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UNIT CELL OF MAGADIITE IN AIR, IN VACUO, AND UNDER OTHER CONDITIONS

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Abstract

Electron diffraction single-crystal patterns and X-ray powder data are used to evaluate unit cell parameters of magadiite. Under normal air conditions, the unit cell is monoclinic with $a=b=7.25$, $c=15.69$ Å, $\beta=96.8°$. The data confirm a similarity with keatite and the a and b parameters are equal to those given by Eugster (1967) when divided by $\sqrt{3}$. A monoclinic cell given by McAtee *et al.* (1968) is not confirmed. *In vacuo*, the structure collapses and the unit cell is monoclinic with $a=b=7.30$, $c=13.73$ Å, $\beta=100.5°$. H-magadiite, in dry air and in vacuo, gives a basal spacing of 11.20 Å. Basal spacings of H-, Na-, and Ca-magadiite are given for various physical conditions and after saturation with liquid ethylene glycol.

Introduction

The hydrous sodium silicate, magadiite, with a composition approximating to $Na_2O\ 14SiO_2\cdot 9H_2O$ or $NaSi_7O_{13}(OH)_3\cdot 3H_2O$, was described first by Eugster (1967) in material from Lake Magadi, Kenya, and subsequently was identified in Oregon and California (Eugster *et al.*, 1967). On the basis of similarities between the X-ray powder diffraction patterns of magadiite and keatite, a form of silica, Eugster (1967) indexed the powder pattern of magadiite using an orthogonal cell with $a=b=12.620$, $c=15.573$ Å. The unit cell parameters were revised subsequently by McAtee, House and Eugster (1968) mainly on the basis of electron diffraction data. They showed electron micrographs in which magadiite appears as very thin plates, more or less rectangular in form and about 1 micron in linear dimensions. Individual crystals were said to give electron diffraction spot patterns with an angle of 84°40′ between two sets of parallel diffraction rows and the non-orthogonality of the pattern was taken as evidence that "magadiite cannot be tetragonal." No spacing measurements were reported from the electron diffraction patterns. With this information, the X-ray powder pattern was re-indexed on a monoclinic cell with a 7.22, b 15.70, c 6.91 Å, and $\beta=95°16'$.

Re-examination of the Electron Diffraction Evidence

Electron micrographs and single crystal diffraction patterns of a sample of magadiite from Trinity County, California, also the source of

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the material studied by McAtee *et al.*, confirm broadly their observations, but the angle between rows of spots appears closer to 90° than their reported value of 84° 40′. The values now obtained lie mainly in the range 88–90° and no conclusive proof has been obtained that the angle departs from 90°. The observed deviations may be due partly to tilting of the crystals on the stage of the instrument. Another aspect of the problem, not recognized in the previous work, is that magadiite shows a structural change when placed in a high vacuum at room temperature. The basal spacings show a reversible shrinkage and re-expansion when the mineral is placed in a high vacuum and then returned to normal atmospheric conditions. This means that electron diffraction data must be applied cautiously when used as an aid in interpreting X-ray powder data recorded under normal atmospheric conditions.

The electron diffraction spot patterns conform so nearly to orthogonal axes and to four-fold diffraction symmetry that a re-consideration of the unit cell parameters seems desirable. This is the more necessary because the observed and calculated $d(hkl)$ values given by McAtee *et al.* (1968) show some considerable discrepancies which, for a number of reflections, amount to several percent in $\Delta d/d(\text{obs})$. Discrepancies of this magnitude probably are not due to experimental errors but are more likely to have arisen from the chosen unit cell parameters.

Accurate spacing measurements have been obtained from electron diffraction spot patterns by shadowing the crystals thinly with aluminum metal, so that each spot pattern carries Al calibration rings (see Brindley and DeKimpe, 1961). The parameters obtained are $a=b=7.38\pm0.03$ Å. These values and the four-fold diffraction symmetry are consistent with the similarity noted by Eugster (1967) between magadiite and keatite, for which the tetragonal a parameter is 7.456 Å (Keat, 1954; Shropshire *et al.*, 1959).

In considering the electron diffraction data for magadiite, it is salutary to remember that micas and clay minerals, which are mainly monoclinic, commonly show hexagonal spot patterns under the same conditions that magadiite shows a tetragonal pattern. Evidently, the electron diffraction data do not prove the unit cell to be tetragonal and do not exclude a lower symmetry.

If a thin platy crystal with axes a and b in the basal plane and c inclined to a at a monoclinic angle β rests on the horizontal stage of the instrument, the reciprocal axes a^* and c^* are related to the horizontal plane as shown in Figure 1. Also, since the crystal is thin normal to (001), the reciprocal lattice nodes are likely to be diffused in the direction c^*. Consequently, the electron diffraction pattern may record the projection of a^* on the horizontal plane and the measured value will be a^*

on the horizontal plane and the measured value will be $a^* \sin \beta^* = 1/a$. Also b^* gives $1/b$. A similar argument holds if α, the angle between c and b is not exactly 90°, and b^* is not exactly in the horizontal plane.

X-RAY POWDER DIAGRAM

The X-ray powder diagram was recorded with a Philips Norelco diffractometer using nickel-filtered CuKα radiation and calibrated with a silicon standard; data were recorded at 0.5° 2θ/min and with a chart speed to give 1° 2θ/in. Samples were prepared using (*i*) a side-filled cavity holder, filled slowly on a vibrating table, and (*ii*) thin slurried samples dried in normal air conditions on glass slides. Arrangement (*i*) has been found very effective in eliminating most, or all, of the preferential orientation which occurs when platy particles are packed in front-filled, or back-filled cavities, and arrangement (*ii*) gives prominence to basal reflections. The patterns were obtained under normal atmosphere conditions, with temperature about 20°C, relative humidity about 60–70 percent.

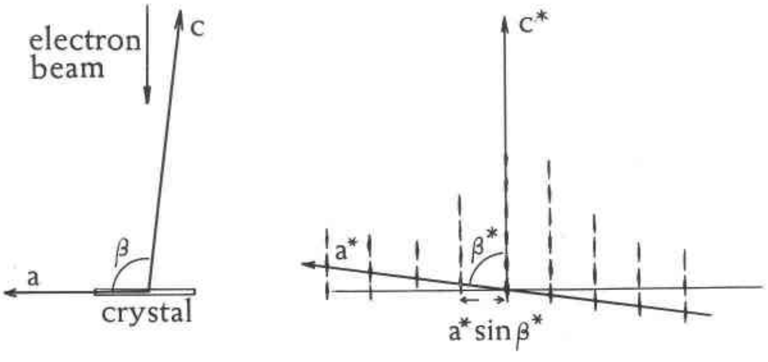

FIG. 1. Lattice and reciprocal lattice of magadiite in electron diffraction.

The powder pattern was indexed as follows: The strong 04 and 40 spots of the electron diffraction pattern correspond to spacings of 1.835 Å. The X-ray diffraction patterns of magadiite in air and in vacuo give clearly defined diffraction peaks of about this value, namely a medium-strong reflection at $d = 1.822$ Å for magadiite in air and $d = 1.826$ Å for magadiite in vacuo. These are outstanding reflections in this region of the X-ray powder diagrams, and were tentatively accepted as 040 reflections. For magadiite in air, observed reflections at 7.24, 3.626, and 2.406 Å may by $0k0$ reflections with $k = 1$, 2 and 3. These are weak reflections and may correspond with the weak spots seen in the electron diffraction patterns. Tentatively, b is estimated as 7.25 Å. From well-oriented samples, $00l$ reflections with $l=1$, 2, 3, 4 and 6 give $d(001)=$ 15.58 Å. A tetragonal cell with $a=b=7.25$ and $c=15.58$ Å does not account for the observed powder pattern. If the unit cell is monoclinic, then $d(001)=c \sin \beta$, and it remains to find β. This has been done by a graphical procedure. With $\beta=90°$, 95°, 100°, 105°, 110°, values of 2θ were calculated for $a=b=7.25$ Å, $c \sin \beta=15.58$ Å, and the results were plotted on a large scale diagram and compared with the observed 2θ values; a second calculation was made with $\beta=94°$, 96°, 98° and 100°, and a reasonable fit was obtained with $\beta \simeq 96.5$–$97.0°$. A further calculation was made with $\beta=96.4$, 96.6, 96.8 and 97.0°, and from the results, a value of $\beta=96.8 \pm 0.2°$ was obtained as giving the best overall agreement. A calculation of β from pairs of reflections indexed as $10l$, $10\bar{l}$, with $l=2$, 3, and 5, gave a value of 96°50′. No further refinement of the parameters was made. The possibility that the unit cell may be triclinic was not explored, but among the lower order reflections there is no obvious indication of a triclinic cell.

DISCUSSION OF THE X-RAY DATA

Table 1 lists the observed and calculated spacings, the percentage deviations, $|d(\text{obs})-d(\text{calc})|/d(\text{obs}) \times 100$, and the peak intensities. The deviations are mainly less than 0.35 percent and for all reflections average 0.24 percent. This is a considerably better agreement than that shown by the results of McAtee *et al.* for which $\Delta d/d$ averages 1.39 percent and for some reflections is as high as several percent. Nearly all reflections can be indexed as $00l$, $0kl$, and $h0l$, and only a few weak reflections are given general indices hkl and one of these has a suspiciously high $\Delta d/d$ value. The layer-like nature of the structure, which is suggested by the platy morphology of the crystals and by the reversible swelling and shrinking behavior described later, may give rise to layer displacements which weaken or eliminate reflections with general indices.

The β-angle, 96.8°, corresponds almost exactly to successive layer displacements of $-a/4$; a displacement of exactly this value makes $\beta=96.6°$. Therefore a larger orthogonal cell exists with $a=b=7.25$ Å and $c=4d(001)=62.32$ Å. Similar results are obtained for many layer silicates where, for example, the layer displacement may be $-a/3$ and the orthogonal cell has $c=3d(001)$. Figure 1 is drawn with $\beta \simeq 97°$ and one sees that the cell dimensions are such that the reflections $40\bar{1}$ and $\bar{4}01$ lie on the plane of projection. Therefore, provided β is not greatly changed when the crystals are dehydrated in the electron microscope, the strong reflections 04 and 40 seen in the electron diffraction patterns may be 040 and $40\bar{1}$ reflections. Analogous results are obtained with layer sili-

TABLE 1. X-RAY POWDER DATA FOR MAGADIITE UNDER NORMAL AIR CONDITIONS

Indices			d(calc), Å	d(obs), Å	Δd/d(obs), %	I(peak)
0kl	h0l	hkl				
001			15.580	15.56	0.13	100
002			7.790	7.77	0.26	9
010			7.250	7.24	0.14	5
	100		7.199			
	$10\bar{2}$		5.630	5.64_4	0.25	4
003			5.193	5.18_7	0.12	18
	102		5.000	5.00_5	0.10	14
		111	4.738	4.69_5	0.92	6
	$10\bar{3}$		4.470	4.46_6	0.09	18
013			4.222	4.23_0	0.19	3
	103		3.993	4.01_1	0.45	8
004			3.895	3.915	0.51	4
020			3.625	3.626	0.03	13
021			3.531	3.544	0.37	19
014			3.431	3.434	0.09	75
022			3.287	3.298	0.33	40
		$12\bar{1}$	3.204	3.197 nr	0.22	11
	$20\bar{3}$		3.137	3.145	0.25	60
	$10\bar{5}$		2.992	2.989	0.10	6
015			2.863	2.866	0.10	6
		$12\bar{3}$	2.816	2.821 sh	0.21	10
	$20\bar{4}$		2.815			
	105		2.744	2.735	0.33	4
						[a]
024			2.654	2.639	—	7
		$21\bar{4}$	2.624			
006			2.597	2.599 sh	0.08	11
	$10\bar{6}$		2.540	2.528 b	—	6
	$20\bar{5}$		2.507			
030			2.417	2.406 b	—	4
	$30\bar{1}$		2.415			
	300		2.400			
	106		2.355	2.353 sh	0.08	12
		$13\bar{1}$	2.279	2.270 b	0.37	5
		310	2.278			
026			2.111	2.103	0.38	4
034			2.054	2.067	0.63	6
	206		1.997	1.997 sh	0.00	12
008			1.948	1.94–1.97 vb	—	5
	304		1.943			
	$10\bar{8}$		1.939			
		$11\bar{8}$	1.873	1.873	0.00	6
	108		1.826	1.822 sh	—	30
		$31\bar{6}$	1.817			
040			1.812			
	$40\bar{1}$		1.812			
				1.785		5
				1.74–1.70 vb		4
				1.674		4
				1.642		5
				1.563		5
				1.493		4
				1.413		3
				1.394		3
				1.371		4

[a] Above this line diffraction data were recorded with 1° slits, and below this line with 4° slits. Approximately, intensities below this line should be divided by 4 to be comparable with those above the line.

nr = not resolved, sh = sharp, b = broad, v = very.

cates; for example, with kaolinite the six-fold group of strong reflections appearing in electron diffraction patterns as 33, 33 and 06, and their negative counterparts, appear in X-ray diffraction patterns as strong reflections with indices 060, $33\bar{1}$, $3\bar{3}\bar{1}$, while 330 and $3\bar{3}0$ appear as weak reflections.

The value now given for the *a* parameter, 7.25 Å is related in a simple way to the larger value, 12.62 Å, given originally by Eugster (1967), as follows: $a\sqrt{3}=7.25\sqrt{3}=12.56$ Å which is very close to Eugster's value, but his tetragonal cell is not confirmed.

MAGADIITE IN VACUUM

When placed in an evacuated chamber on the diffractometer, magadiite collapses to a basal spacing of about 13.50 Å. It readily recovers its original spacing when exposed again to water vapor. The equilibrium vapor pressure has not been determined precisely, but with a simple mercury manometer attached to the vacuum chamber and with an arrangement for introducing controlled amounts of water vapor, it was evident that the normal hydration state of magadiite was re-established at a water vapor pressure of the order of 1 mm Hg. A fraction of a mm Hg water vapor pressure was required to give the collapsed phase.

The side-packed sample holder was not entirely satisfactory for making lattice spacing measurements of the collapsed phase because when the pressure was reduced the sample surface was displaced even though the pressure was reduced extremely slowly. Measurements were made, therefore, on rather thick slurried samples on glass slides, which did not show marked basal plane orientation.

The results are summarized in Table 2. Because many diffraction peaks are broad and poorly resolved, *d*(obs) in many instances cannot be given very accurately. Evidently the collapsed structure is much less regular than the original structure. On the assumption that the unit cell is monoclinic, parameters have been estimated in the same way as for the normal mineral. The basal reflections give $d(001)=13.50$ Å. The *a* parameter is taken equal to the *b* parameter on the basis of the electron diffraction pattern, and the reflection at 1.826 Å, the only clearly defined reflection in this region of the X-ray diffraction pattern, is taken to be 040, which gives $b=7.30$ Å. This is slightly larger than 7.25 Å obtained for normal magadiite and closer to the value 7.38 Å obtained from the electron diffraction measurements. The β angle has been estimated as 100.5° by the graphical procedure previously described.

Table 2 compares calculated spacings based on the monoclinic shaped cell with $a=b=7.30$, $c=13.73$ Å, $\beta=100.5°$, with the observed spacings. A critical discussion of $\Delta d/d$ values is not justified because of the many

Table 2. X-ray Powder Data for Magadiite *in vacuo*

Indices			d(calc), Å	d(obs), Å	I(peak)
0kl	h0l	hkl			
001			13.500	13.50	100
010			7.300	7.4 nr	~5
	100		7.175	7.25	12
002			6.750	6.71	25
011			6.421	6.4 nr	4
	101		5.907	5.89 vb	6
			—	5.32	3
		110	5.117	5.0–5.2 vb	3
		$11\bar{1}$	5.005		
		012	4.956		
			—	4.76 vb	9
003			4.500	4.49	14
	$10\bar{3}$		4.171	4.10–4.25 vb	12
020			3.650	3.64 nr	10
	$20\bar{1}$		3.636		
		$11\bar{3}$	3.621		
	200		3.588	3.581	40
021			3.523	3.53 nr	~10
	$20\bar{2}$		3.439	3.46 nr	~10
	201		3.321	3.314 d?	80
	$10\bar{4}$		3.295		
				2.9–3.2 band	10–20
023			2.835	2.822	11
006			2.250	2.248	4
040			1.825	1.826	10

nr = not resolved, vb = very broad, d = double.

broad and poorly resolved reflections. The angle 100.5° gives a layer displacement larger than $a/4$ which indicates that the interlayer relationships are changed by the removal of water and the collapse of the structure.

Variations in Basal Spacings of Magadiite

Eugster (1967) showed that magadiite when treated with dilute HCl lost its Na_2O content and the resulting composition was consistent with $6SiO_2 \cdot H_2O$ or $H_2Si_6O_{13}$; the basal spacing became 13.68Å. This product, which may be called H-magadiite, was prepared in the present experiments by treating the natural material with N/10 HCl and washing until chloride ion free. A basal spacing of 11.20 Å was obtained under normal air conditions, and this remained unchanged when the sample was maintained in vacuo. Samples heated in air to 200°C and to 400°C, and X-rayed over P_2O_5 gave basal spacings respectively of 11.12 and 10.77 Å; the breadth of the latter peak suggested incipiant breakdown of the structure.

Natural, or Na-magadiite, gives basal spacings of 15.58 Å in normal air conditions and 13.50 Å *in vacuo*. Samples heated in air to 200°C and X-rayed over P_2O_5 still gave a spacing of 15.5 Å, but when heated to 250° and to 400°C, less regular structures were formed. After heating to 700°C, a quartz pattern was obtained.

A calcium saturated, or Ca-magadiite, gave a basal spacing of 15.73 Å in normal air conditions and 13.76 Å *in vacuo*.

Samples treated with liquid ethylene glycol gave the following results: H-magadiite expanded from 11.20 to 15.60 Å, Na-magadiite expanded from 15.58 to 17.83 Å, Ca-magadiite at first showed little change but when left in excess liquid slowly developed a poorly organized 17.2 Å spacing.

CONCLUSIONS

Single crystal, electron diffraction patterns, with Al calibration rings, show an orthogonal pattern with four-fold diffraction symmetry, and with $a=b=7.38 \pm 0.03$ Å. The X-ray powder pattern of magadiite in normal air conditions is indexed with a monoclinic cell with $a=b=7.25$ Å, $c=15.69$ Å, $\beta=96.8$, and $d(001)=15.58$ Å. The a and b parameters correspond to the values given by Eugster (1967) when divided by $\sqrt{3}$, and are consistent with a similarity between magadiite and keatite. The monoclinic cell of McAtee *et al.* (1968) is not confirmed. The observed reflections are mainly of types $00l$, $0kl$ and $h0l$, possibly because of interlayer displacements. The β angle corresponds to layer shifts of $-a/4$. *In vacuo*, the structure collapses to $d(001)=13.50$ Å and the powder pattern is indexed with $a=b=7.30$ Å, $c=13.73$ Å, $\beta=100.5°$. The collapsed structure is considerably less regular than the original mineral. The basal spacings of H-, Na-, and Ca-magadiite are given under vacuum conditions, under normal air conditions, after heating at elevated temperatures, and after saturation with ethylene glycol.

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