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MINERALOGICAL APPLICATIONS

OF ELECTRON DIFFRACTION

II. RESULTS OF STUDIES OF SOME VANADIUM

MINERALS OF THE COLORADO PLATEAU

By Malcolm Ross

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Trace Elements Investigations Report 719

UNITED STATES DEPARTMENT OF THE INTERIOR  
GEOLOGICAL SURVEY

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Geology and Mineralogy

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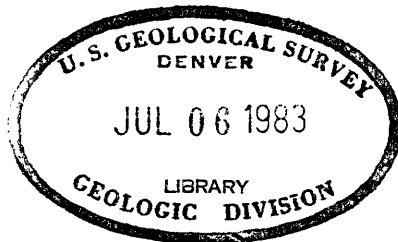
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May 1958



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## MINERALOGICAL APPLICATIONS OF ELECTRON DIFFRACTION

## II. RESULTS OF STUDIES OF SOME VANADIUM

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By Malcolm Ross

## ABSTRACT

A method of obtaining precise unit-cell data from oriented electron diffraction powder patterns is described. Partial unit-cell data obtained from such patterns and a description of the crystal habit are given for the following minerals: hewettite ( $\text{CaV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O}$ ), barnesite ( $\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$ ), a new hydrated calcium vanadyl vanadate, corvusite ( $\text{V}_2\text{O}_4 \cdot 6\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ ), a "corvusite-like" mineral ( $\text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5 \cdot \underline{x}\text{H}_2\text{O}$ ), fernandinite ( $\text{CaO} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ ), navajoite ( $\text{V}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ ), a "corvusite-like" mineral associated with navajoite, steigerite ( $\text{Al}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot 6\frac{1}{2}\text{H}_2\text{O}$ ), fervanite ( $\text{Fe}_4\text{V}_4\text{O}_{16} \cdot 5\text{H}_2\text{O}$ ), and simplotite ( $\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$ ). For many of these minerals the unit-cell data are new. Structural relations between several of these minerals are indicated.

## INTRODUCTION

A large number of fine-grained minerals for which there are no unit-cell data have been described in the literature. Such minerals, particularly those which have layer structures, are not well suited for single crystal X-ray diffraction analysis. On the other hand, the electron diffraction method is better suited for analysis of many fine-grained minerals, particularly those which possess perfect cleavage.

In this paper (Part II) the techniques of interpreting single crystal electron diffraction patterns described elsewhere (Ross and Christ, 1958, hereafter referred to as Part I) have been used in the determination of partial unit-cell data for fine-grained vanadium minerals from the Colorado Plateau. A description of the crystal habit as revealed by electron micrographs is included.

I am especially indebted to Alice D. Weeks for providing a large number of the mineral specimens studied and for her valuable advice concerning their mineralogy. I should also like to thank C. L. Christ and E. J. Dwornik for their advice on various problems, M. E. Thompson for permission to publish data on a new calcium vanadate, and Richard L. Hunt for assistance with some of the experimental work. This work is part of a program being conducted by the U. S. Geological Survey on behalf of the Division of Research of the U. S. Atomic Energy Commission.



## INTERPRETATION OF ELECTRON DIFFRACTION PATTERNS OF ORIENTED POLYCRYSTALLINE MATERIALS

Crystals which possess perfect cleavage tend to orient on the specimen mount so that the cleavage face is parallel to the substrate and with all possible orientations of the crystals around the normal to the cleavage face. The type of crystallographic data that can be obtained from the electron diffraction powder patterns of thin crystals oriented in this way will depend upon the plane of orientation and the crystal system of the material in question (Part I, Table 4). For example, powder patterns of thin colemanite crystals oriented on (010) will give directly  $d_{100}$  and  $d_{001}$  whereas powder patterns of thin  $KClO_3$  crystals oriented on (001) will give directly  $a$  and  $b$ . The theory appropriate to these conclusions is given in Part I.

As the crystals contributing to an oriented powder pattern are very small, the intensity of the diffracted beam will decrease appreciably with slight deviations of the crystal face from the horizontal. As a result the rings are usually sharp and ideal for precise measurement. If a means can be found to index the powder patterns of oriented materials, measurement of the patterns will yield much more accurate unit-cell data than those obtained from the measurement of spot patterns.

Indexing the oriented powder pattern is fairly simple if a photograph can be obtained showing a single crystal pattern superimposed on rings. This type of pattern is readily obtained when a large crystal and a large number of small crystals, oriented randomly in the plane of the substrate, lie in the path of the electron beam.

An example of this type of diffraction pattern may be seen in figure 5. An oriented powder pattern will, in general, show rings (usually weak) that cannot be indexed on the basis of the superimposed spot pattern. Such "extra" rings usually appear because additional reciprocal lattice rods are brought into the sphere of reflection by the incompletely oriented crystals.

#### PREPARATION AND EXAMINATION OF SAMPLES

The vanadium minerals examined in this study have the following characteristics: fine-grained nature; platy, fibrous, or lathlike habit; perfect pinacoidal cleavage and probable layer structure. All the minerals studied tend to orient with a cleavage face parallel to the specimen mount, the "thin direction" of the crystal being parallel to the electron beam. The samples were prepared for examination by grinding lightly in distilled water, placing a droplet of the dispersed material on a collodion mount, and then drying in air. Electron micrographs and SAD (Selected Area Diffraction) spot patterns were usually obtained prior to examination with the electron diffraction unit. External aluminum or  $\beta$ -tin standards were used for most EDU (Electron Diffraction Unit) patterns. A description of the crystal habit as revealed by electron micrographs is given for each mineral. The crystallographic orientation of the minerals is obtained by comparing the relative orientations of the electron micrograph and SAD spot patterns of a single crystal.

The high vacuum (about  $10^{-5}$  cm Hg) in the electron microscope and diffraction unit offers a severe environment for the analysis of many minerals. The heating effect of the electron beam at its highest intensity (at cross-over) can be tremendous, fusing such stable materials as

tourmaline (Barnes, 1950, p. 410) and  $\text{TiO}_2$  (Watson, 1948, p. 718). This heating effect is dependent upon the thickness and density of the sample. Dense, thick particles of a given material are much more readily fused than thin flakes or plates of the same material. Few materials are stable enough to resist alteration on destruction when the beam is at the highest intensity. On the other hand, very unstable materials such as gypsum have been successfully examined at the lower beam intensities with the electron microscope or diffraction unit. The assumption that these instruments are "furnaces" is therefore misleading, for a skilled operator can prepare and examine specimens of many unstable materials in essentially their original state.

Minerals that contain interstitial water between the structural sheets are dehydrated to some extent by the vacuum of the electron microscope and electron diffraction unit. This water is very loosely held by such minerals. Although dehydration does not alter the basic layer structure, it does, commonly, change the dimensions of the crystal in a direction normal to the sheets. Minerals that readily lose interstitial water include the montmorillonite clay minerals, autunite  $[\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 10\text{-}12\text{H}_2\text{O}]$ , tyuyamunite  $[\text{Ca}(\text{UO}_2)_2\text{V}_2\text{O}_8 \cdot 10\text{H}_2\text{O}]$ , carnotite  $[\text{K}_2(\text{UO}_2)_2\text{V}_2\text{O}_8 \cdot 3\text{H}_2\text{O}]$ , and hewettite  $(\text{CaV}_6\text{O}_{16} \cdot 9\text{H}_2\text{O})$ . Most of the minerals examined in this study contain interstitial water.

Minerals that contain water as an integral part of the structure will, upon dehydration, show a complete change in structure. Such transformations have often been observed in the electron microscope and diffraction unit. For example, gypsum has been observed inverting to anhydrate as the intensity of the electron beam is increased.

## EVALUATION OF UNIT-CELL CONSTANTS FROM EDU POWDER PATTERNS

EDU spot patterns superimposed on rings were obtained from all minerals examined in this study. The rings were indexed on the basis of these composite patterns, the sharpest higher order rings being measured to give the unit-cell data. The relation

$$\underline{d}_x \approx D_s \underline{d}_s / D_x$$

was used to calculate the approximate direct lattice spacings (within 0.2 percent). If the precision of measurement is less than 0.2 percent the approximate values of  $\underline{d}_x$  are corrected by multiplying by the proper value of the factor  $(\cos 2 \theta_s) / (\cos 2 \theta_x \cos \theta_s)$ . The value of this factor for each direct lattice spacing is found on the graph shown in Part I, figure 9.

A measuring microscope was used to measure the powder patterns. When more than one powder pattern was used to determine the unit-cell data, the precision of the determination is given. This value includes the maximum and minimum values of the lattice constant as obtained from several measurements.

As the spot and powder patterns give only two dimensions of the reciprocal lattice, no assignment to a crystal system is made. The following conventions are used in designating the unit-cell constants unless some other crystallographic orientation has been assigned from single crystal X-ray study:

- 1) If the spot pattern shows two planes of symmetry, the pattern is assumed to represent a projection of the  $hk0$  reciprocal net. The largest cell constant is taken as  $\underline{a}$ . By symmetry  $\gamma = 90^\circ$ .

- 2) If the spot pattern shows only a center of symmetry, the pattern is assumed to represent a projection of  $h0l$  reciprocal net. A primitive cell with the smallest  $\beta$  angle is chosen (unless the presence of "forbidden reflections" indicate otherwise) with  $\underline{a} > \underline{c}$ .

An attempt is made to predict the systematic absences of reflections by examination of the spot pattern of crystals of varying thicknesses.

#### MINERALOGIC DATA

##### Hewettite and barnesite

Hewettite and metahewettite, of the same composition except for water content ( $\text{CaV}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$ ), were first described by Hillebrand, Merwin, and Wright (1914). These minerals are found as nodular aggregates and coatings of fibers, elongate  $[010]$ , and are deep red in color. Hewettite readily loses water and changes from the  $9\text{H}_2\text{O}$  hydrate to a lower hydrate with  $3\text{H}_2\text{O}$ . Barnes (1955) made dehydration studies of the hewettite minerals and gave evidence that hewettite and metahewettite are structurally identical. He finds that hewettite exists in at least three hydrated forms with  $3\text{H}_2\text{O}$ ,  $6\text{H}_2\text{O}$  (probably), and  $9\text{H}_2\text{O}$ . Barnes (1955, p. 690) suggests that the name metahewettite is unnecessary unless it be retained to designate one of the hydrate phases. Alice D. Weeks suggests (personal communication) that the name metahewettite be used to designate the common  $3\text{H}_2\text{O}$  hydrate phase.

Electron micrographs and SAD patterns were made from an analyzed hewettite collected by Nancy G. Ryan from the Hummer mine, Jo Dandy group, Montrose County, Colo. The electron micrographs show that the crystals are well developed laths elongated  $[010]$ , and flattened  $\{001\}$ . An X-ray

powder pattern of the material showed that only hewettite was present. Measurements of six EDU powder patterns of the hewettite from the Hummer mine give the following results:  $\underline{a} = 12.23 \pm 0.03$  A and  $\underline{b} = 3.605 \pm 0.005$  A ( $\gamma = 90^\circ$ ).

A second sample of hewettite collected by B. N. Webber and L. B. Riley from the Cactus Rat mine, Thompson district, Grand County, Utah, gives electron micrographs and electron diffraction patterns identical to those of the Hummer mine material. The spectrographic analysis of a 10-mg split of the sample used for this study shows:  $> 10\%$  V; 1 -  $10\%$  Ca, Si; 0.1 -  $1\%$  Na, Al, Fe (Katherine Valentine, analyst). An X-ray powder pattern, however, indicates that a small amount of barnesite is in the sample. Measurement of six EDU powder patterns of this material gives the results:  $\underline{a} = 12.22 \pm 0.02$  A and  $\underline{b} = 3.605 \pm 0.003$  A ( $\gamma = 90^\circ$ ). Figure 1 shows a typical hewettite SAD spot pattern.

Barnesite,  $\text{Na}_2\text{V}_6\text{O}_{18} \cdot 3\text{H}_2\text{O}$ , a sodium analog of hewettite described by A. D. Weeks, M. E. Thompson, and A. M. Sherwood (written communication) has the same habit as hewettite and is deep red changing to brownish-red on exposure to air. Barnes and Qurashi (1952), and Barnes (1955) by X-ray analysis found barnesite from Cactus Rat mine, Grand County, Utah, (Harvard no. 98019), to be monoclinic with  $\underline{a} = 12.18 \pm 0.02$  A,  $\underline{b} = 3.614 \pm 0.005$  A,  $\underline{c} = 7.80 \pm 0.03$  A and  $\beta = 95^\circ 0' \pm 20'$ .

Electron micrographs and electron diffraction patterns of barnesite collected by Alice D. Weeks from the Cactus Rat mine, Thompson district, Grand County, Utah, are nearly identical to those of hewettite. Measurement of six EDU powder patterns gives a cell with  $\underline{a} = 12.17 \pm 0.02$  A and  $\underline{b} = 3.604 \pm 0.005$  A ( $\gamma = 90^\circ$ ).

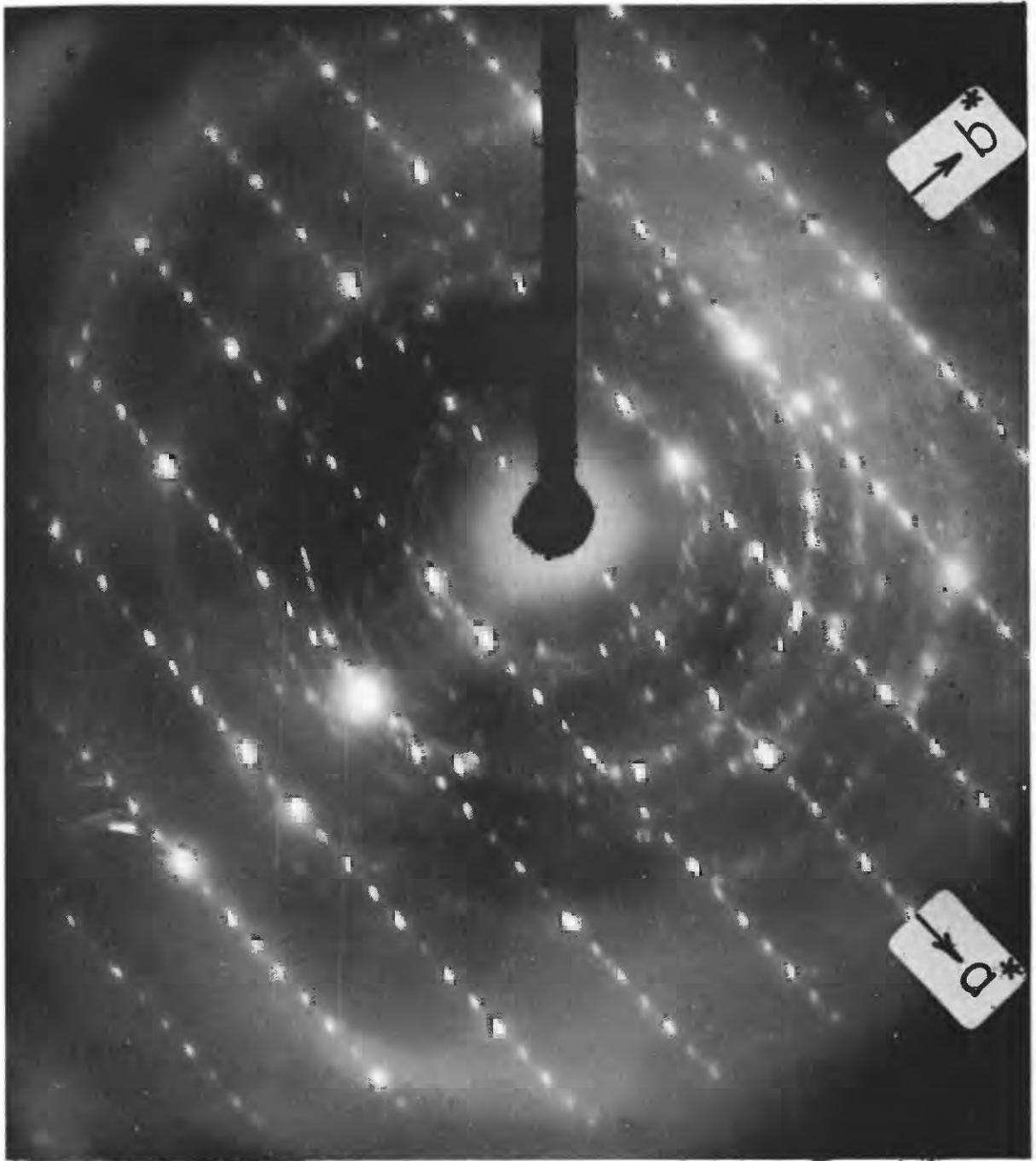


Figure 1.--SAD spot pattern of hewettite.

The similarity between the spacings and intensities of the spot patterns of hewettite and barnesite indicates that the two minerals have similar structures as projected on the a-b plane. The result of the hewettite and barnesite study is summarized in table 1.

---

Table 1.--Electron diffraction and X-ray unit-cell data for hewettite and barnesite

Hewettite	Hewettite <sup>1/</sup>	Barnesite
Hummer mine	Cactus Rat mine	Cactus Rat mine
$\text{CaV}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$	$\text{CaV}_6\text{O}_{16} \cdot n\text{H}_2\text{O}$	$\text{Na}_2\text{V}_6\text{O}_{16} \cdot 3\text{H}_2\text{O}$
Electron diffraction data	Electron diffraction data	Electron diffraction data
$\underline{a} = 12.23 \pm 0.03 \text{ \AA}$	$\underline{a} = 12.22 \pm 0.02 \text{ \AA}$	$\underline{a} = 12.17 \pm 0.02 \text{ \AA}$
$\underline{b} = 3.605 \pm 0.005 \text{ \AA}$	$\underline{b} = 3.605 \pm 0.003 \text{ \AA}$	$\underline{b} = 3.604 \pm 0.005 \text{ \AA}$
$\gamma = 90^\circ$	$\gamma = 90^\circ$	$\gamma = 90^\circ$
		X-ray data <sup>2/</sup> monoclinic
		$\underline{a} = 12.18 \pm 0.02 \text{ \AA}$
		$\underline{b} = 3.614 \pm 0.005 \text{ \AA}$
		$\underline{c} = 7.80 \pm 0.03 \text{ \AA}$
		$\beta = 95^\circ 0' \pm 20'$

Space group:  $\underline{P2}-(\underline{C}_2^1)$  (probable)

<sup>1/</sup> A small amount of barnesite is present in the sample.

<sup>2/</sup> Barnes and Qurashi (1952) and Barnes (1955).



### A new hydrated calcium vanadyl vanadate

A mineral collected by D. P. Elston from the J. J. mine, Bull Canyon mining district, Montrose County, Colo., and to be described by M. E. Thompson appears to be a new calcium vanadyl vanadate. Independently, Alice D. Weeks (personal communication, 1956) found a mineral from the East Carrizo mines, San Juan County, New Mexico, which gives the same characteristic X-ray powder pattern as Miss Thompson's material. The chemical analyses of the vanadates from the East Carrizo mines and the J. J. mine are essentially identical.

Electron micrographs show the sample from the J. J. mine is composed of thin angular flakes and well-developed, sometimes terminated, laths elongated  $[010]$  and flattened  $\{001\}$ . Figure 2 shows an electron micrograph of one of the terminated crystals. Measurement of three EDU powder patterns gives the following results:  $a = 12.18 \pm 0.01$  A and  $b = 3.627 \pm 0.003$  A ( $\gamma = 90^\circ$ ). The intensities of the spots are very close to those of the hewettite patterns. One SAD spot pattern shows very weak spots which appear to triple the cell in the  $b$  direction. As this was the only pattern of many examined that shows such spots, it is difficult to decide on their significance.

Electron micrographs (Fig. 3) show that the sample from the East Carrizo mines is composed of irregularly shaped flakes and long, narrow laths or fibers elongated  $[010]$  and flattened  $\{001\}$ . Spot patterns of this sample are essentially identical to the typical spot patterns of the sample from the J. J. mine. Measurement of five EDU powder patterns gives the following unit-cell data:  $a = 12.15 \pm 0.01$  A and  $b = 3.612 \pm 0.004$  A ( $\gamma = 90^\circ$ ).

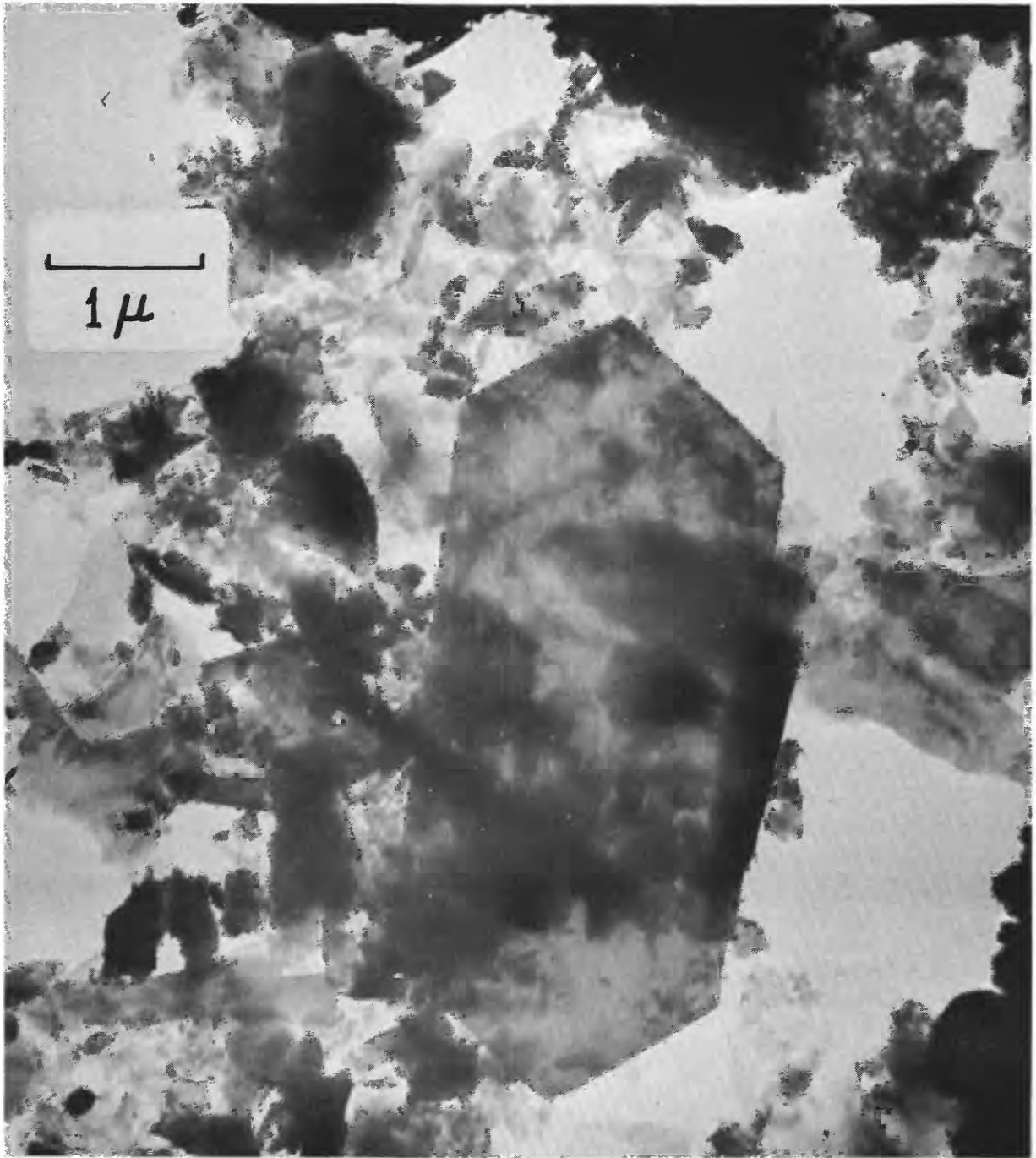


Figure 2.--Electron micrograph of a new hydrated calcium vanadyl vanadate from the J. J. mine.

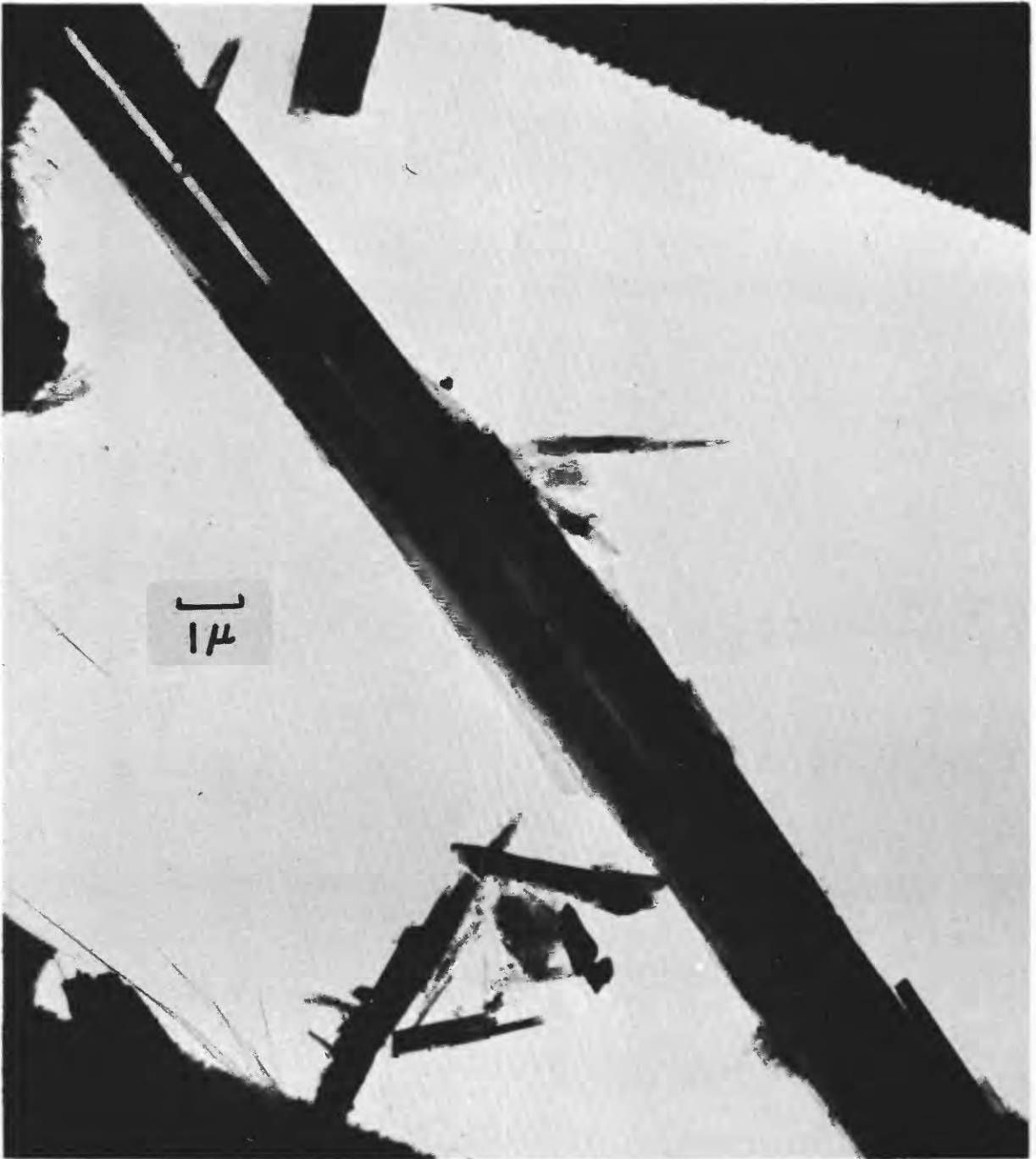


Figure 3.--Electron micrograph of a fiber of a new hydrated calcium vanadyl vanadate from the East Carrizo mines.

The results of the study on this new calcium vanadyl vanadate are given in table 2.

The similarity between the spacings and intensities of the spot patterns of both samples of this new vanadate to those of hewettite indicates that the two minerals have similar structures as projected on the a-b plane.

Table 2.--Electron diffraction unit-cell data for two samples  
of a new calcium vanadyl vanadate

<u>J. J. mine<sup>1/</sup></u>	<u>East Carrizo mines</u>
<u>a</u> = 12.18 ± 0.01 A	<u>a</u> = 12.15 ± 0.01 A
<u>b</u> = 3.627 ± 0.003 A	<u>b</u> = 3.612 ± 0.004 A
$\gamma$ = 90°	$\gamma$ = 90°

1/ One SAD spot pattern showed weak spots which appear to make b = 3 x 3.627 A.

#### Fernandinite, corvusite, and the "corvusite-like" minerals

A number of vanadium (IV, V) minerals have been loosely described as corvusite or "corvusite-like" and are characterized by their massive or sometimes fibrous appearance and dark-brown, blue-black, or dark-green color. Fernandinite is probably closely related to this group of minerals.

Schaller (1915) described fernandinite from Minasragra, Peru, as a massive dull green mineral with a probable formula of  $\text{CaO} \cdot \text{V}_2\text{O}_4 \cdot 5\text{V}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ .

Electron micrographs of the type fernandinite from Minasragra, Peru, (USNM R-5706) disclose angular plates or flakes flattened {001}. Measurement of four EDU powder patterns gives a cell with a = 11.69 ± 0.04 A

and  $\underline{b} = 3.674 \pm 0.004$  A ( $\gamma = 90^\circ$ ). The spot patterns of fernandinite show only those reflections for which  $h + k = 2n$ . Due to the thinness of the fernandinite crystals "forbidden reflections" (where  $h + k = 2n + 1$ ) should appear because of projection of reciprocal lattice rods of the upper levels ( $\ell = 1, 2, 3$ , etc.) into the sphere of reflection. The fact that "forbidden reflections" do not appear probably indicates that reciprocal lattice points for which  $h + k = 2n + 1$  are missing in the upper  $\ell$  levels. If such reciprocal lattice points are missing, fernandinite has a C-centered cell.

Henderson and Hess (1933) proposed the formula  $V_2O_4.6V_2O_5.xH_2O$  for corvusite. Their original material was a brown massive sample (USNM 96807) and a bluish-black massive sample (USNM 96806).

Electron micrographs of the brown corvusite (USNM 96807) show that it is a poorly crystallized, very fine grained material with an average particle size of less than 0.2 microns. The individual particles are irregularly shaped flakes. Spot patterns show only those reflections for which  $h + k = 2n$  indicating a probable C-centered cell. Measurement of six EDU powder patterns gives the following unit-cell data:

$\underline{a} = 11.6 \pm 0.1$  A and  $\underline{b} = 3.65 \pm 0.01$  A ( $\gamma = 90^\circ$ ).

Weeks and Thompson (1954) studied "corvusite-like" minerals from several localities and found them commonly massive and blue-black to greenish black in color. An excellent sample of a "corvusite-like" mineral studied by Weeks and Thompson (personal communication) was collected by Daniel Milton from Incline No. 2, Monument No. 2 mine, Apache County, Ariz. It is a fibrous blue-black material with a probable formula of  $V_2O_4.5V_2O_5.xH_2O$ . Electron micrographs show that the crystals of this mineral are long, well-developed laths, elongated [010] and flattened {001},

similar to well-crystallized hewettite. Spot patterns show only those reflections for which  $h + k = 2n$  indicating a probable  $C$ -centered cell.

Measurement of six EDU powder patterns gives the following results:

$\underline{a} = 11.69 \pm 0.03 \text{ \AA}$  and  $\underline{b} = 3.662 \pm 0.008 \text{ \AA}$  ( $\gamma = 90^\circ$ ).

The similarity between the spacings and intensities of the spot patterns of fernandinite, corvusite, and the "corvusite-like" mineral indicates that they have similar structures as projected on the  $\underline{a-b}$  plane. Weeks and Thompson (1954, p. 47) have noted that the X-ray powder patterns of fernandinite and corvusite are similar. The chemical analyses and diffraction data for these minerals are given in table 3.

Table 3.--Chemical analyses and electron diffraction unit-cell data  
for fernandinite, corvusite, and a "corvusite-like" mineral

Brown corvusite <sup>1/</sup> (USNM 96807)		Blue-black "corvusite-like" mineral <sup>2/</sup> Monument no. 2 mine, Arizona		Fernandinite <sup>3/</sup> Minasragra, Peru	
$V_2O_4 \cdot 6V_2O_5 \cdot xH_2O$		$V_2O_4 \cdot 5V_2O_5 \cdot xH_2O$		$CaO \cdot V_2O_4 \cdot 5V_2O_5 \cdot 14H_2O$	
CaO	0.40	CaO	2.5	CaO	3.83
Fe <sub>2</sub> O <sub>3</sub>	12.20	Fe <sub>2</sub> O <sub>3</sub>	2.3	Fe <sub>2</sub> O <sub>3</sub>	0.90
V <sub>2</sub> O <sub>4</sub>	7.62	V <sub>2</sub> O <sub>4</sub>	13.3	V <sub>2</sub> O <sub>4</sub>	11.63
V <sub>2</sub> O <sub>5</sub>	50.68	V <sub>2</sub> O <sub>5</sub>	68.1	V <sub>2</sub> O <sub>5</sub>	63.33
H <sub>2</sub> O	15.83	H <sub>2</sub> O	11.4	H <sub>2</sub> O	18.07
K <sub>2</sub> O	2.15	K <sub>2</sub> O, Na <sub>2</sub> O, Al <sub>2</sub> O <sub>3</sub>	1.2	K <sub>2</sub> O	0.59
Na <sub>2</sub> O	1.24	SiO <sub>2</sub> + insol	0.7	MgO	0.07
MgO	2.07	Total	99.5	MoO <sub>3</sub>	1.58
MoO <sub>3</sub>	0.28	H <sub>2</sub> O (-)	6.8	Total	100.00
UO <sub>3</sub>	2.94				
Sol. SiO <sub>2</sub>	4.21				
Total	99.62				
$a = 11.6 \pm 0.1 \text{ \AA}$		$a = 11.69 \pm 0.03 \text{ \AA}$		$a = 11.69 \pm 0.04 \text{ \AA}$	
$b = 3.65 \pm 0.01 \text{ \AA}$		$b = 3.662 \pm 0.008 \text{ \AA}$		$b = 3.674 \pm 0.004 \text{ \AA}$	
$\gamma = 90^\circ$		$\gamma = 90^\circ$		$\gamma = 90^\circ$	
hkℓ: $h + k = 2n$		hkℓ: $h + k = 2n$		hkℓ: $h + k = 2n$	

<sup>1/</sup> Henderson and Hess (1933, p. 201). E. P. Henderson, analyst, recalculated after deducting insoluble.

<sup>2/</sup> Robert Meyrowitz, analyst, U. S. Geological Survey.

<sup>3/</sup> Palache, Berman, and Frondel (1951, p. 1062). W. T. Schaller, analyst, recalculated to 100 after deducting insoluble.

## Navajoite

Navajoite, described by Weeks, Thompson, and Sherwood (1955) as a hydrated vanadium pentoxide, is a dark brown, soft, fibrous mineral similar to hewettite in habit.

Chemical analysis of navajoite by A. M. Sherwood shows:

V <sub>2</sub> O <sub>5</sub>	71.68%
V <sub>2</sub> O <sub>4</sub>	3.08
Fe <sub>2</sub> O <sub>3</sub>	3.58
SiO <sub>2</sub>	1.20
CaO	0.22
H <sub>2</sub> O	20.30
Total	<u>100.06</u>

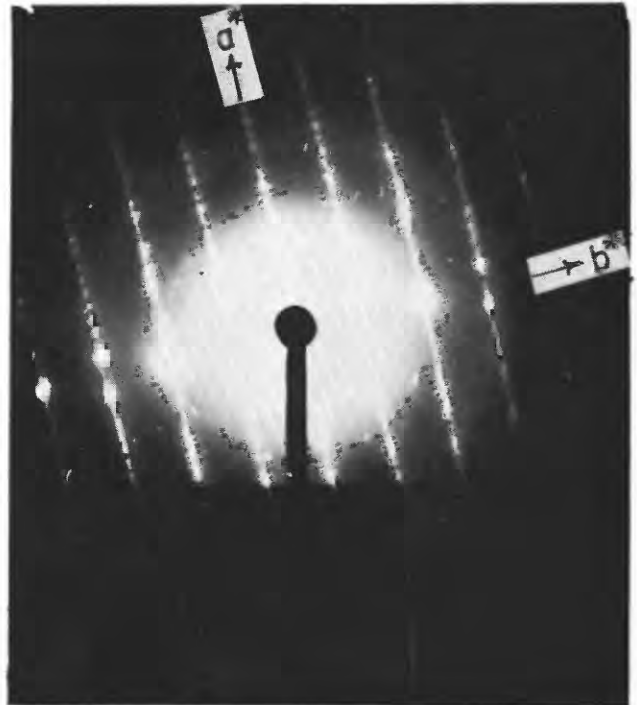
They give the formula V<sub>2</sub>O<sub>5</sub>·3H<sub>2</sub>O for navajoite and suggest that the CaO can be accounted for by 3 percent hewettite, SiO<sub>2</sub> by quartz, and Fe<sub>2</sub>O<sub>3</sub> by substitution of iron for vanadium in the navajoite structure. Weeks and others indexed an X-ray photograph of the zero layer ( $k = 0$ ) obtained by rotating a fiber bundle around [010] in a powder camera and found a cell with  $a = 17.43$  Å,  $b = 3.65$  Å,  $c = 12.25$  Å and  $\beta = 97^\circ$ . The  $b$  dimension was determined from an X-ray photograph of a small bundle of fibers rotated around [010] in a Weissenberg camera.

Electron micrographs (fig. 4A) of a portion of "navajoite-like" material (Sample A) collected by Alice D. Weeks from the South Rim workings of the Monument No. 2 mine, Apache County, Ariz., (the type locality) show characteristic thin well-developed laths and thicker rods of fibers. The laths and fibers are elongated [010] and flattened {001}.

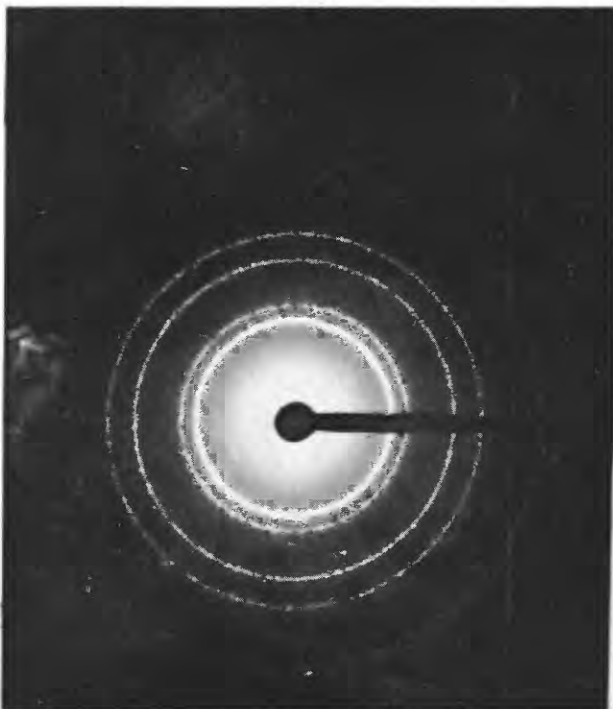




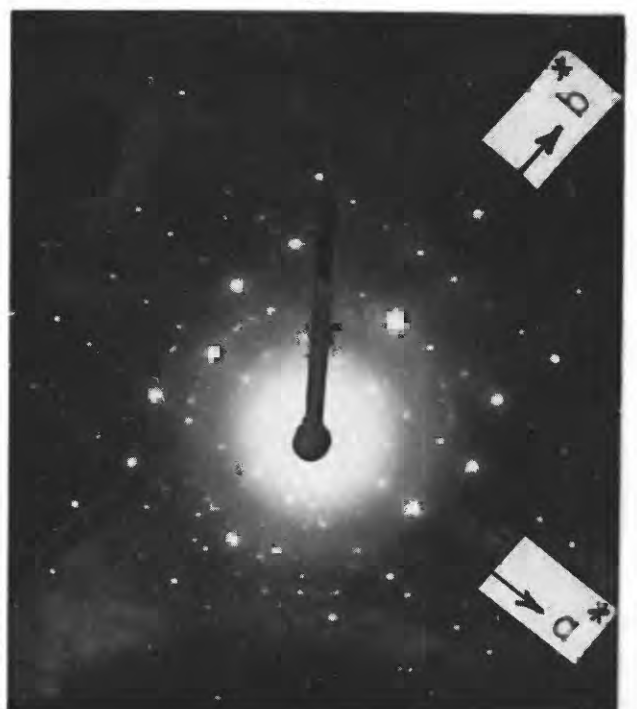
A



B



C



D

Figure 4.--Electron micrograph and diffraction patterns of navajoite and a "corvusite-like" material associated with navajoite.  
 A. Electron micrograph of sample A. B. SAD spot pattern of navajoite. C. Aluminum standard. D. SAD spot pattern of a "corvusite-like" mineral associated with navajoite.

The typical EDU spot pattern obtained from Sample A is shown in figure 5. From this pattern the strongest rings could be indexed. Measurement of four powder patterns gives the following unit-cell data:  $a = 11.86 \pm 0.02$  A and  $b = 3.644 \pm 0.002$  A ( $\gamma = 90^\circ$ ). Reflections appear only when  $h + k$  is even, indicating a probable  $C$ -centered cell. A few spot patterns were obtained from Sample A (fig. 4B) which are quite different from the "typical" pattern and indicate that a second phase is present in a minor amount. Examination of one of these spot patterns shows a probable  $C$ -centered cell ( $h + k = 2n$ ) with  $a = 35$  A,  $b = 3.6$  A and  $\gamma = 90^\circ$ . The electron diffraction powder patterns of Sample A show several weak reflections which cannot be indexed on the basis of the "typical" spot pattern but can be on the basis of the "second type" of spot pattern. Also, just outside the strong 020 ring ( $d = 1.822$  A) of the major phase is a weak but sharp ring with a spacing of 1.805 A which probably represents the 020 reflection of the second phase.

Another sample of "navajoite-like" material (Sample B) was collected by R. G. Coleman from the South Rim workings of the Monument No. 2 mine. Sample B occurred as a seam in sandstone and is dark brown in color and very fibrous. The X-ray powder pattern of Sample B is similar but not identical to the X-ray powder pattern of Sample A.

Electron micrographs of Sample B show that the crystal habit is identical to that of Sample A. Electron diffraction patterns, however, show that the predominant phase in Sample B is identical to the second phase in Sample A. Measurement of seven EDU powder patterns of Sample B, indexed from the pattern shown in figure 6, gives the following unit-cell data:  $a = 34.7 \pm 0.2$  A and  $b = 3.606 \pm 0.004$  A ( $\gamma = 90^\circ$ ). The  $hkl$  reflections appear only when  $h + k$  is even. A few spot patterns (fig. 4D)

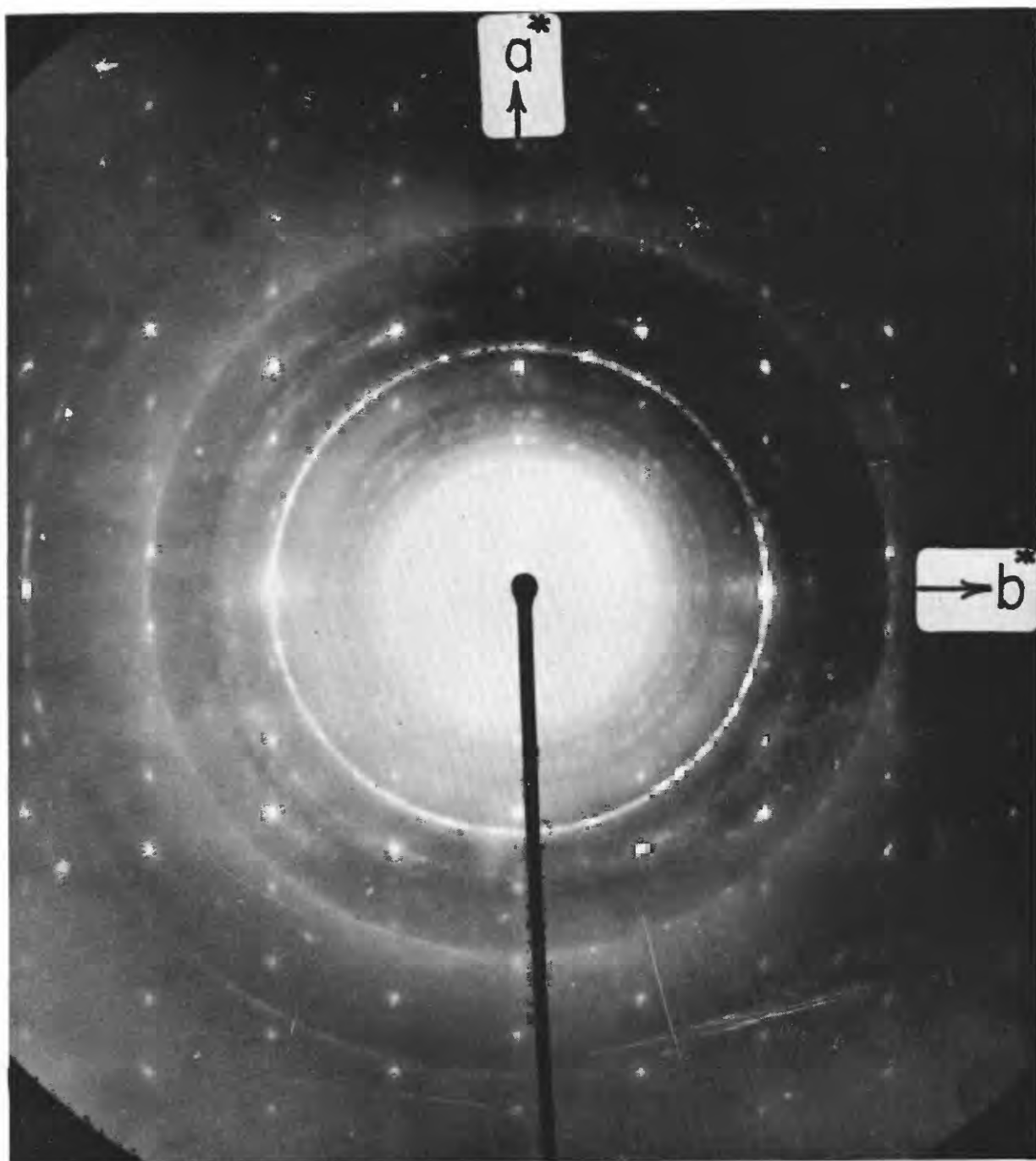


Figure 5.--EDU pattern of a "corvusite-like" mineral associated with navajoite showing spots superimposed on rings.

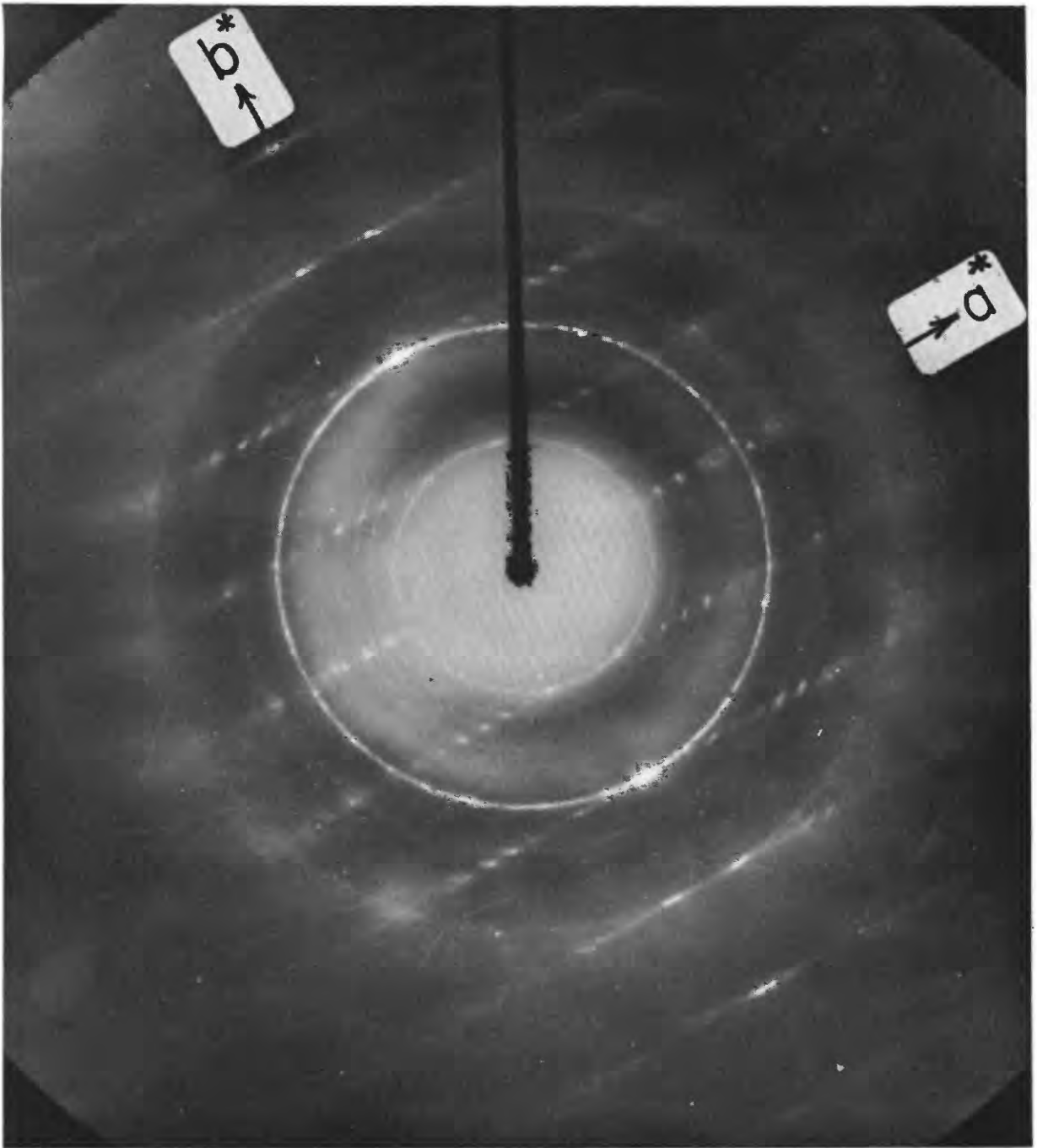


Figure 6.--EDU pattern of navajoite showing spots superimposed on rings.

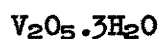
were obtained from Sample B which were identical to the spot patterns of the major phase in the Sample A. Measurement of one of these spot patterns gives a cell with  $\underline{a} = 12 \text{ \AA}$  and  $\underline{b} = 3.6 \text{ \AA}$  ( $\gamma = 90^\circ$ ). Reflections appear only when  $h + k = 2n$ .

The above data indicate that both samples from Monument No. 2 mine contain two phases. The major phase in Sample B is navajoite, whereas the major phase in Sample A appears to be a "corvusite-like" mineral. This apparent "corvusite-like" mineral may represent a stage in the oxidation of corvusite to navajoite, and its presence in navajoite samples may account for the appearance of  $V^{+4}$  in the chemical analysis of navajoite. The reason why so little navajoite appeared in Sample A may be due to sampling. Electron diffraction data show that the  $17.4 \text{ \AA}$  reflection is a 200 reflection instead of a 100 reflection as Weeks and others had assumed from X-ray studies. Combination of the electron diffraction data with the X-ray data of Weeks and others would suggest that navajoite is monoclinic, C-centered with the following unit-cell constants:  $\underline{a} = 34.8 \text{ \AA}$ ,  $\underline{b} = 3.606 \text{ \AA}$ ,  $\underline{c} = 12.25 \text{ \AA}$ , and  $\beta = 97^\circ$ . The results of this study are summarized in table 4.

Table 4.--Electron diffraction and X-ray unit-cell data for  
navajoite and a "corvusite-like" mineral associated  
with navajoite.

Sample A <sup>1/</sup> Electron diffraction data	Sample B <sup>2/</sup> Electron diffraction data
Major phase ("corvusite-like" mineral)	Minor phase ("corvusite-like" mineral) <sup>4/</sup>
$\underline{a} = 11.86 \pm 0.02 \text{ \AA}$	$\underline{a} = 12 \text{ \AA}$
$\underline{b} = 3.644 \pm 0.002 \text{ \AA}$	$\underline{b} = 3.6 \text{ \AA}$
$\gamma = 90^\circ$	$\gamma = 90^\circ$
$hkl: h + k = 2n$	$hkl: h + k = 2n$
Minor phase (navajoite) <sup>3/</sup>	Major phase (navajoite)
$\underline{a} = 35 \text{ \AA}$	$\underline{a} = 34.7 \pm 0.2 \text{ \AA}$
$\underline{b} = 3.6 \text{ \AA}$	$\underline{b} = 3.606 \pm 0.004 \text{ \AA}$
$\gamma = 90^\circ$	$\gamma = 90^\circ$
$hkl: h + k = 2n$	$hkl: h + k = 2n$

Navajoite (type material)



X-ray data<sup>5/</sup>  
monoclinic

$$\underline{a} = 17.43 \text{ \AA}$$

$$\underline{b} = 3.65 \text{ \AA}$$

$$\underline{c} = 12.25 \text{ \AA}$$

$$\beta = 97^\circ$$

<sup>1/</sup>"Navajoite-like" material collected by A. D. Weeks from the South Rim workings, Monument No. 2 mine, Apache County, Ariz.

<sup>2/</sup>"Navajoite-like" material collected by R. G. Coleman from the South Rim workings, Monument No. 2 mine, Apache County, Ariz.

<sup>3/</sup>Cell data obtained from measurement of an EDU spot pattern.

<sup>4/</sup>Cell data obtained from measurement of an SAD spot pattern.

<sup>5/</sup>Weeks, Thompson, and Sherwood (1955, p. 211).

## Steigerite

Henderson (1935) describes steigerite as a hydrous aluminum vanadate,  $\text{Al}_2\text{O}_3 \cdot \text{V}_2\text{O}_5 \cdot 6\frac{1}{2}\text{H}_2\text{O}$ , canary yellow in color with a waxy luster.

Electron micrographs of steigerite from Gypsum Valley, Colo., (USNM E-5108) show that the material is composed of thin poorly developed laths and angular flakes, many of which are less than one micron in size. The laths and flakes are flattened  $\{010\}$ . Measurement of seven powder patterns indexed from an EDU spot pattern gives the following unit-cell data:  $a = 12.92 \pm 0.03$  Å,  $c = 10.98 \pm 0.04$  Å and  $\beta = 121^\circ 13' \pm 30'$ . A primitive cell with the smallest  $\beta$  angle was chosen.

## Fervanite

Hess and Henderson (1931) describe fervanite from Gypsum Valley, Colo., as a hydrous ferric vanadate with the formula  $\text{Fe}_4\text{V}_4\text{O}_{16} \cdot 5\text{H}_2\text{O}$ . The mineral is fibrous, golden brown, with a brilliant luster. Extinction is slightly inclined to the length of the fiber with  $2V$  small, suggesting monoclinic symmetry (Hess and Henderson, 1931, p. 274).

Fervanite collected by H. T. Evans from the Hummer mine, Montrose County, Colo., was examined. The material is golden brown and very fibrous, closely resembling hewettite in habit. Electron micrographs (fig. 7) show that the material is composed of long narrow fibers elongated  $[001]$  and flattened  $\{010\}$ . The width of the fibers in the  $a$  direction averages about 0.5 microns. Measurement of four EDU powder patterns gives a cell with  $a = 9.02 \pm 0.01$  Å,  $c = 6.65 \pm 0.03$  Å and  $\beta = 103^\circ 20' \pm 20'$ . A primitive cell with the smallest  $\beta$  angle was chosen.

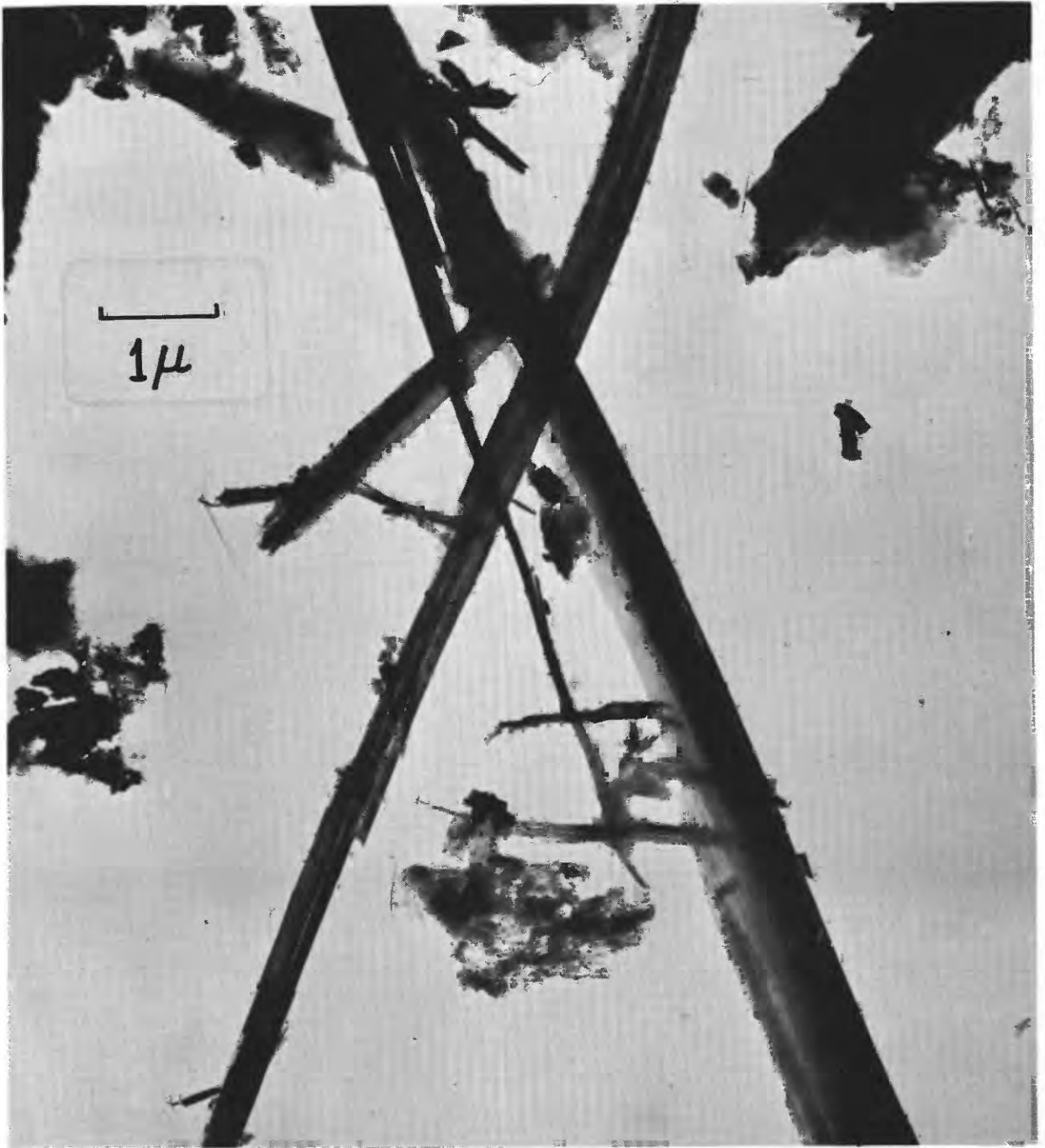


Figure 7.--Electron micrograph of fervanite.



## Simplotite

Simplotite,  $\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$ , described by Thompson, Roach, and Meyrowitz (1958) occurs as hemispherical aggregates of dark green, platy crystals. They found by X-ray techniques that the mineral was monoclinic, pseudotetragonal with  $a = 8.39 \pm 0.03$  A,  $b = 17.02 \pm 0.05$  A,  $c = 8.37 \pm 0.03$  A, and  $\beta = 90^\circ 25' \pm 5'$ .

Electron micrographs of the type material collected by C. H. Roach from the Peanut mine, Montrose County, Colo., show that it is composed of irregularly shaped plates or flakes varying greatly in size. Measurement of four EDU powder patterns of simplotite gives a cell with  $a = c = 8.336 \pm 0.002$  A and  $\beta = 90^\circ 0' \pm 30'$ . Figure 8 shows an SAD spot pattern of simplotite superimposed on the rings of the aluminum standard. The tetragonal symmetry is apparent.

## DISCUSSION

The electron diffraction technique can be used to determine unit-cell constants of crystals that may be too fine grained to give useful optical or X-ray data. The importance of the technique for the study of layer lattice minerals which are unsuitable for single crystal X-ray diffraction analysis cannot be overstressed, particularly in view of the recent successful applications of electron diffraction methods to the complete solution of crystal structures (Pinsker, 1953; Cowley, 1953a, b).

No attempt is made to determine completely the unit-cell of minerals examined in this study either by correlation with X-ray powder patterns or by examination of electron diffraction patterns of "oblique textures."<sup>1/</sup>

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<sup>1/</sup> An "oblique textured" pattern refers to an electron diffraction obtained from a polycrystalline specimen which has preferred orientation, the plane of orientation being inclined from a normal to the electron beam.

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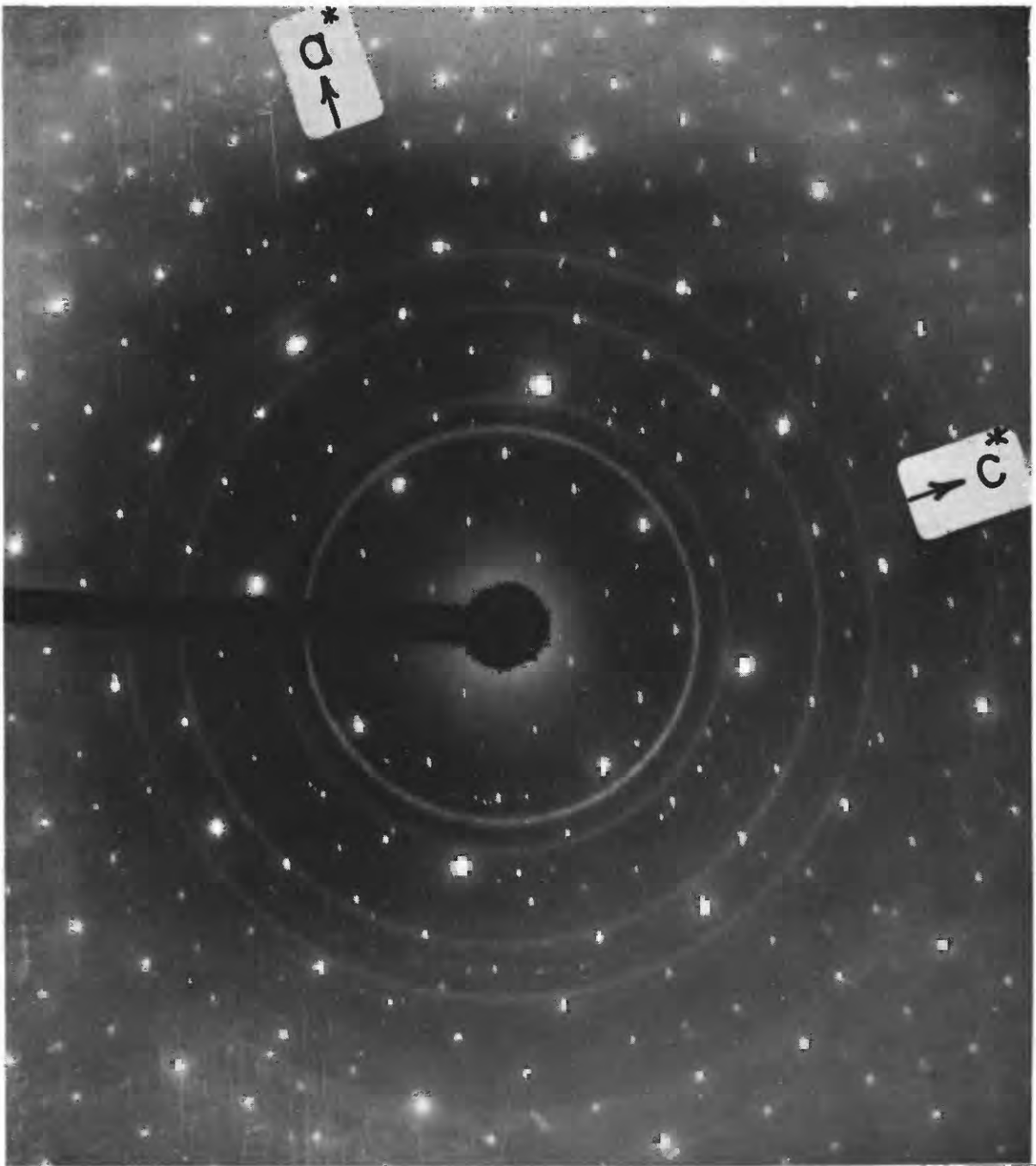


Figure 8.--SAD spot pattern of simplotite superimposed on the powder pattern of the internal aluminum standard.

The use of X-ray powder patterns in connection with the "two-dimensional" electron diffraction data to determine completely the unit-cell of layer lattice minerals presents a number of problems. In general, the X-ray pattern of this type of mineral shows weak and broad or diffuse rings, making measurement difficult. Moreover, indexing of the X-ray powder pattern with electron diffraction unit-cell data is often ambiguous because a series of closely spaced reflections may appear only as broad bands in the X-ray pattern. Indexing of the X-ray pattern by direct comparison with an indexed EDU oriented powder pattern is usually impossible because, due to orientation effects, the EDU pattern includes only a restricted number of reflections; whereas the equivalent reflections in the X-ray pattern are usually very weak or missing entirely. The direct lattice spacings given by EDU powder patterns of nonorthogonal crystals may be different from the direct lattice spacings given by the X-ray powder pattern and thus cause further difficulty in indexing. The reasons for the differences in the values of the lattice spacings obtained by the two methods for nonorthogonal crystals are discussed in Part I.

Electron diffraction powder data cannot, in general, be compared to ASTM X-ray data for the identification of fine-grained minerals because of the variations between X-ray and electron diffraction powder patterns mentioned above. In the U. S. Geological Survey laboratory a set of standard EDU powder and spot patterns is used to identify unknown materials.

Electron diffraction patterns of "oblique texture" have been used by Pinsker and coworkers to find the unit-cell and space group of a number of compounds. Pinsker (1953, p. 93) gives a general account of the interpretation of patterns of "oblique texture." It is beyond the scope of this

paper to discuss the use of this type of pattern in evaluation of the unit-cell of layer lattice minerals except to point out that in many cases minerals of this type are so thin in one direction that patterns of "oblique texture" give no information about the axial length in the thin direction of the crystal.

Little use was made in this paper of SAD spot or powder patterns for the determination of unit-cell data; however, SAD patterns give the same unit-cell data as do the EDU patterns. Measurements of SAD patterns are not very precise, particularly if the patterns are not internally standardized.

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