THE STRUCTURE OF POLLUCITE

by

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Abstract

Náray-Szabó concluded that pollucite must be pseudocubic and proposed a tetragonal structure, in spite of evidence of isometric symmetry. In recognizing the known similarity to analcite he assumed the cell formula to be $16(CsAlSi_2O_6.H_2O)$. From powder data he deduced that the general features of the structure consist of the analcite framework $(Si,Al)_{48}O_{96}$ with 16 Cs occupying the large voids at $\frac{1}{8} \frac{1}{8} \frac{1}{8}$ etc.

The structure determination reported here was made on a specimen from Rumford, Maine. The space group is verified to be Ia3d, as determined by Strunz, and the cell edge is a=13.69Å. Integrated intensities, measured with a single-crystal diffractometer and, using CuKα radiation, were corrected for Lorentz and polarization factors, absorption, and anomalous scattering. Interpretation of a three-dimensional Patterson function located the Cs at $\frac{1}{8} \frac{1}{8} \frac{1}{8}$. A Fourier synthesis phased upon the cesium revealed the $(Si,Al)_{48}O_{96}$ - framework. The parameters for these

atoms were then refined by least squares. Computations, based on an

analysis by Foote, indicated 12Cs, 4Na, and $4H_2O$ per cell. Either

$\left| 12Cs+4H_2O \right|$ or $\left| 12Cs+4Na \right|$ must occupy the voids at $\frac{1}{8}\frac{1}{8}\frac{1}{8}$ etc. A

Fourier difference synthesis, based upon calculated structure factors,

but omitting H_2O and Na, showed residual electron-density peaks near

$\frac{1}{4}\frac{1}{8}$ 0, lying midway between the Cs locations. These represent the H_2O

molecules lying between Na ions (or Na and Cs). The final model was

refined by least squares to an $\underline{R}$ factor less than 5.5%.

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Introduction

Pollucite is a mineral whose chemical composition and structure are not clearly understood. It is a rare mineral, which contains as one of its essential constituents the rare element cesium. To discover the exact nature of the composition and structure of pollucite was the object of the present investigation. Only a vague understanding of these can be obtained by a study of the current literature. The unsatisfactory state of knowledge about pollucite can best be seen in the light of the following historical account.

Johann F.A. Breithaupt discovered pollucite in specimens he obtained from the island of Elba. He announced his discovery of this new mineral in the WIENER ZEITUNG in 1844. On the island of Elba, Breithaupt noted two unknown minerals, which always occured together in the cavites (Drussen) of the granite. Not only did they always occur together, but in addition they were strikingly similar in their physical appearance. For this reason Breithaupt named these two minerals Castor and Pollux after the inseparable companions of ancient mythology.

Castor, or castorite, was later identified with petalite ($LiAlSi_4O_{10}$), the mineral in which arfvedson first discovered the element lithium in 1817. Pollux, whose genitive form is pollucis, became known as pollucite. The fact that pollucite contains cesium remained unknown for twenty years after the mineral was found, because at that time the element cesium was still to be discovered.

Table 1

Chemical analysis of pollucite as

reported by Plattner in 1846

SiO_2	46.200
Al_2O_3	16.394
Fe_2O_3	0.862
K_2O	16.506
Na_2O (with trace of Li)	10.470
H_2O	2.321
	———————
	92.753

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Plattner made a chemical analysis of Breithaupt's pollucite in 1846 and obtained the following results given in Table 1.

Since cesium was unknown at that time, Plattner reported the cesium content in terms of potassium. Thus, he was not able to explain the low summation of the oxides.

In the course of their investigation of the sun's atmosphere in 1860, R. Bunsen and G.R. Kirchoff were systematically comparing the spectra of the sun with that of the flame spectra of purified elements. Upon examining the flame spectra of "certain mineral water concentrates" theu found two unknown blue lines, and on this basis announced the discovery of the element cesium (Latin caesius, meaning "sky blue").

Four years later in 1864, M.F. Pisani examined a mineral specimen from a private collection of a Mr. Adam, and a test of the physical properties with further examination by the blowpipe confirmed the identity of the specimen as pollucite. But, to Pisani's great surprise, the spectrograph showed the strong characteristic blue lines of cesium. Pisani proceeded to obtain additional specimens fo pollucite from which he made an analysis. His results are shown in Table 2.

<center>Table 2</center>

<center>Chemical analysis of pollucite</center>

<center>reported by Pisani in 1864</center>

	% Oxide	% Oxygen		Oxygen Ratio
SiO_2	44.03	23.48		15
Al_2O_3	15.97	7.43	} 7.63	5
Fe_2O_3	0.68	0.20		
CaO	0.68	0.19		
Cs_2O (+K_2O trace)	34.07	1.97	} 3.16	2
Na_2O (+Li_2O trace)	3.88	1.00		
H_2O	2.40	2.13		2

<center>————— —————</center>

<center>101.71</center>

Pisani knew that pollucite had been examined optically by Alfred Des Cloiseaux, who had concluded that the mineral was cubic, because it was isotropic. One of Pisani's crystals which weighed twenty grams had distinct faces of the cube and trapezohedron forms. These appeared similar to those found on crystals of analcime. On the basis of these findings, Pisani stated that pollucite should be classified in the mineralogical realm with either analcime or leucite.

Pisani's results give the ratios of the oxygen atoms alloted to the oxides $SiO_2:Al_2O_3:Cs_2O:H_2O$ to be 15:5:2:2 respectively. The numbers of the oxygens in the oxides have the highest common factor of 6;therefore, the least rational oxygen ratio for an oxide formula would be 90:30:12:12. This gives an oxide formula for Pisani's analysis of $45SiO_2 \cdot 10Al_2O_3 \cdot 12Cs_2O \cdot 12H_2O$.

After Pisani published his analysis of pollucite, George J.Brush published a recalculation of Plattner's original analysis, made with certain assumptions about the method of analysis that Plattner had used. The recalculated analysis agreed fairly well with that of Pisani's for pollucite.

K.F. Rammelsberg was not satisfied with Pisani's analysis, so he made another analysis of the pollucite from Elba, which he reported in 1878. From this analysis the concluded that the true formula for the composition of pollucite should be $R'_4Al_2(SiO_3)_5$, where R' includes H,Cs, Na, and K. Two years later Rammelsberg published another analysis of

pollucite which he said confirmed this formula.

In 1890, pollucite was found in a new locality at Hebron, Maine. H.L. Wells analysed specimens from Hebron and published his results with a discussion of the composition of pollucite. Wells discredited Rammelsberg's conclusions and argued that the true composition of pollucite should be represented by the formula $H_2R'_4Al_4(SiO_3)_9$, where R' includes Cs, K, Na, Li, and Ca. Wells also made a recalculation of Plattner's original analysis of pollucite which he said was in agreement with his formula for the mineral.

Pollucite was soon found at other localities such as Rumford, Maine. Specimens from these new localities were also analysed, but new significant information on the nature of pollucite was not forthcoming until x-ray methods of analysis appeared.

In 1932, B.Grossner and E. Reindl examined pollucite from Rumford, Maine using the rotating-crystal and powder methods. They found their material to be isometric, having a cell whose edge was $\underline{a}$=13.66kX ($\rightleftharpoons$13.69Å) and which contained $16CsAlSi_2O_6 \cdot \underline{x}H_2O$. They noted the similarity of these data with the cell and composition of analcime, for which $\underline{a}$=13.68kX ($\rightleftharpoons$13.71Å) with $16NaAlSi_2O_6 \cdot H_2O$ per cell. A few years later, Hugo Strunz determined the space group from powder photographs as $Ia3d$ with cell edge $\underline{a}$=13.71kX ($\rightleftharpoons$13.74Å) and proposed a composition $CsAlSi_2O_6 \cdot \frac{1}{2} H_2O$. He also noted the similarity of composition, cell edge, and optics of pollucite, analcime and leucite.

The structure of pollucite was first investigated by St. V. Náray-Szabó in 1938 on specimens from Elba and Buckfield, Maine. With oscillating-crystal photographs he verified the space group $\underline{Ia}$ 3d and found a cell edge of $\underline{a}$=13.74 kX($\dot{\sim}$13.77Å).

Despite the confirmation of the isometric space group, and despite the fact that all crystals of pollucite were known to be optically isotropic, Náray-Szabó decided that pollucite could only be pseudocubic. He concluded that the mineral was actually tetragonal with space group $\underline{I}$ 4/$\underline{acd}$.

He recognizing the previously known similarity of pollucite to analcime, Náray-Szabó, following the example of Strunz, assumed a corresponding formula analogous to that of analcime, namely $CsAlSi_2O_6 \cdot \underline{x}H_2O$. The analcime structure had been solved by W.H. Taylor some seven years earlier. It consists of an open framework of SiO_4 and AlO_4 tetrahedra, within whose interstial spaces Na and H_2O are located. Náray-Szabó adopted this framework, which, if referred to the isometric space group $\underline{Ia3d}$, can be described by placing Si and Al together in equivalent position 48$\underline{g}$ and oxygens in 96$\underline{h}$. This framework has a large void centered around 16$\underline{b}$ at $\frac{1}{8} \frac{1}{8} \frac{1}{8}$.

Náray-Szabó found good agreement between his powder data and calculated $F_{\underline{hkl}}$ values when he placed the Si, Al, and oxygen atoms in the positions of the analcime framework and the Cs atoms in the void at $\frac{1}{8} \frac{1}{8} \frac{1}{8}$.

The structure based on $\underline{Ia3d}$ makes no distinction between Si and Al atoms, since they are lumped together in $48\underline{g}$. Náray-Szabó preferred a structure in which these chemically different atoms could be assigned to distinct positions in a subgroup of $\underline{Ia3d}$. He found by trial that very good agreement with his data was obtained with the tetragonal subgroup $\underline{I4/acd}$ when he placed Cs in $16\underline{f}$, Al in $16\underline{f}$, Si in $32\underline{g}$ and distributed the 96 oxygens in 3 sets of $32\underline{g}$ positions with different parameters. The location of the water molecules was not determined, and the fact that the crystals contained sodium was neglected.

W.E. Richmond and F.A. Gonyer (1938) were dissatisfied that the formulas for pollucite presently accepted differed so significantly. Accordingly Gonyer made new analyses of the Greenwood, Maine pollucite. The analyses indicated the composition $Cs_{15}Al_{15}Si_{33} \cdot 4H_2O$ for one example, and $Cs_{14}Al_{14}Si_{34}O_{96} \cdot 9H_2O$ for another. In examining other analyses the authors suggested $Cs_{14+\underline{x}}Al_{14}(Al_{\underline{x}}Si)_{34}O_{96} \cdot (4 \text{ to } 9)H_2O$ as a more general formula.

About this same time Percy Quensel published an analysis of pollucite from the Varuträsk pegmatite in Sweden. Quensel noted that this analysis conformed closely to that by Wells for pollucite from Hebron. He made the following comparison of oxide ratios:

	SiO_2	Al_2O_3	R_2O	H_2O
Pollucite, Varuträsk	9.60	2	1.97	1.21
Pollucite, Hebron	9.06	2	2.08	1.04

In 1944, Nel published an analysis of pollucite from Karibib, South

West Africa. A formula based upon 96 oxygen atoms (excluding those with water) yielded the following composition:

$(Cs\ Rb\ K)_{10.03}Na_{3.97}Al_{14.81}Si_{33.39}O_{96} \cdot 5.85\ H_2O$. Nel stated that the unit cell formula for the Karibib pollucite was theoretically

$Cs_{10}Na_4Al_{14}Si_{34}O_{96} \cdot 6H_2O$. From his study if previously reported analysis of pollucite Nel concluded that the number of Cs atoms plus water molecules always summed to 16 per cell.

Nel suggested that pollucite and analcime were members of a series which were related by the replacement of Cs^+ by Na^+ plus H_2O. Nel thought that Na^+ plus H_2O would together occupy the space otherwise occupied by Cs^+, or vice versa. According to Nel the end members of the series would be Pollucite: $Cs_{16}Al_{16}Si_{32}O_{96}$ and Analcime: $Na_{16}Al_{16}Si_{32}O_{96} \cdot 16H_2O$. In support of his suggestion, Nel noted that there was a linear variation of the refractive index with the weight percentage of water in the known examples of pollucite and analcime.

Symmetry, cell, and cell content.

Clear, colorless pollucite from Rumford, Maine was used in the
present investigation. A small specimen, which came from the original
Brush collection, was obtained from the M.I.T. reference collection.
Several small fragments were examined optically and found to display
no birefringence. Their index of refraction was measured by the immersion
technique and found to be near 1.525, which is within the range of the
many published values.

One fragment was mounted for examination by the precession method.
A series of orientation photographs were taken, some of which showed
the symmetries 4mm, 6mm, and 2mm. This appeared to confirm the cubic
symmetry, and allowed adjustment of the crystal so that [110] was the
dial axis.

With this setting a simple rotation about the dial axis permitted
taking precession photographs with the possible symmetry axes [001],
[1$\bar{1}$1] and [1$\bar{1}$0] as precessing axes. It permitted also conveniently meas-
uring the interaxial angles on the dial. The relationships are illus-
trated in Fig. 1. Zero-level and upper-level precession photographs
were taken in each of the three directions indicated. The zero-level
photographs reproduced in Fig. 2 and Fig. 3 show the symmetries 4mm
and 2mm respectively. The first-level photograph shown in Fig. 4 shows
the symmetry 3m. These symmetries and interaxial angles are consistent

Fig. I
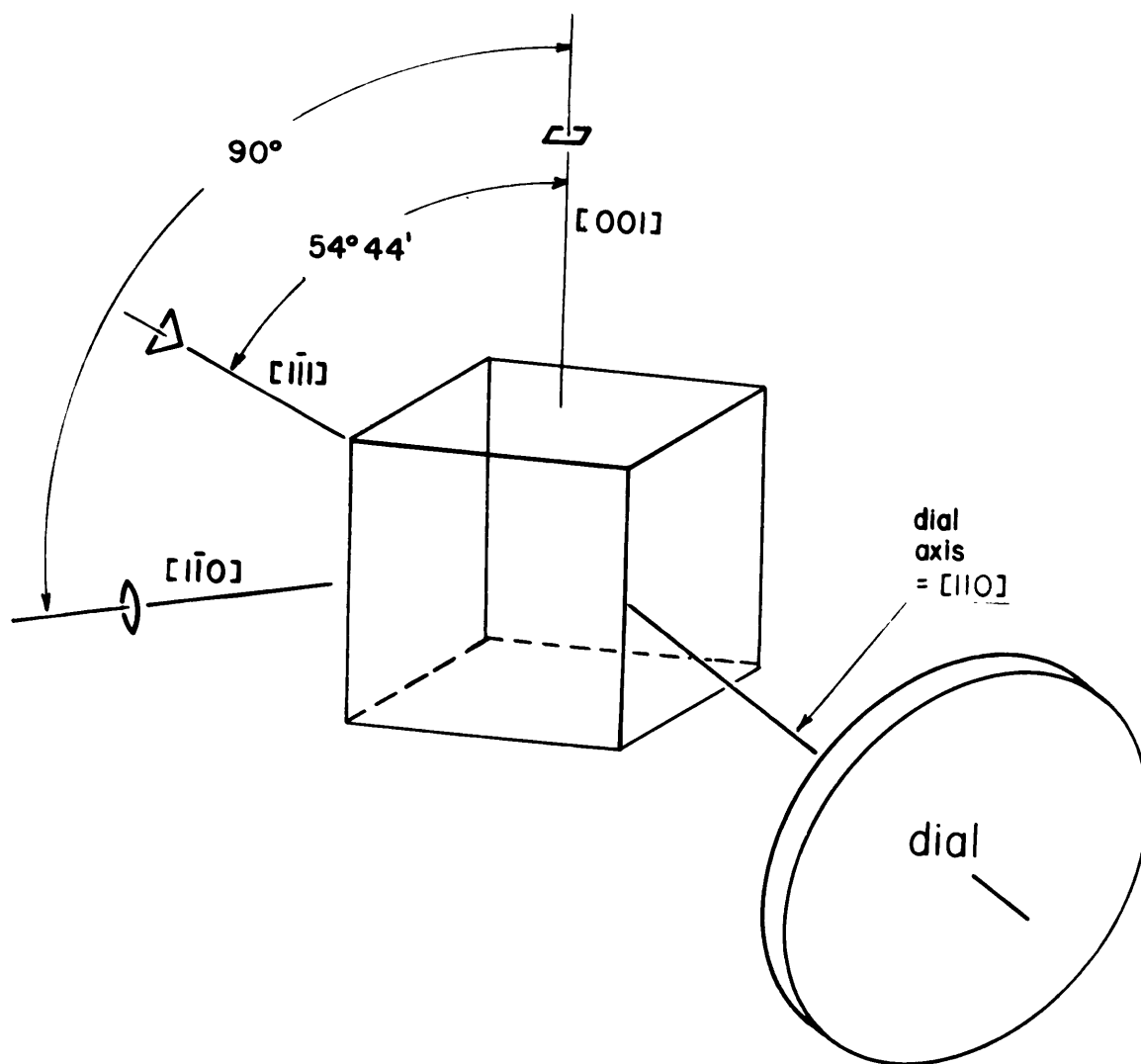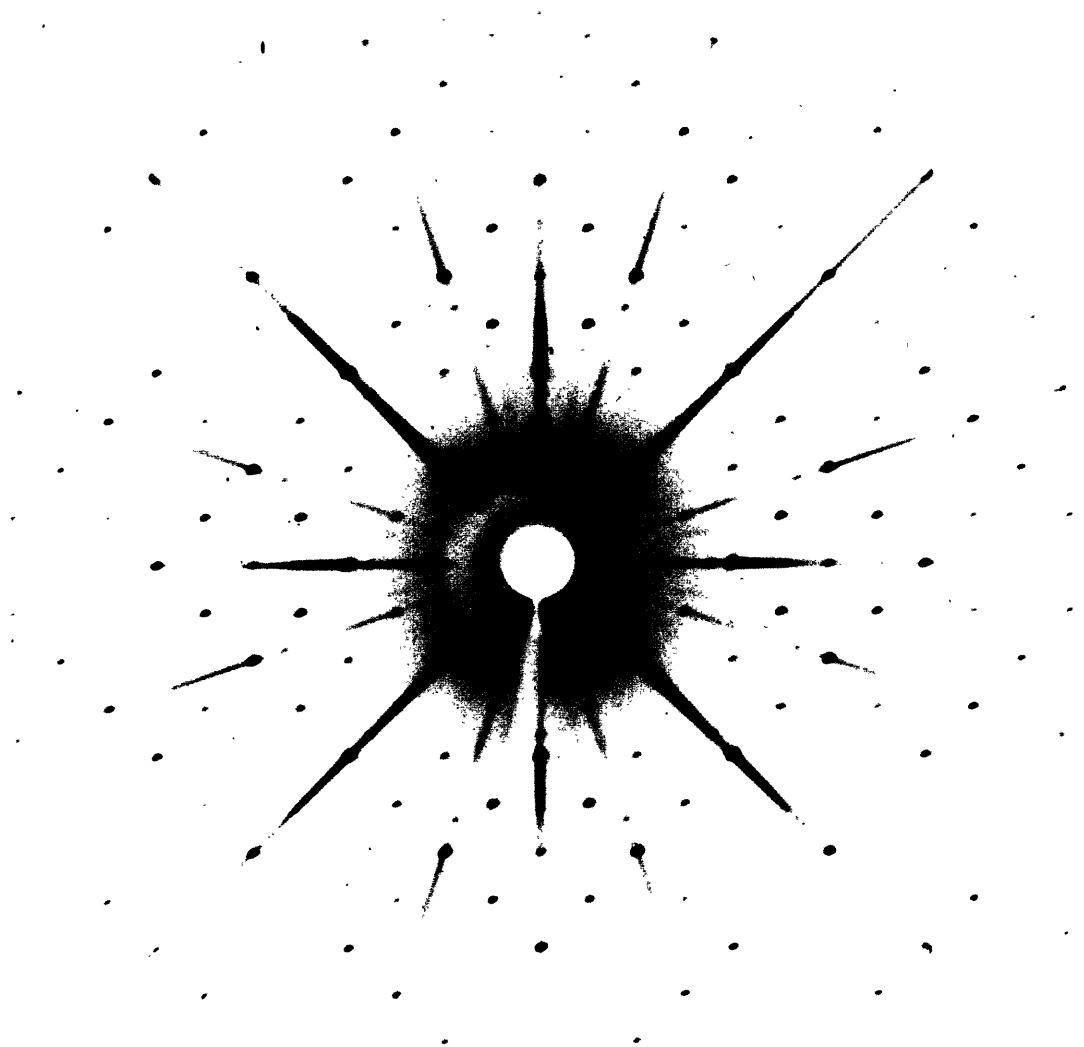
Fig. 2. Zero-level precession photograph (0kl), a axis.
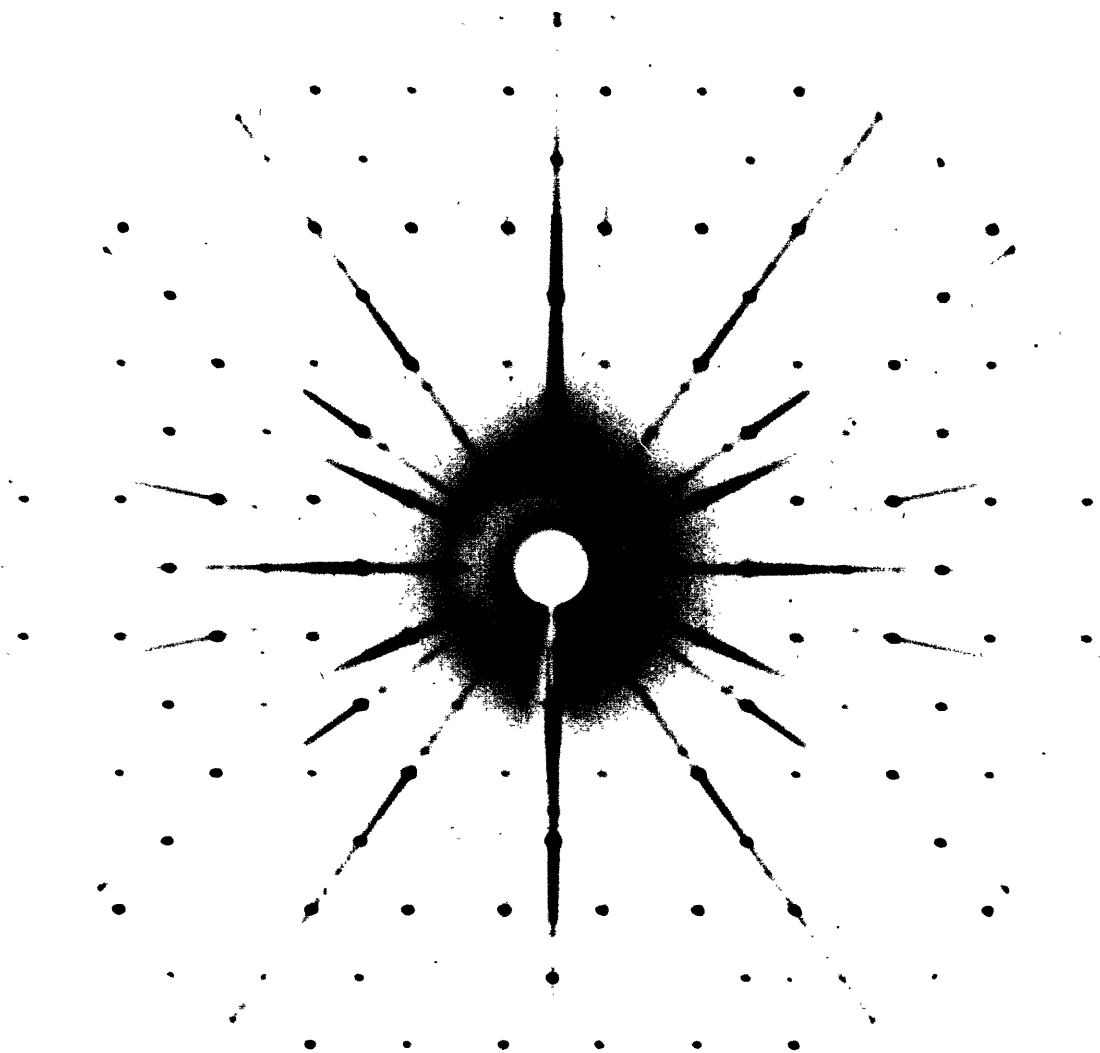
Fig. 3. Zero-level precession photograph (h$\bar{k}$0) [1$\bar{1}$0] axis.
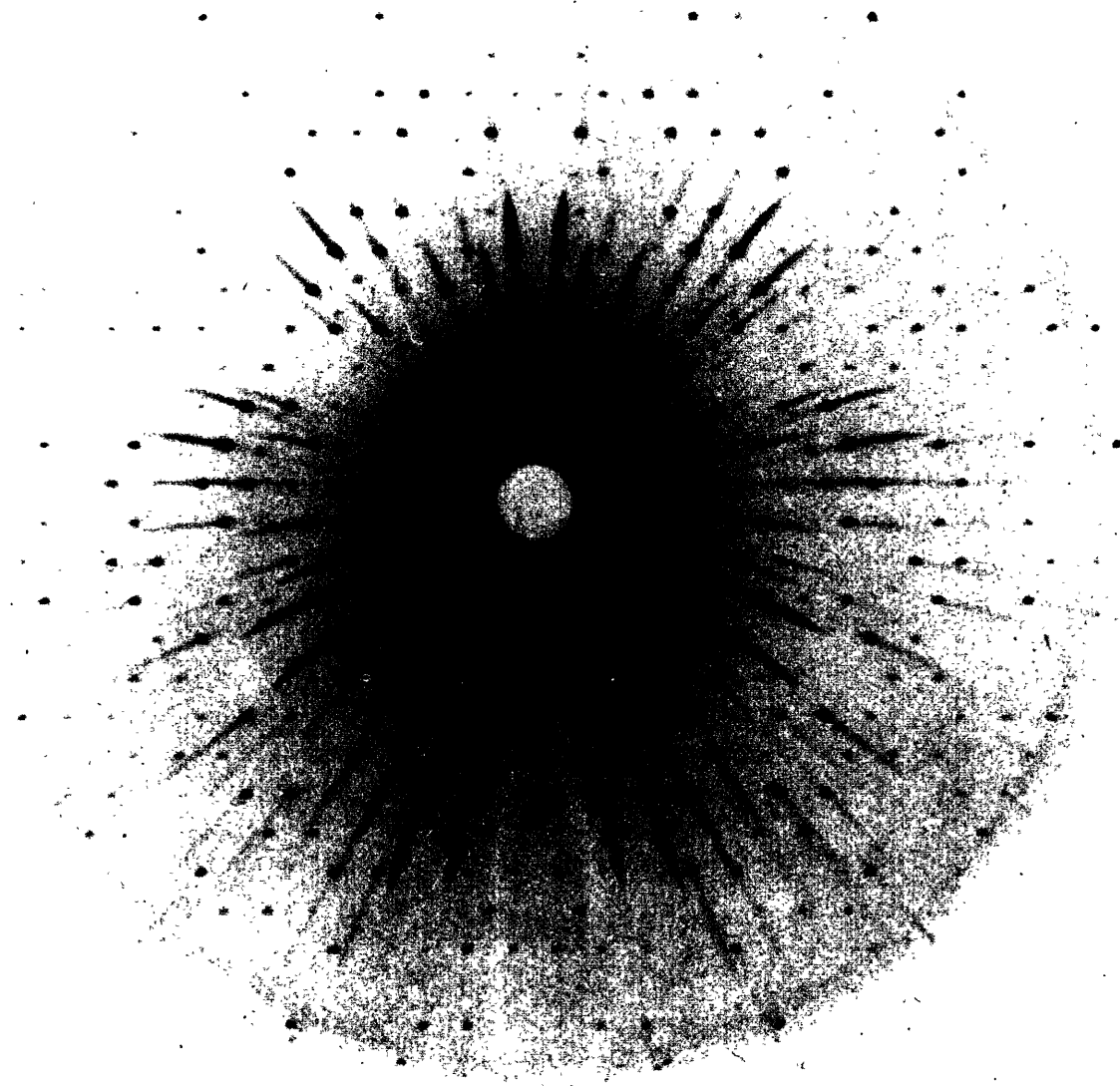
Fig. 4. First-level precession photograph (hkl) $[1\bar{1}\bar{1}]$ axis.

with a cubic crystal, and so provide convincing evidence that the

Friedel symmetry of pollucite is $\frac{4}{m} \; \bar{3} \; \frac{2}{m}$. The zero-level photographs

were supplemented by cone-axis photographs in each of the directions

[001], [1Ī1], and [1Ī0] . The cone axis photographs provided further

confirmation of the symmetry along each axis, and measurements of the

diameters of all the cone-axis rings allowed computations for the set-

tings of the upper level precession photographs.

After the cone-axis photographs were measured, first-level and

second-level precession photographs were taken. When those taken in

the [001] direction were superimposed, the pattern of points with re-

spect to the crystal axes was that shown in Fig. 5. This pattern of

points is indicative of the reciprocal lattice type $\underline{F}^*$. Because the

reciprocal of $\underline{F}^*$ is $\underline{I}$, the crystal lattice is body centered.

A search for systematic extinctions of certain reflections was

then made by comparing each zero-level photograph with an upper-level

photograph taken in the corresponding axial direction. The patterns of

missing points in the zero-level precession photographs was compared

with the patterns illustrated in The precession method by M.J.Buerger.

The pattern of missing points on the zero-level photographs taken in

the[001]direction revealed: (1) an axial glide isogonal with (001)

having glide component $\frac{a}{2}$ and; (2) screw axes 4_1 (or 4_3) isogonal with

the 4-fold axis of the point group. The pattern of missing points in

the zero-level photographs taken in the [1Ī0] directions showed a diamond
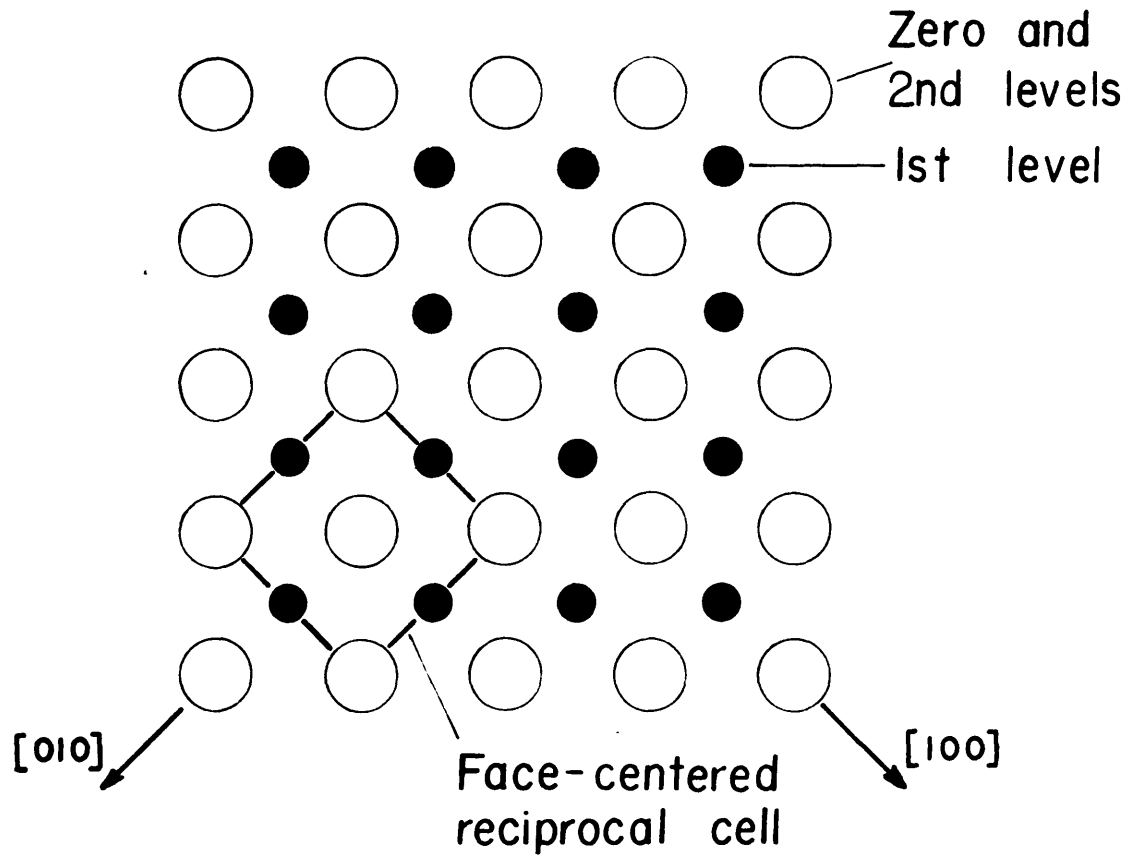
Fig. 5

glide isogonal with (1Ī0) having glide components $\frac{a}{4}\,\frac{a}{4}\,\frac{a}{4}$.

The qualitative information derived from the precession photographs could now be expressed by the diffraction symbol, which consists of the Friedel symmetry followed by the lattice type and the space group symmetry elements discovered in the systematic extinctions of certain reflections. The full diffraction symbol for pollucite is m̄3̄mIa3d. This diffraction symbol is consistent with only one space group, namely Ia3d. Thus the space group which had been derived for pollucite by Strunz in 1936, has been verified.

Although cell dimensions for pollucite were known from the literature, it was desirable to check these values and to obtain more accurate dimensions, if possible, for use in subsequent computations. Measurements were therefore made of the row spacings in the directions [100], [1Ī1] , and [1Ī0] on the zero-level precession photographs. These measurements allowed computations of the cell edge. In making these computations it was necessary to keep in mind the fact that a reciprocal cell translation is reciprocal to the parallel spacing magnitude of the direct cell, and generally not to the magnitude of identity period of the direct cell. The average value of the cell edge, as deduced from measurements on the precession photographs was $13.68 \pm .02\text{Å}$.

Similar values close to this one for the cell edge were also obtained from measurements on the cone-axis photographs, a front reflection rotation photograph, and a back reflection rotation photograph. The latter yielded a fairly precise average value of $a=13.70 \pm .02\text{Å}$. The

Precision obtained in measurements on the other photographs was much
less.

The most precise measurements for the computation of the cell
edge were obtained from a precision, back-reflection Weissenberg photo-
graph. This film was indexed with the aid of a Wooster-type chart and
front-reflection Weissenberg photographs of the zero and first levels.
The measurements of the different reflections, which included those
for $K\alpha_1$, $K\alpha_2$, and $K\beta$ wavelengths, resulted in computed values for
the cell edge $\underline{a}$ which differed systematicaly as a function of 2θ. The
values of $\underline{a}$ were plotted against $\cos^2\theta$ in Fig. 6. A graphical extra-
plolation of the data points to $\cos^2\theta = 0$ ($\theta = 90$) was made, beacause at
$\theta = 90$ many of the systematic errors are negligable, This extrapolation
gave the most precise determination of the cell edge $\underline{a} = 13.692 \pm .006 \overset{\circ}{A}$.
The precision is governed mainly by one's ability in measuring dis-
tances on the film, and can be estimated by repeated measurements of
the reflections.

The unit cell content and the ideal chemical formula of pollucite
from Rumford, Maine were determined using the procedures outlined in
Crystal structure analysis by Buerger. The chemical mass of the unit
cell was computed with the relationship $\underline{NM} = \underline{GV}$; where $\underline{N}$ is the number of
formula units per unit cell, $\underline{M}$ is the collective mass of the atoms in
formula unit, $\underline{G}$ is the density of the unit cell, and $\underline{V}$ is the volume of
the unit cell. The scheme of units observed was as follows:
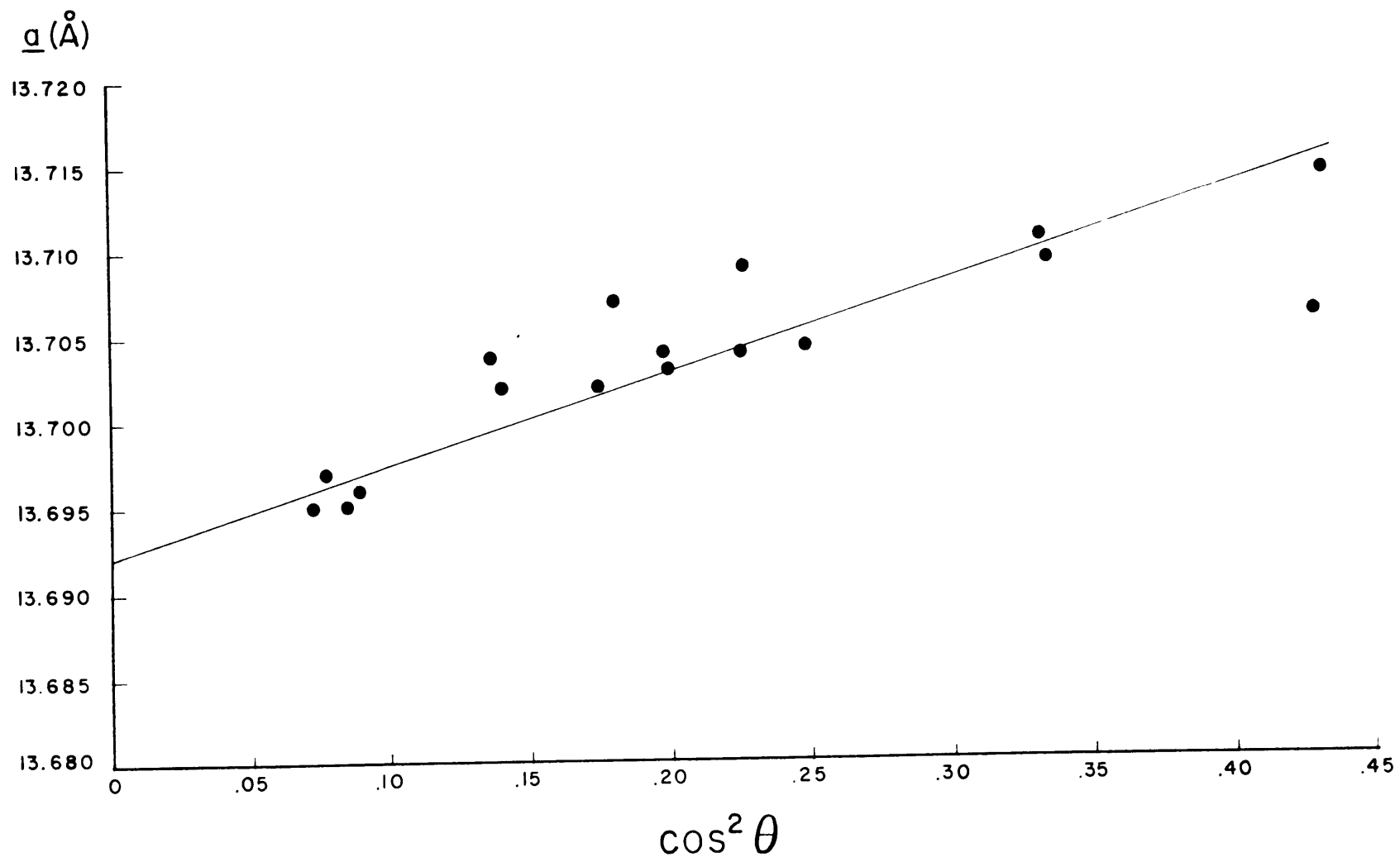
Fig. 6

$$NM(\text{ atomic-weight units}) \quad \frac{G(g./cc.) \times V(\overset{o}{A}^3) \times 10^{-24} \ (cc./\overset{o}{A}^3)}{1.660 \times 10^{-24} \ (g./ \text{ atomic-weight unit})}$$

The specific gravity of two small fragments was determined with a Berman torsion density balance. These gave an average value of $2.94^{\pm}.001$. With a cell edge of a $13.69\overset{o}{A}$, the cell volume is $2,566\overset{o}{A}^3$. For this specific gravity and cell volume, the cell mass is 4,545 chemical mass units.

The pollucite from Rumford, Maine had been analysed by H.W.Foote. The results of his analysis are given in column 2 in Tables 3 and 4. In Table 3 the total number of oxygen atoms, metal atoms and water molecules per unit cell have been computed on the basis of 4,545 chemical mass units. The results indicate that there are 96 oxygens per unit cell. This conclusion is acceptable on the grounds that one of the possible multiplicities of the space group Ia3d is 96.

In table 4 the number of atoms and water molecules per cell has been computed by assuming 96 oxygens per cell on a water-free basis. The results are consistent with those in Table 3. The cell mass computed in Table 4 is 4,574 chemical mass units, and is only slightly greater than that computed on the basis of a specific gravity of 2.94. Indeed, if the cell volume is $2,566\overset{o}{A}^3$, then the cell mass of Table 4 gives a specific gravity of 2.96. Foote stated that the pollucite for his analysis ranged between 3.029 and 2.938 in specific gravity.

It is regrettable that the specific gravity values cannot be more precisely determined, in order to provide a check on the chemical analyses.

Table 3

Computation of the cell content of Rumford pollucite
based upon a cell mass of 4,545 atomic weight units

Oxide	Average weight % oxide (H.W. Foote)	Mass per cell (At. Wt. units) (4,545) x wt. %	"Molecular" weight of oxide	Number of "molecules" of oxide	Number of metal atoms or molecules per cell	Number of oxygen atoms per cell
SiO_2	43.65	1,983.72	60.09	33.01	33.01	66.02
Al_2O_3	16.84	765.31	101.96	7.51	15.02	22.53
Cs_2O	36.14	1,642.42	281.82	5.83	11.66	5.83
K_2O	0.38	17.27	94.20	0.18	0.36	0.18
Na_2O	2.09	94.98	61.98	1.53	3.06	1.53
Li_2O	0.08	3.64	15.48	0.24	0.48	0.24
H_2O	1.58	71.80	18.00	3.99	3.99	
	100.76	4,579				96.33

Table 4

Computation of cell content and cell mass of Rumford pollucite based upon 96 oxygens per cell.

Oxide	Average weight % oxide (H.W.Foote)	Corrected average weight % oxide	Metals water and oxygen	Atomic (or molecular weight)	Weight % metals water	$\dfrac{\text{Weight}}{\text{Atomic wt.}}$	Atomic % (or molecular % H_2O)	Number of atoms and molecules per cell for 96 oxygens	Number of atoms x At. wt.
SiO_2	43.65	43.32	Si	28.09	20.25	0.7209	20.17	32.98	926.4
Al_2O_3	16.84	16.71	Al	26.98	8.84	0.3277	9.17	14.99	404.4
Cs_2O	36.14	35.87	Cs	132.91	33.83	0.2545	7.12	11.64	1547.1
K_2O	0.38	0.38	K	39.10	0.32	0.0082	0.23	0.38	14.9
Na_2O	2.09	2.07	Na	22.99	1.54	0.0670	1.87	3.06	70.3
Li_2O	0.08	0.08	Li	6.939	0.07	0.0101	0.28	0.46	3.2
H_2O	1.58	1.57	H_2O	18.02	1.57	0.0871	2.44	3.99	71.9
			Ox	16.00	33.58	2.0988	58.72	96.00	1536.0
	100.76	100.00			100.00	3.5743	100.00		4,574.

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If pollucite is a stoichiometric compound, then in order to establish charge balance, the number of Al atoms per cell should equal the number of total alkali atoms per cell. In Tables 3 and 4, the number of Al atoms is about 15, while the number of all alkali atoms is closer to 16 (actually 15.55). To arrive at an idealized cell formula it is necessary to decide whether there are 15 or 16 total alkali atoms, and consequently whether there are 15 or 16 aluminum atoms. Since the space group $\underline{Ia3d}$ has 16-fold, 24-fold, 32-fold, 48-fold, and 96-fold equipoints, it is reasonable make the number of each kind of atom, or sum of chemically similar atoms, conform to the numbers 16, 24, 32, 48, and 96. Thus it is reasonable to conjecture that there are 16 alkali atoms, and consequently 16 Al atoms per cell. Since there are 16 Al atoms, there can be only 32 Si atoms per cell. A spectrographic analysis made by Mr. Phillip Fenn in the M.I.T. Cabot Laboratory showed the Cs:Na ratio was actually 4:1 . This would indicate, on the basis of 3 Na atoms per cell, that the analysis should have given 12 Cs atoms per cell. This would bring the actual alkali total closer to 16 atoms per cell. If the Li and K are included with Na, then the idealized cell formula for pollucite from Rumford, Maine can be written as: $Cs_{12}Na_4Al_{16}Si_{32}O_{96} \cdot 4H_2O$.

Intensity measurement.

For measurement of diffracted intensities several small spheres were prepared in an anular, plastic sphere grinder, which employs a tangential jet of water. These spheres were exceptionally round, having no visible eccentricity. No birefringence could be detected with a polarizing microscope when they were immersed in a liquid whose refractive index was that of pollucite, 1.52. One sphere, which had a radius of 0.17 mm, was chosen for intensity measurements. After it had been oriented on the precession camera, it was remounted for ratation about the a axis. A front-reflection Weissenberg photograph was then taken, and no detectable splitting of reflections was seen that might indicate that the crystal was twinned.

The integrated intensities were measured on a single crystal diffractometer having equi-inclination Weissenberg geometry. CuKα radiation (nickel filtered) and a proportional counter were used for the data collection.

The final orientation of the crystal on the diffractometer was effected by the Fankucken method. This method for accurately orienting a crystal is evidently in common use, but the sole description of the method lies within two brief paragraphs in an article by I. Fankucken. The method allows a stack of crystal planes, ussually (001), to be oriented so that they are perpendicular to the direction of the rotation axis of the instrument. Consequently, a rational direction, usually c,

can be made the axis of rotation of the crystal.

For equi-inclination Weissenberg geometry, the Fankucken method
is here described for the common case. The crystal is oriented for
rotation about c by using some less accurate means, such as the preces-
sion camera or optical goniometer; it is then placed on the diffracto-
meter. The counter is then set so that it is receiving impulses of the
$K\alpha_1$, line from a reflection of the class 00L, where L is greater than
zero. For this class of reflections the azimuth angle T is zero, but
the equi-inclination angle μ is greater than zero. The angle μ is a func-
tion of the index L. If the crystal were already in perfect orientation
for rotation about c, then the crystal could be precisely set at the
critical angle of reflection of the $K\alpha_1$ line if an accurate setting of
the equi-inclination angle μ could be made. This ideal situation is
illustrated in Fig. 7a. If μ is accurately set and the c axis is oriented
parallel to the rotation axis (dial axis), then the stack of planes
normal to c remains perpendicular to the axis of rotation throughout
any rotation of the dial. Consequently, the intensity received by the
counter during a rotation of 360° on the dial is a constant maximum
value, because the stack of planes maintain the inclination angle μ with
the x-ray beam throughout the rotation.

Usually the crystal is not yet in perfect orientation when placed
on the diffractometer. In this circumstance, the inclination angle
varies between $\mu + \Delta\mu$ and $\mu - \Delta\mu$ in a 180° rotation of the dial. This is
illustrated in Fig. 7b. In a 360° rotation of the dial there are two
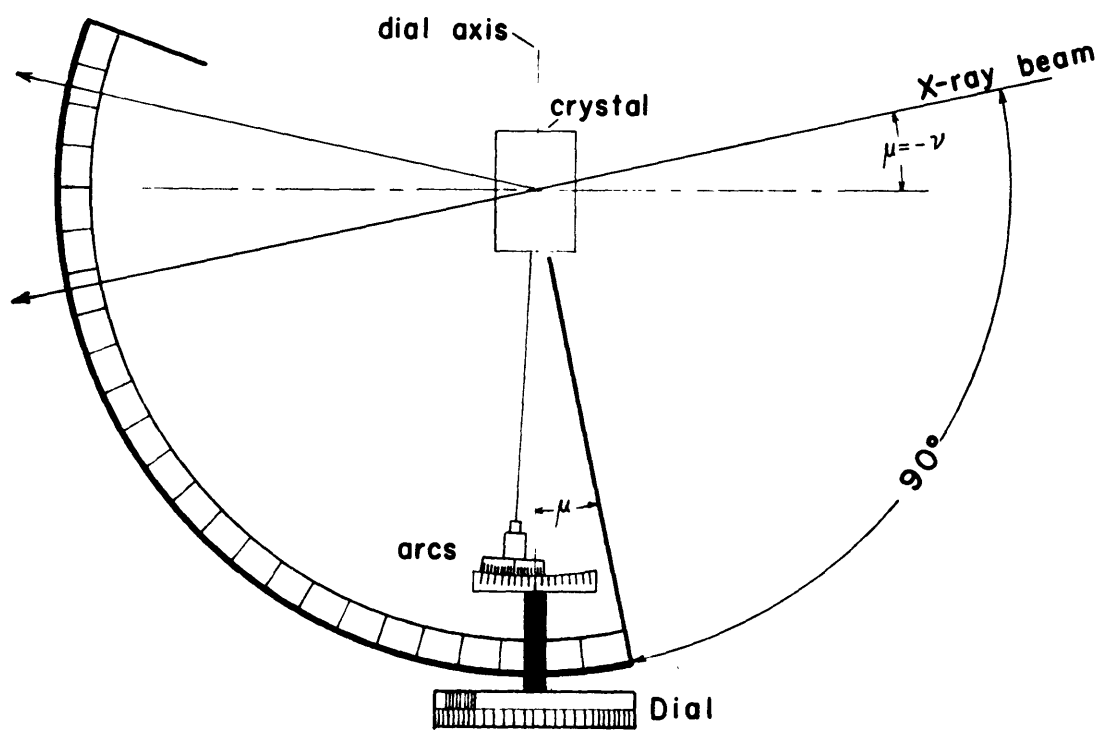
Fig. 7a
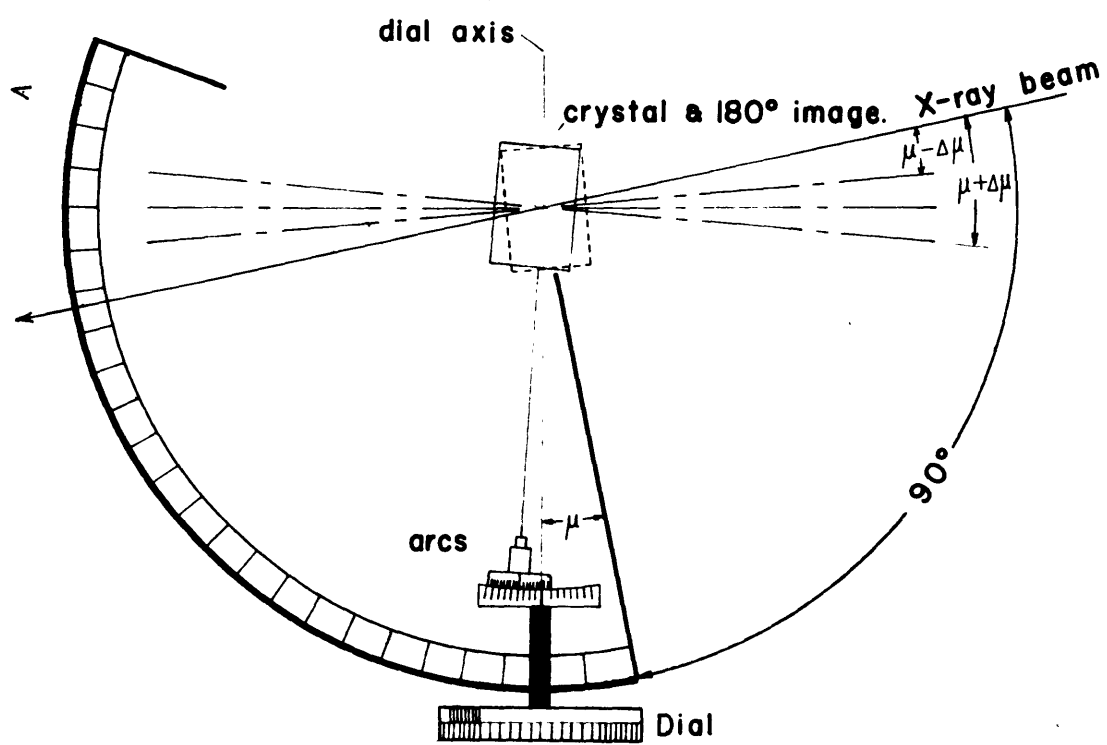
Fig. 7b

positions 180° apart at which the inclination angle is equal to μ , and
at these two positions the reflected intensity is a maximum. For all
other positions the reflected intensity is noticeably less. If μ were ac-
curately set to within a few seconds of arc, the crystal could be easily
oriented by adjusting the arcs of the goniometer head so that the reflected
intensity remained a maximum during a 360° rotation of the dial. The arc
that is to be adjusted must be set parallel to the plane containing the
x-ray beam and the rotation axis.

It so happens that the diffractometer usually cannot be visually
set with an accuracy better than 5 minutes of arc and, therefore, the
equi-inlination angle is usually a little off from its precise setting.
In this case, when the crystal is not yet perfectly aligned, the reflec-
ted intensity passes through two maxima whose peaks are not exactly
180° in separation. The setting of angle μ must then be adjusted so that
these maxima occur 180° apart. Fankucken suggests turning the dial to
"the angle setting at which the maximum should have been," and by this
he probably means 180° from one of the two maxima. At this position of
the dial one can adjust the inclination angle until the reflected inten-
sity is a maximum. By repeating this process several times, the maxima
become separated by 180°. The inclination angle is then locked and the
goniometor arcs adjusted so that the reflection remains at a maximum
during rotation of the dial. Then the stack of planes normal to c are
automatically perpendicular to the rotation axis of the dial.

The parameters Υ and φ for the diffractometer settings were obtained

with a program written by C.T. Prewitt for the IBM 7.094 computer. This program also computes the Lorentz-polarization factor and $\sin\theta$ for each reflection. Further preparations for collecting intensities included selecting the most suitable settings in the counter circuitry and adjusting the diffractometer so that the crystal would remain within a cross section of the x-ray beam having constant intensity.

The intensity data consisted of a variable-time scan count and two fixed-time background counts. The average background counts was subtracted from the scan count to obtain the correct measure of the integrated intensity.

Intense reflections which exceeded 10,000 counts per second were above the linearity range of the counter and, therefore, were collected using an aluminum foil as an absorber. The absorption of the foil was found by measuring several intense reflections within the linearity range, both with and without the foil. The ratio of the different values obtained gave a most satisfactory scale factor for the reduction of the intensities due to the absorber.

Two hundred and seven independent reflections were measured, and the resulting integrated intensities were corrected for Lorentz, polarization and absorption factors using the IBM 7094 programs GAMP and ABSRP 2 written by H.H. Onken and C.T. Prewitt respectively.

Structure determination.

Pollucite can be thought of as a structure containing a set of heavy atoms. Each Cs atom has 55 electrons and behaves as a heavy atom compared to the other atoms of Si, Al, Na, O, and H, which have 14, 13, 11, 8, and 1 electron respectively. Náray-Szabó concluded that the Cs atoms would occupy one equi-point at $\frac{1}{8}\,\frac{1}{8}\,\frac{1}{8}$ (16$\underline{b}$) in space group $\underline{Ia3d}$. If the Cs atoms in pollucite do actually occupy only one equipoint, it could be expected that the major features of a Patterson function would permit the Cs location to be unambiguously determined.

The corrected values of the integrated intensities were used as the coefficients, $\underline{F}\,(\underline{hkl})^{2}$'s, for computing a three-dimensional Patterson function. The computations were made using the program MIFR 2A written for the IBM 7094 computer by D.P.Shoemaker, L. Katz, and K. Seff. The peak heights of the most prominent peaks corresponded to the expected peak height for a pair of Cs atoms as calibrated from the height of the origin peak. The location of these in the Patterson function required the location of the Cs atoms at $\frac{1}{8}\,\frac{1}{8}\,\frac{1}{8}$ etc. (equipoint 16$\underline{b}$). This confirmed Náray-Szabó's location for the Cs atoms.

Since the structure is centrosymmetrical and the origin is chosen at a symmetry center, then the structure factors $\underline{F}(\underline{hkl})$ are all real quantities with positive or negative signs. It was anticipated that most of the signs of the structure factors would be determined by the contribution of the Cs atom alone. If the Cs atoms are to occupy a special

position in a centro-symmetrical structure, then their contribution to
the structure factors would always be a relatively large in-phase value.
On the other hand, it was expected that the atoms in the residual part
of the structure would be more or less uniformly, but randomly distributed.
Waves scattered by this kind of distribution tend to annul one another.
For this reason the contributions of the atoms in the residual part of
the structure would rarely be a maximum, and in most reflections would
be far less than their in-phase maximum value. On this basis one may an-
ticipate that the contribution of the Cs atoms for all or most reflections
would usually be greater than the contribution of the residual part of
the structure. In other words, the contribution of the Cs atoms was expec-
ted to dominate each $\underline{F}$(hkl), and thus determine its sign. The result of
this reasoning is that the observed structure factors can be correctly
phased by giving them the signs of the calculated structure factors
computed for the contribution of the Cs atoms alone. Then, a preliminary
Fourier synthesis phased upon the Cs atoms should give a first approx-
imation of the actual structure of pollucite. This approach to the solu-
tion of the structure is one example of the heavy atom method, and it
proved to be a fruitful approach for pollucite.

A Fourier synthesis was made using the observed $\underline{F}$ (hkl) 's and
the phases determined by the Cs atoms. The computations were made using
the M.I.T. version of the Los Alamos Fourier program GINPUT GENFOR. The
contoured Fourier maps showed peaks not only at the locations of the Cs
atoms, but also in the regions of Náray-Szabó's (Si, Al) and O atoms

of the framework. Because of this result it was decided to test the structure proposed by Náray-Szabó for the space group $\underline{Ia3d}$. Structure factors for all reflections were calculated using the coordinates reported by Náray-Szabó and the simplified composition $(CsAlSi_2O_6)$ assumed by him. For the purpose of these calculations, a preliminary choice was made for scale factor and reasonable isotropic temperature factors. The discrepancies in the calculated and observed structure factors gave a residual of R=23.9%, where

$$\underline{R} = \frac{\sum ||\underline{F}_{obs}| - |\underline{F}\ calc||}{\sum |\underline{F}\ obs|}$$

This low $\underline{R}$ value, in conjuction with the results found by the Fourier synthesis, indicated that Náray-Szabó's structure was basically correct.

A decision was still required between isometric and tetragonal symmetries and between the possible assignments of Cs, Na, and H_2O to the voids in the framework. The computations based on the analysis given by Foote indicated that there are 12 Cs, 4 Na, and 4 H_2O per cell. Because the 12 Cs atoms occupy an equipoint of multiplicity 16 in both the cubic and the tetragonal space groups, it was reasonable to predict that the remaining 4 positions might be filled with either the 4 Na atoms or the 4 water molecules, In this case either $|12Cs+4H_2O|$ or $|12Cs+4Na|$ must occupy the voids centered about equipoint 16b at $\frac{1}{8} \frac{1}{8} \frac{1}{8}$. An attempt was made to refine in the isometric system structures with these two alternative assignments of atoms to voids. The water molecule was represented by a fully ionized oxygen atom, O^{-2}. Both models were to be refined with 4 atoms missing. Their composition, in comparison to the complete formula

for pollucite, can be summarized as follows:

Rumford, Me. Pollucite...$Cs_{12}Na_4Al_{12}Si_{32}O_{96} \cdot 4H_2O$

Model 1 (H_2O missing).....$(Cs_{12}Na_4)$ $(Al_{12}Si_{32}O_{96})$

Model 2 (Na missing) .....$(Cs_{12}, 4.H_2O)$ $(Al_{12}Si_{32}O_{96})$
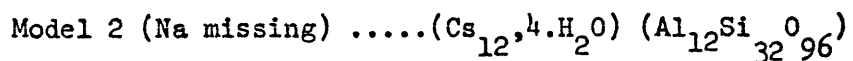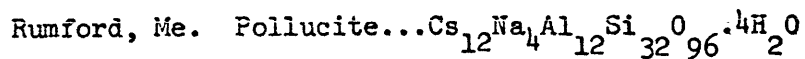
It was anticipated that once the paramenters of the atoms in these two
incomplete models were refined, a Fourier difference synthesis would
reveal the positions of the missing atoms (Na or H_2O), and that a deci-
sion could then be made as to which atoms were to be assigned to the
different voids.

Refinement.

A least-squares refinement of the pollucite structure was carried out, using the full-matrix program SFLSQ 3 written by C. Prewitt for the IBM 7094 computer. For the alternative models, atomic scattering factor curves were computed for the combinations: $12Cs^{\circ}+4Na^{+1}$, and $12Cs^{\circ}+4O^{-2}$. Atomic scattering factors for half-ionized oxygen atoms, and a combined scattering curve for $12Al^{+1.5}+32Si^{+2}$ were used in each model. The initial isotropic temperature coefficients were choosen arbitrarily to be: $B(Cs+Na)=1.3$, $B(Cs+O^{-2})=1.3$, $B(Si+Al)=0.4$ $B(O^{-1})=0.8$. At this stage of refinement, an arbitrary weighting scheme was used which gave equal weights to all reflections. Both models were refined with one cycle of least-squares, allowing only the scale factor to vary, followed by one cycle with fixed scale factor and isotropic temperature coefficients, allowing the free coordinates to vary, followed by one cycle in which only the individual isotropic temperature coefficients were allowed to vary. This greatly lowered the sum of all the discrepancies in the $F(hkl)$'s from a value of $R=23.9\%$ to a value of $R=9.7\%$ for both models. That both models should refine to the same R value is not surprising, because both models are essential equivalent in distribution of scattering power. The reason for this is that Na^{+1} and O^{-2} are isoelectronic ions, each having 10 electrons, and although the scattering power of O^{-2} falls off much more rapidly that Na^{+1} with increasing $(\sin\theta)/\lambda$, a difference due to this effect is not noticeable in the two combined scattering curves for $12Cs^{\circ}+4Na^{+1}$ and $12 Cs^{\circ}+4O^{-2}$ which represent the two models.

Thus both models should give equivalent structure factors, and accually did so at this stage of the refinement.

A Fourier difference synthesis based upon calculated structure factors at $\underline{R}$ 9.7% (omitting H_2O and Na in models 1 and 2 respectively) showed residual electron-density peaks near $\frac{1}{4} \frac{1}{8} O(24\underline{c})$, lying midway between the Cs locations. These must represent the 4 missing Na ions or water molecules. But, because of their location, these peaks cannot be accepted as representing the $4Na^+$ ions, for the Na^+ ions would touch the Cs^+ ions. The ionic radius of Cs is approximately $1.7\overset{o}{A}$. In pollucite the Cs atoms lie on equivalent positions which are $4.8\overset{o}{A}$ apart. Thus the space between two Cs ions is $4.8\overset{o}{A}$ - 2x $1.7\overset{o}{A}=1.4\overset{o}{A}$. Because the ionic diameter of Na is approximately $1.9\overset{o}{A}$, the Na ions cannot occupy these positions between the Cs ions. On the other hand, if the 4 Na ions go with the 12 Cs ions to fill the large voids, the H_2O molecules can occupy $\frac{1}{4} \frac{1}{8} O(24\underline{c})$ if each H_2O resides between $2Na^+$ ions or between a Na^+ and a Cs^+ ion where the spaces between these pairs of ions would be $2.8\overset{o}{A}$ and $2.1\overset{o}{A}$ respectively. Because the diameter of a H_2O molecule is approximately $2.8\overset{o}{A}$ the space available between two Cs^+ ions is insufficient to accommodate the H_2O molecule. Therefore, the H_2O molecules are definitely associated with the Na^+ ions (and Li^+) in pollucite.

The final model to be refined had the following assignments of atoms:

$12Cs+4Na$	in the large voids,	16$\underline{b}$,	at $\frac{1}{8} \frac{1}{8} \frac{1}{8}$
$4H_2O$	between the large voids,	24$\underline{c}$,	at $\frac{1}{4} \frac{1}{8} 0$
12 Al+32Si	in the framework,	48$\underline{g}$,	at x, $\frac{1}{4}$-x, $\frac{1}{8}$
96 O	in the framework,	96$\underline{h}$,	at xyz

At this point in the refinement a correction was applied for ef-
ects of anomalous scattering of the atoms. The dispersion corrections
for the atomic scattering factors f are given in Table 5A. The values
of the corrections for the Cs atom with CuKα radiation are relatively
large, while the values for the other atoms in pollucite are relatively
small. Because 12 Cs plus 4Na atoms, and 32 Si plus 16 Al atoms occupy
the same equipoints respectively, the values of $\Delta f'$ and $\Delta f''$ for these
pairs of atoms were averaged according to the ratios of atoms in each
pair. The final values of the dispersion corrections are given in Table 5B.

Before proceeding to anisotropic temperature refinement, a new
weighting scheme was introduced which is based upon the discrepancies
between $\left| F_{obs} \right|$ and $\left| F_{calc} \right|$. This particular type of weighting scheme
is one first suggested by A. de Vries in 1965. The reflections were sorted
ine the order of increasing $\left| F_{obs} \right|$, and grouped into sets of 10 reflec-
tions. For each group a residual R was calculated using the program ROFF
written by B.J. Wuensch. This R value computed for a group of 10 reflec-
tions is a statistical measure of the probable error in the observed
structure factors of the group.

In Fig.8 these R values are plotted against the corresponding
average values of $\left| F_{obs} \right|$ taken over each group of 10 reflections. A
weighting scheme was then obtained which is based on the inverse of this
curve. Equal weights, $W=1$, were assigned to reflections having
$\left| F_{obs} \right| \geq 200$, and different weights were assigned to reflections having
$\left| F_{obs} \right| < 200$ by using $W = \left| F_{obs} \right| / k$ where $k = 200$. The least-squares

Table 5A

Dispersion corrections, at $(Sin \theta)/\lambda = 0$ and with CuKα radiation, for scattering factors of atoms in pollucite.

Atom	Atomic Number	Δf'	Δf"
O	8	0.0	0.1
Na	11	0.1	0.2
Al	13	0.2	0.3
Si	14	0.2	0.4
Cs	55	-1.7	8.3

Table 5B

Final dispersion corrections for scattering factors of atoms and atom pairs in pollucite.

Atom or atom pair	Equipoint	Δf'	Δf"
O	96h	0.0	0.1
32Si+16Al	48g	0.2	0.4
$H_2O=O$	24c	0.0	0.1
12Cs+4Na	16b	-1.3	6.1
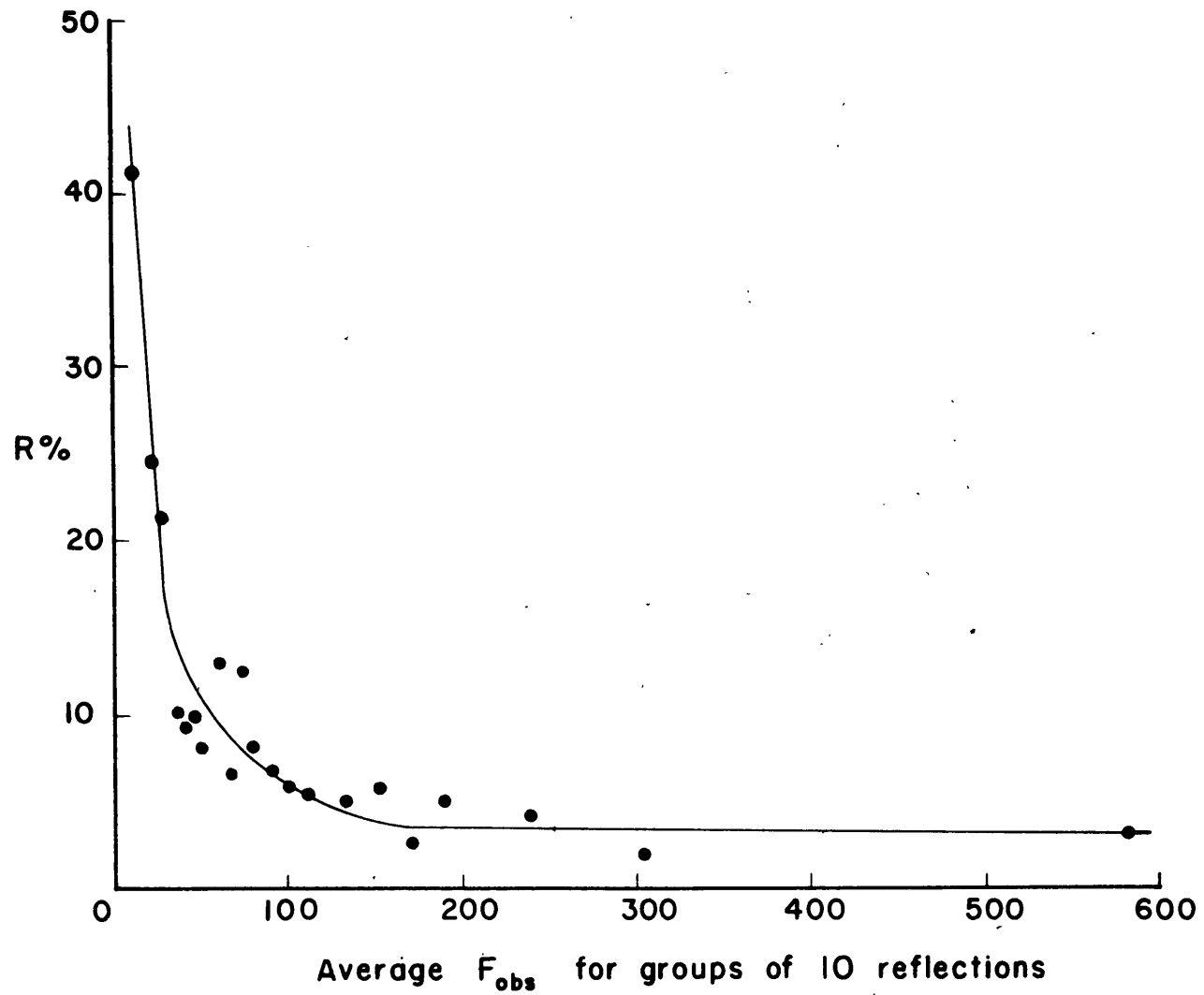
Fig. 8

program SFLSQ-3 minimizes the value of $\underline{W} \, (\, |\underline{F}_{obs}| - |\underline{F}_{calc}| \,)^2$.

The last stage of the refinement of the pollucite structure included the application of anisotropic temperature factors to the calculated structure factors. The mathematical expression of the anisotropic temperature motion of the individual atoms involves a symmetric tensor with six independent components, or thermal parameters, β_{ij}. The least-squares program SFLSQ 3 computes a temperature correction of the form

$$T = e^{-(h^2 \beta_{11} + k^2 \beta_{22} + l^2 \beta_{33} + 2hk \, \beta_{12} + 2hl \, \beta_{13} + 2kl \, \beta_{23})}$$ which is applied to each atom's contribution to $\underline{F}_{calc}$. The restrictions among the thermal parameters β_{ij}, which are imposed by symmetry relations for atoms in special positions, were determined by the method suggested by Henri A. Levy in 1956. The determination of the restrictions on the β_{ij}'s for the atoms in special positions is shown in Table 6.

With isotropic temperature factors the final model, which now included the 4 missing water molecules, had a residual of $\underline{R}=8.6\%$. With the new weighting scheme and the corrections for anomalous scattering, several cycles of anisotropic temperature refinement lowered the residual from $\underline{R}=8.6\%$ to $\underline{R}=5.5\%$. The pollucite structure was then considered to be well refined . The final valves for $\underline{F}_{obs}$ and $\underline{F}_{calc}$ are given in Table 7, and the final parameters are given in Table 8.

Table 6

Determination of the restrictions on the β_{ij}'s.

Cs and Na, equipoint symmetry 32.

The 3-fold axis transforms position xyz to $\bar{z}\bar{y}\bar{x}$. This transformation imposes all the necessary restrictions, since those imposed additionally by the 2-fold axes are redundant.

β_{ij}	$(xyz \longrightarrow \bar{z}\bar{y}\bar{x})$ $x_i x_j$	$x'_i x'_j$	$\beta_{ij} = \beta'_{ij}$	Restrictions
β_{11}	x^2	z^2	$\beta_{11} = \beta_{33}$	$\beta_{11} = \beta_{33}$
β_{22}	y^2	y^2	$\beta_{22} = \beta_{22}$	$\beta_{22} = \beta_{22}$
β_{33}	z^2	x^2	$\beta_{33} = \beta_{11}$	
β_{12}	xy	yz	$\beta_{12} = \beta_{23}$	$\beta_{12} = \beta_{23}$
β_{13}	xz	xz	$\beta_{13} = \beta_{13}$	$\beta_{13} = \beta_{13}$
β_{23}	yz	xy	$\beta_{23} = \beta_{12}$	

Si and Al, equipoint symmetry 2

The 2-fold axis transforms position xyz to $\bar{y}\bar{x}\bar{z}$.

β_{ij}	$(xyz \longrightarrow \bar{y}\bar{x}\bar{z})$ $x_i x_j$	$x'_i x'_j$	$\beta_{ij} = \beta'_{ij}$	Restrictions
β_{11}	x^2	y^2	$\beta_{11} = \beta_{22}$	$\beta_{11} = \beta_{22}$
β_{22}	y^2	x^2	$\beta_{22} = \beta_{11}$	
β_{33}	z^2	z^2	$\beta_{33} = \beta_{33}$	$\beta_{33} = \beta_{33}$
β_{12}	xy	xy	$\beta_{12} = \beta_{12}$	$\beta_{12} = \beta_{12}$
β_{13}	xz	yz	$\beta_{13} = \beta_{23}$	$\beta_{13} = \beta_{23}$
β_{23}	yz	xz	$\beta_{23} = \beta_{13}$	

Table   7

Final $\underline{F}_{obs}$ and $\underline{F}_{calc}$ of pollucite

H	K	L	$\underline{F}_{obs}$	$\underline{F}_{calc}$
2	2	0	58.50	46.92
4	0	0	614.71	637.19
4	2	0	59.88	48.18
4	4	0	349.25	350.05
6	2	0	52.61	47.13
6	4	0	105.06	99.42
8	0	0	361.49	349.13
8	2	0	70.28	62.05
6	6	0	74.65	69.17
8	4	0	225.66	218.35
8	6	0	102.84	97.59
10	2	0	30.53	30.49
10	4	0	61.40	58.79
8	8	0	154.53	153.56
10	6	0	37.81	36.02
12	0	0	147.08	142.81
12	2	0	58.12	54.82
12	4	0	108.65	107.75
10	8	0	62.11	60.49
12	6	0	94.58	95.96
10	10	0	26.50	23.76
12	8	0	77.22	77.98
14	4	0	26.14	27.91
14	6	0	6.54	1.52
12	10	0	47.00	51.12
16	0	0	43.20	42.31
16	2	0	44.15	48.62
14	8	0	6.91	4.87
16	4	0	34.12	33.31
2	1	1	40.60	36.75
3	2	1	138.62	124.38
4	3	1	69.82	64.65
5	2	1	78.43	73.15
6	1	1	49.59	51.94
5	4	1	21.66	20.73
6	3	1	106.37	103.93
7	2	1	133.35	127.54
6	5	1	56.52	54.67
7	4	1	81.25	75.77
8	3	1	78.42	74.15

H	K	L	$\underline{F}_{obs}$	$\underline{F}_{calc}$
9	2	1	27.88	20.41
7	6	1	110.15	111.62
8	5	1	15.86	17.38
9	4	1	24.79	21.09
10	1	1	186.31	185.19
10	3	1	155.32	154.42
8	7	1	100.89	98.07
9	6	1	21.50	17.66
11	2	1	41.40	39.90
10	5	1	155.50	156.74
11	4	1	57.37	56.87
12	5	1	14.74	12.35
13	2	1	39.37	40.00
9	8	1	26.05	22.14
10	7	1	97.40	99.80
12	3	1	27.81	26.22
11	6	1	44.60	45.15
10	9	1	77.92	79.60
13	4	1	36.61	36.07
11	8	1	74.64	75.34
12	7	1	32.55	30.79
14	1	1	122.42	123.33
14	3	1	99.29	100.97
13	6	1	26.81	26.66
14	5	1	91.28	92.28
11	10	1	32.11	32.10
15	2	1	20.85	21.21
13	8	1	40.97	42.55
15	4	1	37.42	39.50
14	7	1	63.65	67.86
15	6	1	28.84	31.59
16	3	1	6.46	4.65
12	11	1	19.80	18.46
13	10	1	42.47	44.73
14	9	1	40.15	42.85
16	5	1	4.94	6.47
2	2	2	15.94	.00
3	3	2	277.63	259.58
4	2	2	44.68	34.55
5	3	2	152.36	139.79
5	5	2	96.13	90.77
6	4	2	39.92	35.23
7	3	2	229.40	218.77
8	2	2	28.12	25.16
7	5	2	126.58	117.27
8	4	2	38.66	32.69
9	3	2	24.83	19.27
7	7	2	212.41	208.27
8	6	2	32.90	31.76

H	K	L	F_{obs}	F_{calc}
9	5	2	66.24	66.28
10	4	2	40.85	22.09
11	3	2	81.74	76.90
9	7	2	46.09	42.09
11	5	2	91.62	90.94
12	2	2	20.52	17.98
21	4	2	40.11	38.15
10	8	2	24.34	21.63
11	7	2	94.75	91.80
13	3	2	50.14	51.87
12	6	2	27.35	25.90
13	5	2	52.12	56.84
11	9	2	81.49	82.91
12	8	2	15.90	11.41
14	4	2	7.18	3.83
13	7	2	62.14	62.95
15	3	2	31.96	32.72
11	11	2	71.90	74.03
12	10	2	17.93	18.95
15	5	2	55.95	57.94
13	9	2	80.43	89.63
16	2	2	14.32	11.66
16	4	2	32.76	37.88
15	7	2	51.56	56.79
5	4	3	29.67	25.55
6	3	3	194.80	184.44
6	5	3	93.70	90.95
7	4	3	33.12	26.35
7	6	3	162.41	158.10
8	5	3	41.82	37.61
9	4	3	34.81	13.53
10	3	3	157.27	151.33
8	7	3	38.63	37.19
9	6	3	20.71	16.92
10	5	3	119.43	118.44
11	4	3	20.54	19.31
9	8	3	19.21	21.07
10	7	3	91.47	90.82
11	6	3	53.61	52.46
12	5	3	8.36	3.96
10	9	3	26.45	23.68
13	4	3	14.35	12.32
11	8	3	28.60	27.48
12	7	3	9.50	8.21
14	3	3	90.69	93.64
13	6	3	23.94	25.09
14	5	3	62.00	62.51
11	10	3	14.16	12.79

H	K	L	$\underline{F}_{obs}$	$\underline{F}_{calc}$
12	9	3	14.10	12.28
13	8	3	14.93	12.83
15	4	3	12.87	14.81
14	7	3	48.28	51.84
15	6	3	22.92	22.21
12	11	3	4.30	1.90
13	10	3	15.76	14.61
4	4	4	209.13	200.73
6	6	4	56.68	49.69
7	5	4	54.94	48.32
8	4	4	155.31	149.72
8	6	4	41.81	34.33
9	5	4	26.62	19.01
8	8	4	128.58	128.67
9	7	4	32.35	32.52
10	6	4	20.72	19.87
11	5	4	46.27	44.95
12	4	4	98.62	99.36
11	7	4	8.01	2.61
12	6	4	57.58	56.83
13	5	4	35.40	36.08
10	10	4	10.85	7.21
11	9	4	31.11	31.16
12	8	4	88.32	90.06
13	7	4	5.91	5.56
14	6	4	9.89	10.49
12	10	4	27.19	28.38
15	5	4	30.15	30.48
14	8	4	9.76	12.27
13	9	4	17.41	15.56
6	5	5	74.98	67.47
7	6	5	91.50	88.66
8	7	5	71.23	66.06
9	6	5	53.56	53.55
10	5	5	163.98	162.32
9	8	5	22.76	22.72
10	7	5	71.38	70.45
11	6	5	79.96	82.15
10	9	5	110.12	113.52
11	8	5	61.13	60.02
12	7	5	14.14	9.06
13	6	5	38.93	41.32
14	5	5	94.10	95.91
11	10	5	51.77	54.33
13	8	5	38.96	44.44
14	7	5	38.23	38.20
7	7	6	145.23	140.71

H	K	L	$\underline{F}$ obs	$\underline{F}$ calc
8	6	6	51.71	50.43
9	7	6	24.05	22.55
9	9	6	85.86	92.27
10	8	6	21.29	24.46
11	7	6	53.76	49.85
12	6	6	47.10	44.95
11	9	6	58.84	64.30
12	8	6	25.25	23.20
13	7	6	28.79	29.48
11	11	6	35.56	37.45
12	10	6	21.41	24.38
9	8	7	43.74	45.93
10	7	7	52.60	53.20
10	9	7	16.98	11.54
11	8	7	9.75	2.00
11	10	7	14.31	14.42
12	9	7	16.54	14.88
13	8	7	9.87	10.01
8	8	8	139.45	142.54
10	10	8	10.26	13.48
11	9	8	40.35	44.79
12	8	8	104.11	115.49
10	9	9	103.13	114.41

Table 8

Final parameters for pollucite

Atoms	Coordinates	Positional parameters			Avg. B
		x	y	z	(Standard deviations in parentheses)
Cs+Na	$\frac{1}{8}$ $\frac{1}{8}$ $\frac{1}{8}$				1.972 A^2 (.037)
Si+Al	$\underline{x}$ $\frac{1}{4}$ $-\underline{x}$ $\frac{1}{8}$	.6623 (.0002)			0.235 A^2 (.064)
Oxygen	$\underline{x}$ $\underline{y}$ $\underline{z}$	.1037 (.0006)	.1341 (.0007)	.7207 (.0005)	1.665 A^2 (.151)
H$_2$0	$\frac{1}{4}$ $\frac{1}{8}$ 0				1.690 A^2 (.888)

Atoms	Thermal parameters					
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cs+Na	.00281 (.00005)	.00281 (.00005)	.00281 (.00005)	.00034 (.00008)	.00034 (.00008)	.00034 (.00008)
Si+Al	.00068 (.0001)	.00068 (.0001)	.00045 (.0002)	-.0002 (.0003)	.00026 (.00027)	.0000
Oxygen	.0044 (.0006)	.00038 (.0005)	.00032 (.0003)	.00012 (.0004)	.00053 (.0003)	.00026 (0004)
H$_2$0	Not refined at this date............................ (Note: the last cycles of refinement indicated that there may be 6 H$_2$0 rather than 4H$_2$0)					

Description of the structure.

In pollucite each SiO_4 and AlO_4 tetrahedron is linked by the sharing of every corner oxygen atom so that each oxygen atom is common to two tetrahedra. This particular arrangement of tetrahedra provides a framework which was first noted in analcime by W. H. Taylor in 1930. Consequently, this arrangement is conveniently referred to as the analcime framework. It is common not only to pollucite and analcite, but also to other members of the analcime family. This framework, which conforms to $Ia3d$ is illustrated in Fig. 9, which shows the lower half of four contiguous cells. The arrangement of tetrahedra in the framework is easily visualized in terms of rings or loops of tetrahedra. These loops contain 4 tetrahedra, 6 tetrahedra, and 8 tetrahedra. In Fig. 9 one 4-membered loop, one 6-membered loop, and one 8-membered loop are designated with the number 4, 6, and 8 respectively. Referring to the distribution of symmetry in $Ia3d$ one notes that: the 4-membered loops are normal to $\bar{4}$ axes; the 6-membered loops are normal to $\bar{3}$ axes; and the 8-membered loops are normal to 2-fold rotation axes.

It is convenient to visualize the framework as being comprised solely of 6-membered loops with the exception of the oxygens which link one 6-membered loop to another, each octant of the cell contains one entire 6-membered tetrahedral loop which encircles an inversion center in the middle of the octant and lies normal to the 3-fold axis which coincides the body diagonal of the octant. Thus in each cell one may visualize eight 6-membered loops of tetrahedra, none of which
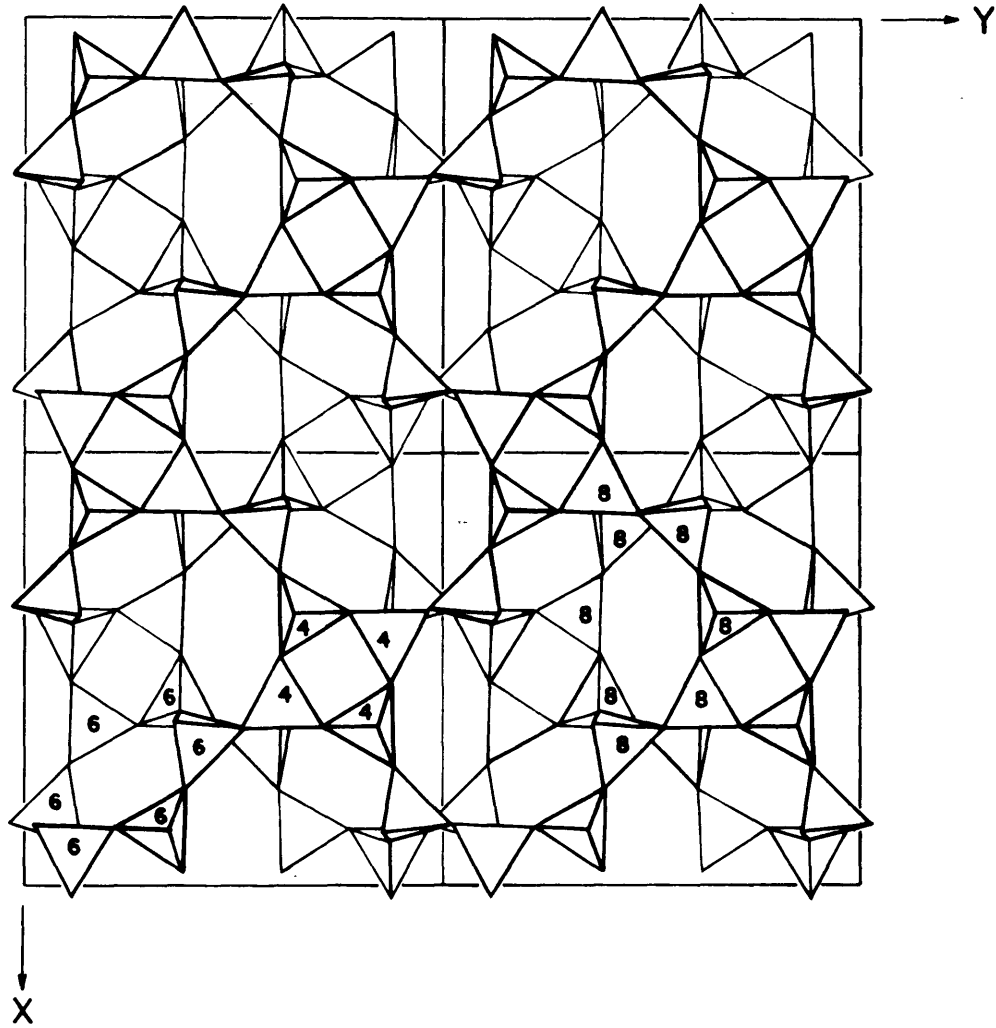
Fig. 9. Projection on (OOI) of the (Si, AI)−O
Framework of pollucite, showing the
lower half of four cells. Modified
after Náray−Szabó (1938).

share tetrahedra with each other. In this manner it is easy to see that there are 8x6= 48 (Si,Al) atoms in a cell. Since there are twice as many oxygen atoms ($4 \times \frac{1}{2} \times 48$), it follows that there are 96 oxygen atoms in a cell.

The framework is a relatively open structure and provides a considerable amount of space which may be occupied by other atoms. In some respects the framework may be thought of as a three-dimensionally infinite anion, because the oxygens as a whole would be electrically deficient if bonded only to Al and Si atoms in tetrahedral coordination. Thus the framework readily accepts positively charged ions in the open spaces which it provides.

In every unit cell there are 16 very large voids in the framework. These voids contain the equipoint 16b at $\frac{1}{8}$ $\frac{1}{8}$ $\frac{1}{8}$; they lie on 3-fold rotation axes which do not intersect one another. Along each individual 3-fold axis these voids are connected to one another by open windows which are framed by the 6-membered loops described above. In this way the voids are joined through windows to form continuous open channels along the 3-fold axes.

In pollucite the Cs and other alkali atoms occupy the centers of the voids at the equipoint 16b . The alkali atoms are the only atoms in pollucite which occupy the 3-fold axes. In other words, along the channelways there are no water molecules between the alkali atoms in these particular directions. The distribution of the Cs and other alkali atoms in pollucite is illustrated in Fig. 10.
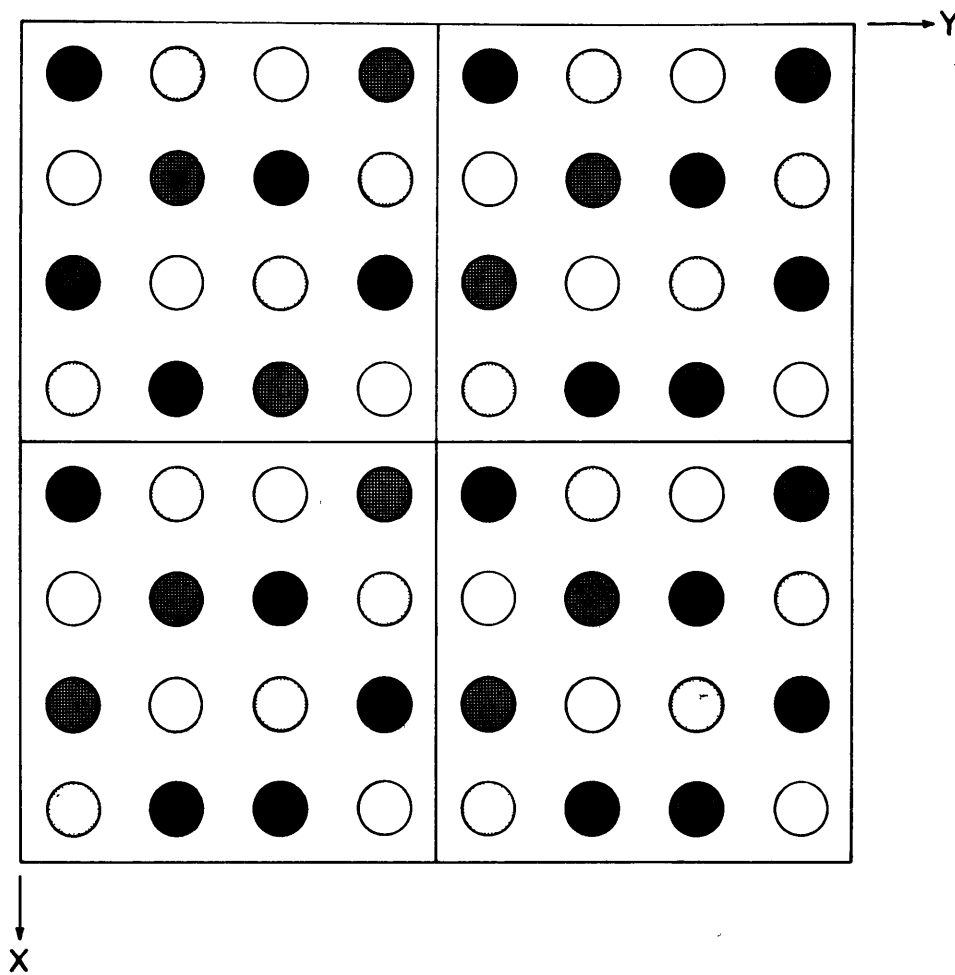
Fig. 10. The distribution of cesium atoms in pollucite.
(four cells are shown; shading indicates height)

Key: ● $\frac{1}{8}$c   ● $\frac{3}{8}$c   ○ $\frac{5}{8}$c   ○ $\frac{7}{8}$c

The channels, like the 3-fold axes which they include, do not intersect with one another. But they do adjoin and communicate with each other by way of open windows, which are framed by 8-membered loops of tetrahedra. These are centered about the equipoint $24\underline{c}$ which is occupied by the water molecules in pollucite. Thus each water molecule is lying between two alkali atoms that occupy different, but adjoining channels.

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