. 4a structure (in which case simple 120° twinning ("trilling") might be expected) it seems probable that the 15° patterns are from a variant of the "true" tochilinite structure in which mackinawite-like sulfide layer and brucite-like hydroxide layers are intensely disordered by rotation of integral multiples of ±45° (for the sulfide) and ±60° (hydroxide) about the c (layer-stacking) axis. It is not clear why ±45° disorder is observed in the sulfide layer. The 15° angle between the pairs of coplanar a_S and a_H vectors is thus found in each of the 24 possible positions. The $[MS_4]$ tetrahedra are hence oriented such that the c axis is parallel with tetrahedral two-fold axes. The absence of the mackinawite-like 110 reflections, present in Fig. 4b, in this pattern, further suggest that the sulfide layers comprise only fragments of the tetrahedral arrangement present in "true" tochilinite, and that order is, at best, short range.

The pattern of Fig. 4e, which was obtained from a thin tube, shows intervals of ~30° between most adjacent intense spots on the rings (although some intensity in the 15° positions is present on the sulfide rings), which is perhaps the situation expected from a pair of layers with hexagonal geometry, such as those of Fig. 4a. However,

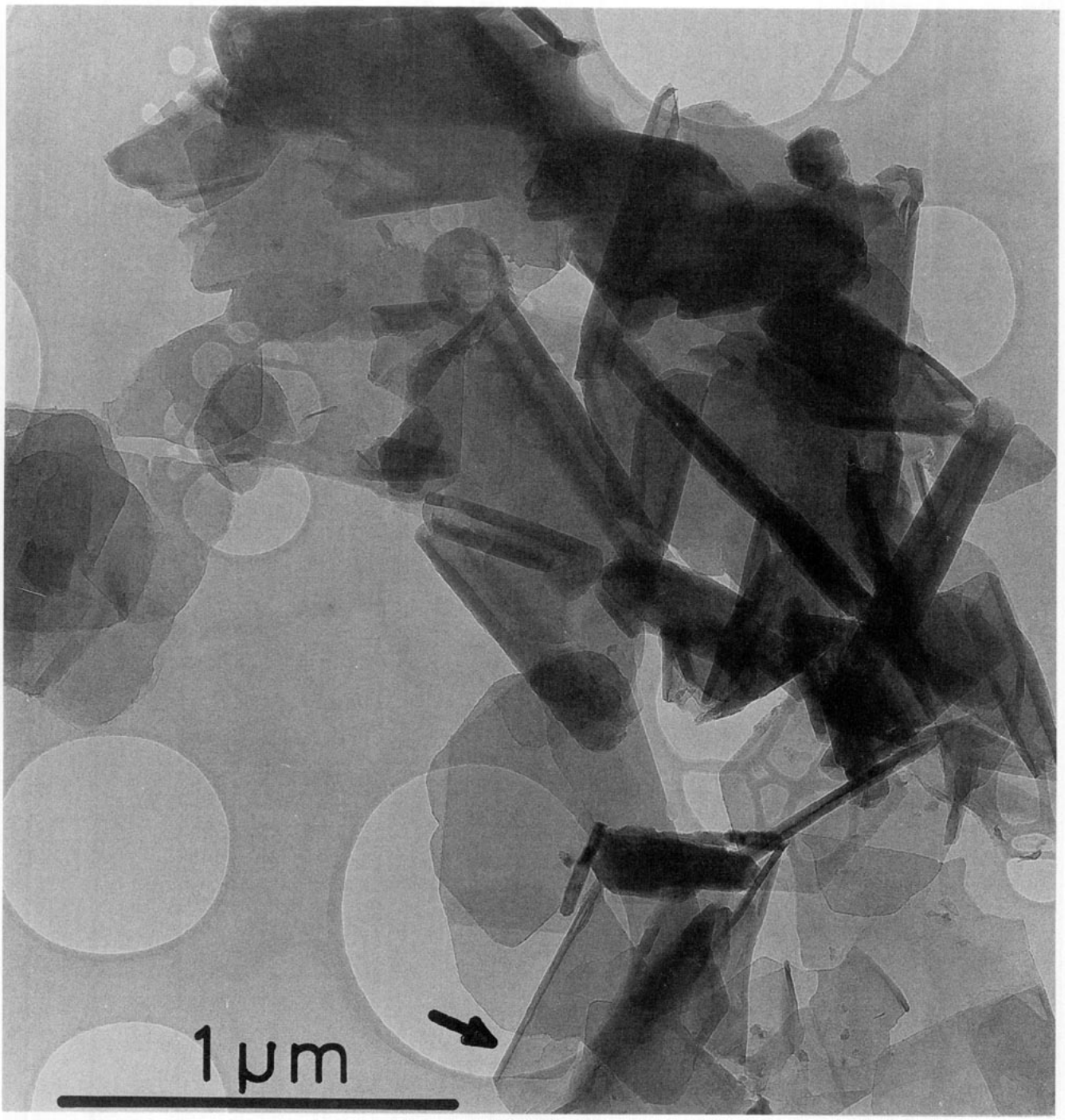

FIG. 1. Low magnification TEM image of the reaction product, showing a mixture of plate-like and tubular tochilinite crystals.

from these [001] zone-axis patterns it is not possible to determine whether extensive layers with tetrahedra/octahedra in the same relative orientation are rotated (a rotation-twinning arrangement) or instead the platelet layers consist of nanocrystalline "islands" which are misoriented from one to the next in a mosaic arrangement. The former structure might show some increase in the stacking-vector (~10.4 Å) if the layer-to-layer rotation is ordered, or else streaking of certain *hkl* reflections if disordered. However, such ordering is not necessarily a prerequisite and in these thin, poorly crystallized materials, might be difficult to observe. The layer spacing observed from a tubular crystal (Fig. 4c) was only that expected for a single layer-pair repeat. On the other hand,

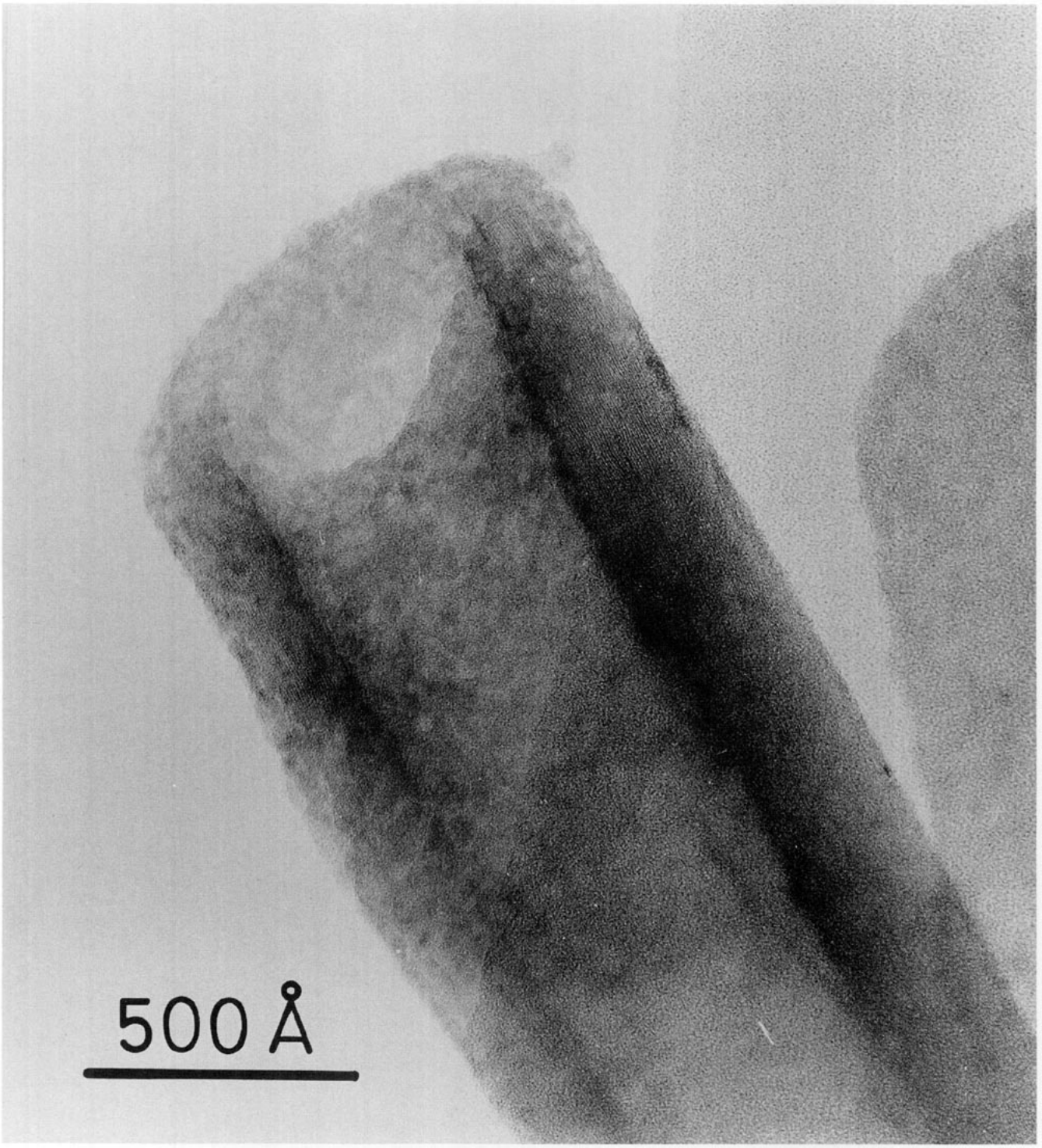

FIG. 2. High magnification TEM image of the end of one well-formed tube, tilted slightly to show the tube wall ends. The layering in the tube walls is visible where the beam is approximately parallel with the layers, as is the mottled, disordered appearance of the walls normal to the electron beam.

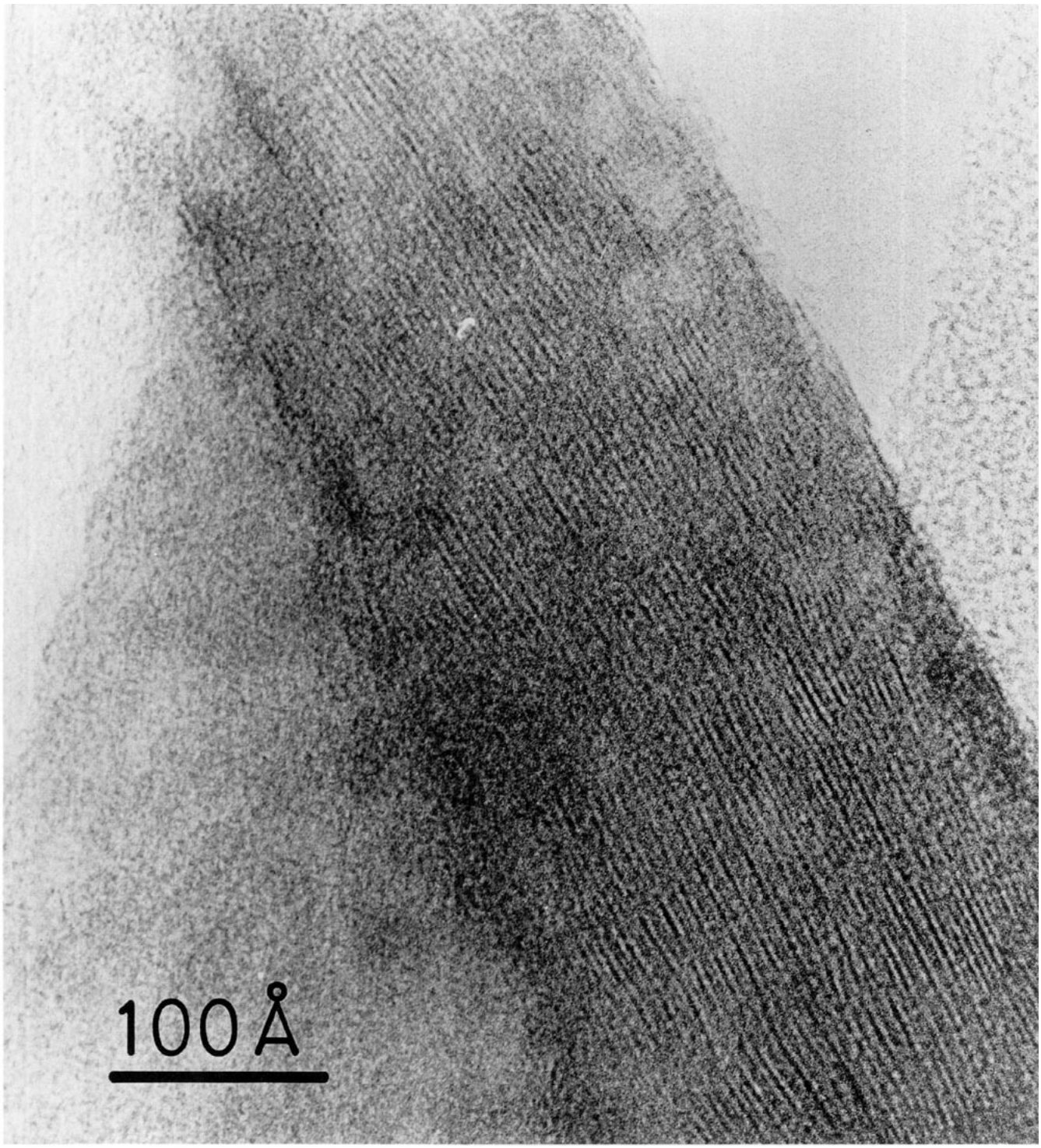

FIG. 3. Enlargement of part of the tube end shown in Fig. 2, to illustrate the individual, highly distorted layers in the structure. There are about twenty 10.4-Å layer-pair repeats in the wall structure. In the lower left of the figure, the "mottling" can be seen to consist of partly crystalline, better ordered islands, although only a few fringes at best are visible in these areas.

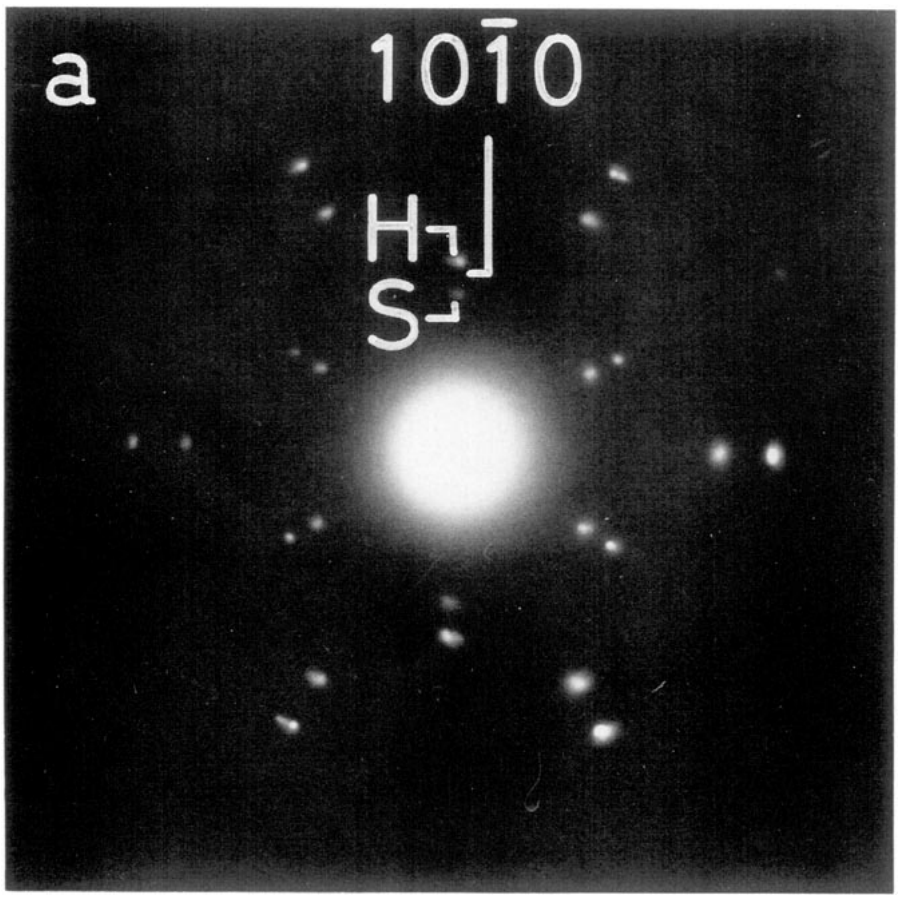

FIG. 4. (a) Selected area diffraction pattern (SAD) from a plate-like crystal showing the "valleriite-like" double-hexagonal symmetry. Two independent lattices are present corresponding to the sulfide (S) and hydroxide (H) layers. (b) SAD from the relatively rare plate-like form of the synthetic tochilinite, with the tetragonal S lattice. Reciprocal unit cells S and H are outlined. (c) SAD from a well-formed tube, showing strong 00*l* reflections arising from the layer repeat of ~10.4 Å. Other reflections are strongly steaked by the clyindrical morphology. The orientation of the tube axis is indicated by an arrow. (d) An example of the 15° rotation "twinning" commonly observed from plate-like crystals. Rings *p*, *s* are sulfide layer 100 and 110 reflections and *q*, *r* hydroxide layer 100 and 110 reflections respectively. Note the good order in the hydroxide layers but strong disorder in the sulfide layers. (e) A pattern from a thin tube, shows intervals of ~30° between adjacent groups of intense spots on the rings.

the complete absence of lattice fringes in the [001] images of the platelets and also, except for tiny "islands", in the tubes (Fig. 3) points towards a strongly disordered layer arrangement, perhaps supporting the mosaic structure. As was reported for the sulfide layers in our study of synthetic valleriite (4), the reflections from the sulfide layers of the present material were invariably the most highly disordered, by rotation of the a_S vector with respect to a_H. This is responsible for the "ring" plus "spot" appearance of the patterns such as Fig. 4e. This level of disorder in the sulfide layer is probably sufficient to preclude detailed observation of the origin of the 15° structure.

We obtained EDX point analyses from both plate-like and tubular forms of the product, and from these spectra obtained reliable Fe/S, Mg/Al, and (Mg + Al)/Fe ratios (Table 2). The oxygen analyses suggested H layer compositions of $M(OH)_{1.85}$ (tubes) and $M(OH)_{1.92}$ (plates), but since the oxygen K_α emission is close to the lower energy limit of the ultrathin window EDX system we elected to use the "ideal" value of $M(OH)_{2.0}$ for both forms in the calculations below. The analyses suggest the following compositions for the two forms of the crystallites:

$$\text{tubes: } 2Fe_{0.79}S \cdot 1.92[(Mg_{0.69}Al_{0.31})(OH)_2)]$$

$$\text{plates: } 2Fe_{0.71}S \cdot 1.64[(Mg_{0.70}Al_{0.30})(OH)_2)].$$

Thus, two forms have nearly the same $M(OH)_2$ layer composition but differ slightly in the Fe/S and the interlayer ratios. Assuming that the S is all present as S^{2-} and that the Mg and Al in the hydroxide layer are di- and trivalent, respectively, electroneutrality is maintained with an Fe oxidation state of about +3. The different interlayer composition ratios (k = 1.92 and 1.64) in the above formulations may reflect a real difference in the

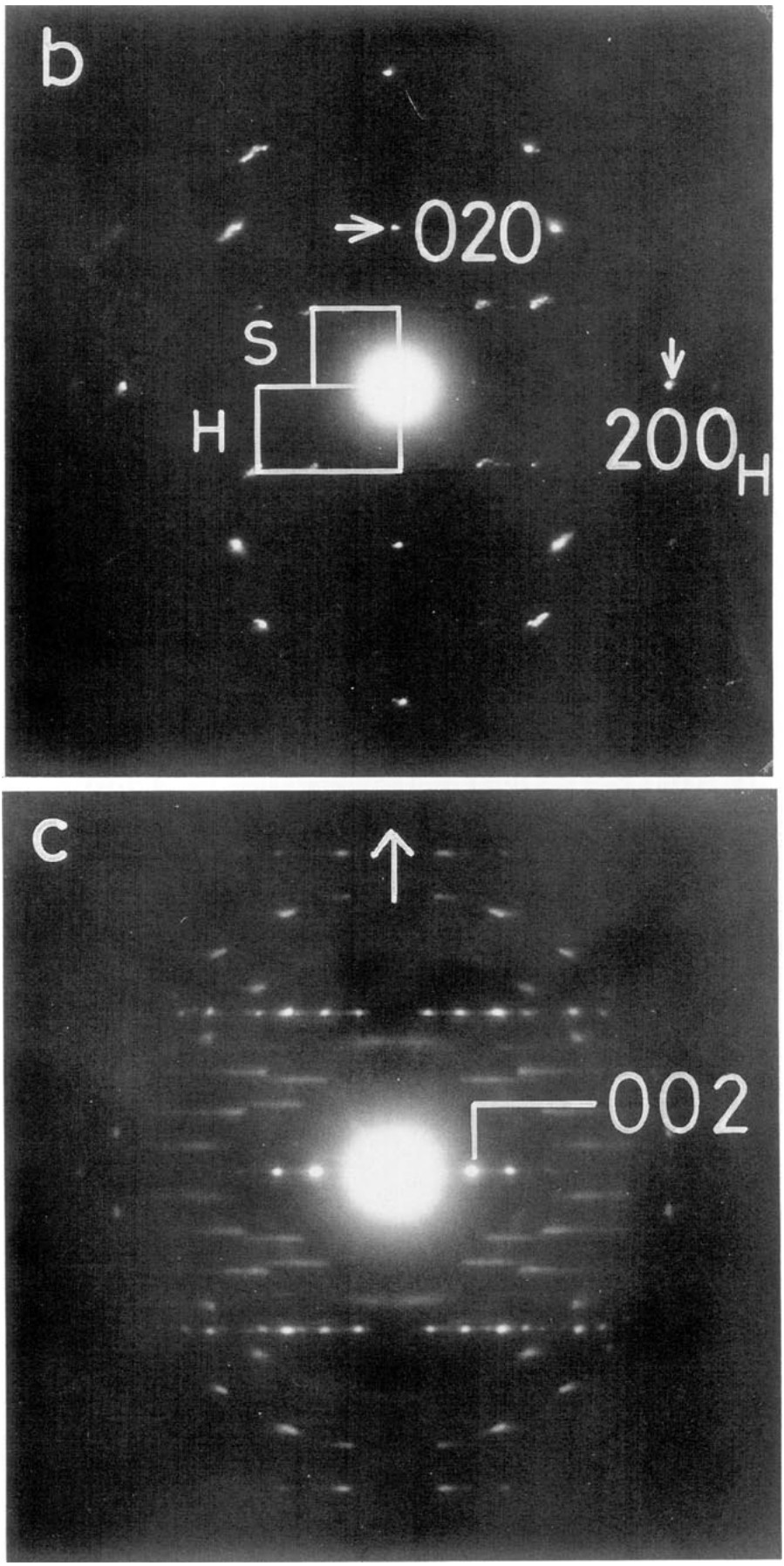

FIG. 4—*Continued*

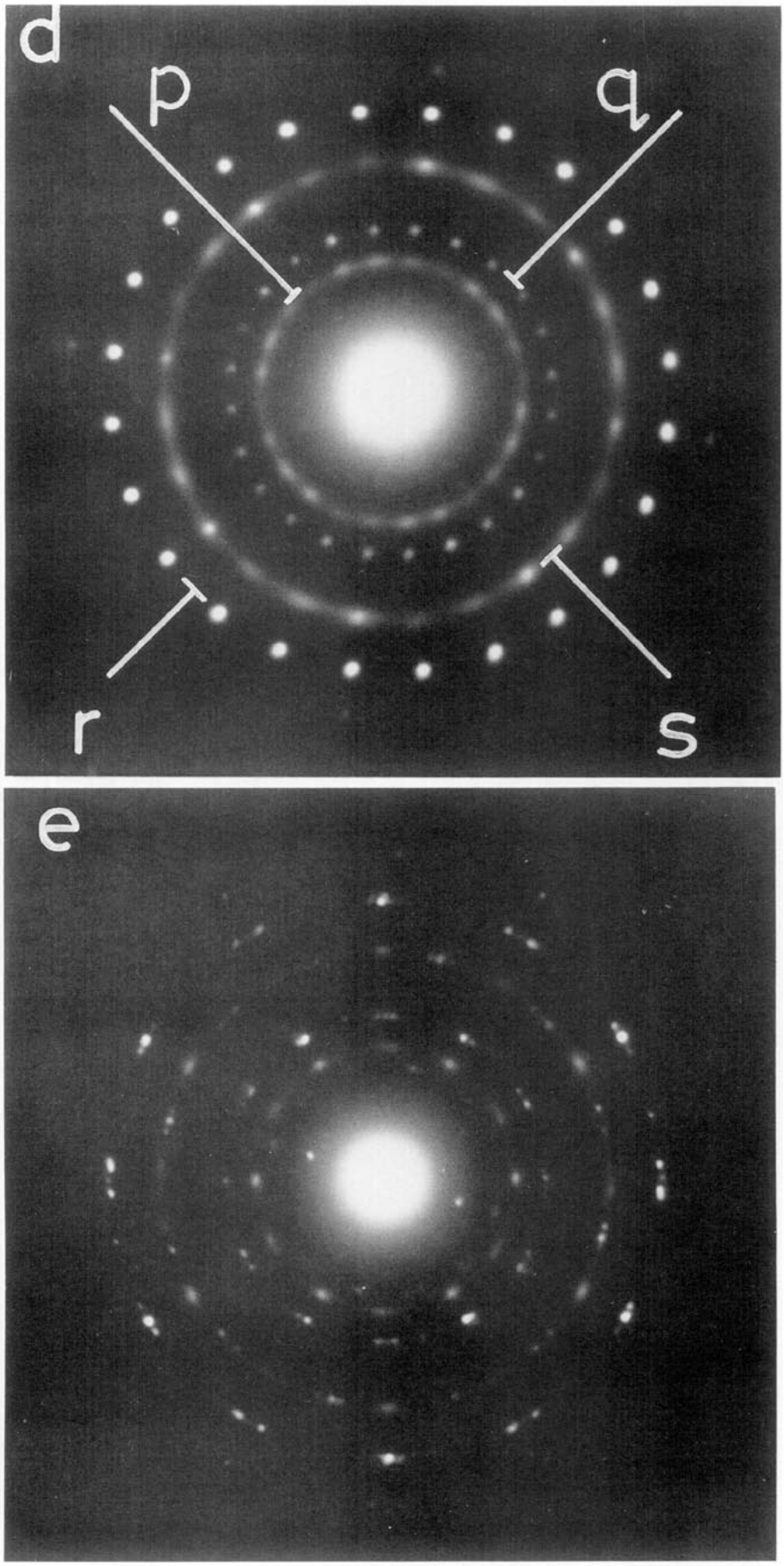

FIG. 4—*Continued*

TABLE 2
Elemental Ratios for Synthetic Tochilinites[a]

Ratio	Tube-like product[b]	Plate-like product[c]
Mg/Al	2.19	2.28
(Mg + Al)/Fe	1.22	1.16
Fe/S	0.79	0.71
O/(Mg + Al)	1.85	1.92

[a] From EDX analyses.
[b] Average of 8 analyses.
[c] Average of 6 analyses.

cell parameters of the component layers which determine this ratio (assuming that the layer stacking sequence is . . . S H S H . . .). But we consider that neither the EDX data nor the electron diffraction results are sufficiently accurate to unequivocally specify this structural parameter. However it is clear that the k values derived from EDX data in the present study are of the same magnitude as those which can be derived from the cell parameters ($k \approx 1.5$–1.7) and also those obtained from numerous elemental analyses of natural tochilinite samples (usually $k \approx 1.5$–2 in Table 1).

4. CONCLUSIONS

The present study has shown that a tochilinite-like phase can be synthesized hydrothermally from mixed sulfide/hydroxide gels of Fe/Mg/Al. The material has a structure consisting of negatively charged layers of FeS alternating in an incommensurate manner with hexagonal, positively charged, hydrotalcite layers, with an interlayer repeat spacing of about 10.4 Å. The disordered and nanocrystalline nature of the material poses difficulties both in characterization and in adequate description. Study by a combination of powder XRD, high resolution TEM, EDX, and SAD techniques enables four different structural modifications to be distinguished, one isostructural with valleriite and the others with the previously reported forms of natural tochilinite, plate-like and tubular. The plate-like form existed with two different degrees of rotational disorder within the sample. The plate-like and tubular forms differed slightly but significantly in elemental composition. Although all four modifications showed considerable disorder, the nature of the disorder could be rationalized in terms of the above structural model.

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REFERENCES

1. N. I. Organova, V. A. Drits, and A. L. Dmitrik, *Sov. Phys. Crystallogr.* **17,** 667 (1973).
2. M. E. Zolensky and I. D. R. Mackinnon, *Am. Mineral.* **71,** 1201 (1986).
3. H. T. Evans and R. Allman, *Z. Kristallogr.* **127,** 73 (1968).
4. A. E. Hughes, G. A. Kakos, T. W. Turney, and T. B. Williams, *J. Solid State Chem.* **104,** 422 (1993).
5. A. B. Makeev, T. L. Evstifneeva, N. V. Troneva, L. N. Vyalsov, A. I. Gosschkov, and N. V. Trubkin, *Mineral. Zh.* **6**(5), 91 (1986).
6. M. Huhma, Y. Vuorelainen, T. A. Hakli, and H. Papunen, *Bull. Geol. Soc. Finl.* **45,** 103 (1973).
7. D. J. Barber, A. Bourdillon, and L. A. Freeman, *Nature (London)* **305,** 295 (1983).
8. N. I. Organova, V. A. Drits, and A. L. Dmitrik, *Am. Mineral.* **59,** 190 (1974).
9. K. Tomeoka and P. R. Buseck, *Nature (London)* **306,** 354 (1983).
10. I. D. R. Mackinnon and M. E. Zolensky, *Nature (London)* **309,** 240 (1984).
11. E. Makovicky and B. G. Hyde, *Struct. Bonding* **46,** 103 (1981).
12. N. I. Organova, V. A. Drits, and A. L. Dmitrik, *Sov. Phys. Crystallogr.* **18,** 606 (1974).
13. N. I. Organova, V. A. Drits, and A. L. Dmitrik, *Kristallografiya* **17,** 761 (1972).
14. D. C. Harris and D. J. Vaughan, *Am. Mineral.* **57,** 1037 (1972).
15. J. L. Jambor, *Bull. Geol. Surv. Can.* **65,** Paper 76-1B (1976).
16. Y. Muramatsu and M. Nambu, *Ganseki Kobutsu Kosho Gakkaishi* **75,** 377 (1980).
17. N. I. Organova, A. J. Gorshkov, Y. P. Dikov, V. A. Kul'bachinskii, I. P. Laputina, A. V. Svivtov, S. F. Sluzenikin, and A. I. Panomarenkov, *Izv. Akad. Nauk SSSR Ser. Geol.* **6,** 84 (1988).
18. Z. Johan, *Neues Jahrb. Mineral. Monatsh.* **6,** 269 (1990).