THE CRYSTAL STRUCTURE OF RHODIZITE

by

Karlheinz Jürgen Taxer

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Certified by . . . .
Thesis Supervisor

Accepted by . . . .
Chairman, Departmental Committee
on Graduate Students

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Abstract

The space group of rhodizite has been confirmed to be $\underline{P\bar{4}3m}$ with the cell constant $a = 7.319 \pm 0.001$ Å. A new analysis and determination of the density of the Manjaka (Madagascar) material by Frondel and Ito suggested to them the formula $CsB_{11}Al_4Be_4(OH)_4O_{25}$.

Intensities of 504 of the 760 reflections of the asymmetric Friedel unit were measured using filtered $Mo\underline{K}\alpha$ radiation and a scintillation detector. After these were corrected for Lorentz, polarization and absorption factors, a three-dimensional Patterson function was computed. The structure deduced from this and three-dimensional electron-density and electron-density difference maps was refined to $R \approx 12\frac{1}{2}\%$. This structure has an ideal composition $CsB_{12}Be_4Al_4O_{28}$. The non-alkali part, $B_{12}Be_4Al_4O_{28}$, consists of close-packed oxygen atoms held together by Be and B atoms in tetrahedral coordination and Al in octahedral coordination, all forming a connected network. The omission of 4 oxygens from the close-packed set provides a hole which houses the alkali. The sum of the valences of the atoms of the network suggests that it is formally neutral; if so, the alkali would appear to be un-ionized. Alternatively, the alkali may contribute one electron to a possible metallic bond between the Al atoms. Such a metallic bond is suggested by the short Al-Al distance, which is 2.95 Å.

Thesis Supervisor: Martin J. Buerger
Title: Professor of Mineralogy and Crystallography

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Acknowledgments

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CHAPTER I

Introduction

Rhodizite contains both very large and very small ions, and its crystal chemistry is therefore of special interest. Its composition, moreover, has been problematical ever since a variety of it from the Ural Mountains was first described by Rose (27) in 1834. Strunz (30) tried to solve the structure in 1943. In 1938 he determined the unit cell and space group (29) and computed the cell content from an analysis done by Pisani (24) in 1911. Very recently Frondel *et al*. (11) analysed rhodizite from a new locality, namely Manjaka, Madagascar. He found a composition quite different from that given by Strunz, and computed a new cell content based on a new determination of the density. The number of boron atoms per cell, eleven, seemed unusual, since this would require at least three kinds of boron atoms on very special positions. Also, the presence of hydroxyls and the total of 29 oxygen atoms seemed improbable. A determination of the crystal structure, therefore, appeared to be quite a new problem; it seemed certain that Strunz's analysis was not right and could be disregarded. It was also obvious that, because of the unusual number of atoms required by Frondel's analysis, some corrections in the published composition were necessary.

Since rhodizite contains a heavy alkali atom, it was treated as a heavy atom problem. It was also expected that the image of the structure from the heavy atom would stand out among all the peaks in the Patterson map, since the other atoms in rhodizite are weak scatterers.

CHAPTER II

Previous Work on Rhodizite

Rhodizite was first found in the Ural Mountains and was described by Rose in 1834. It has since been found sparingly in pegmatite at five other localities in Madagascar (Lacroix, 16 and Behier, 1). The chemical analysis of the mineral by older methods presented difficulties, especially in view of the small size of the samples hitherto available, and its composition has remained problematical. The first analysis of rhodizite from the Ural Mountains was made by Damour (9) in 1882. Dana's System of Mineralogy (23) reports that the beryllium content was incorrectly determined as Al_2O_3; the analysis is also otherwise unreliable, and is therefore not listed in Table 1.

All the other analyses have been made on samples from Madagascar. In 1910 Pisani (24) analysed rhodizite from Antandrokomby, Madagascar; this analysis was used by Strunz (19) in 1938 in the first x-ray work on rhodizite, in which he determined the unit cell and computed the cell content. Pisani stated that there was an admixture of spodumene in his sample. The density of the Antandrokomby material was determined as 3.38 g/cm^3. Strunz presented the formula $NaKLi_4Al_4Be_3B_{10}O_{27}$ based on these data. He determined the space group as $P\bar{4}3m$, and the measurement of the cell dimension gave the value of a as 7.318 ± 0.00 Å.

The 1951 edition of Dana's System of Mineralogy (23) says that rhodizite is a complex borate of beryllium, aluminum and alkali and quotes Strunz's formula. Strunz himself, in the third edition of Mineralogische Tabellen (31), listed rhodizite as a member of the rhodizite-boracite group, belonging to the class of borates without water. The third analysis was made by Duparo, Wunder and Sabot (10) in 1911; they stated that rhodizite contained an admixture of albite.

Numerous well-crystallized specimens of rhodizite were collected by Frondel in 1963 in Manjaka, Madagascar. In this locality the mineral rhodizite is associated with rubellite, pink spodumene, albite, microcline and quartz as the chief minerals, and with pink beryl, manganapatite, behierite and lithium mica as accessory minerals. Frondel and Ito (11) examined the sample and performed a new chemical analysis, the results of which are given in Table 2. They describe their material as strongly piezoelectric and pyroelectric, density 3.44 ± 0.0 g/cm^3, isometric, space group $P\bar{4}3M$ with $\underline{a} = 7.317$ Å. Aided by a knowledge of the space group, Frondel and Ito gave a different interpretation of the composition than did Strunz, as indicated by the following comparison of the content of one cell:

Strunz: $NaKLi_4Al_4Be_3B_{10}O_{27}$

Frondel and Ito: $(Cs_{.44}K_{.31}Rb_{.16}Na_{.03})\ Al_4Be_4B_{11}O_{25}(OH)_4$

Frondel and Ito (alternative): $(Cs_{.44}K_{.31}Rb_{.16}Na_{.03})\ Al_4Be_4B_{12}O_{27}(OH)_3$

The alternative formula was discounted by Frondel and Ito on the basis of density. The measured density was 3.44 g/cm^3, which compares well with 3.47, the density calculated for the preferred formula, but poorly with that calculated for the alternative formula, which is 3.59.

The structure of rhodizite was investigated by Strunz (30) in 1943, who based his study on the cell content he had computed in 1938. His results showed the following distribution of atoms in the cell:

O(1)	in	12i	$x = 1/4$	$z = 0$
O(2)	in	12i	$x = 1/4$	$z = 1/2$
B	in	12i	$x = 1/8$	$z = 3/8$
(3 Be replace 2 B?)				
Li	in	4e	$x = 1/4$	
Al	in	4e	$x = 3/4$	
(Na,K)	in	1a and 1b	000 and $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$	

The agreement between the calculated and observed structure factors was said to be good.

Strunz's results could not be used as a start in finding the structure of rhodizite because his information on

TABLE 1

Chemical analyses of rhodizite (23)

	Antandrokomby material (Madagascar)	Sahatany Valley material (Madagascar)	Manjaka material (Madagascar)
	Analyst: Pisani (1910)	Analysts: Duparo, Wunder and Sabot (1911)	Analysts: Ito and Haramura (1964)
Li_2O	7.30	0.68	-
Na_2O	3.30	1.78	0.12
K_2O		1.41	1.79
Rb_2O	5.90	2.29	1.83
Cs_2O		3.47	7.54
BeO	10.10	14.93	12.20
Al_2O_3	30.50	27.40	24.41
Fe_2O_3			0.12
B_2O_3	40.60	43.33	46.82
SiO_2	1.36	3.18	0.45
Ign.	0.45	1.42	4.10
Rem.	-	0.11	0.53
Total	99.51	100.00	99.92
Density (g/cc)	3.25	3.344	3.44
Remarks	The sample had spodumene admixed.	Remainder is MgO. The sample had albite admixed.	Remainder is Li_2O, 0.00x, SnO_2, 0.1, H_2O, 0.43. Also Ga, Pb, Cu in range 0.0x; Mn 0.00x; traces of Mg, Ag, Tl, Yb. Alkalis determined by high-temperature flame photometry

TABLE 2

Chemical analysis of the Manjaka rhodizite and its interpretation in terms of content of cell (11)

Chemical analysis		Cell content			
	Weight percent	Based upon 29 oxygen atoms per cell			Based upon cell mass of 811 atomic units
Na_2O	0.12	Na	0.03	0.74	0.93
K_2O	1.79	K	0.31		
Rb_2O	1.83	Rb	0.16		
Cs_2O	7.54	Cs	0.44		
BeO	12.20	Be	4.03		3.9
Al_2O_3	24.41	Al	3.96		3.9
Fe_2O_3	0.12	Fe	0.01		
B_2O_3	46.82	B	11.1		10.9
SiO_2	0.45				
Ign.	4.10	H	3.8		3.7
Rem.	0.53	O	29		28.5
Total:	99.92				

its composition was probably wrong. His results should not prejudice the interpretation of the Patterson map and electron-density maps and the recognition in them of the image of the structure.

CHAPTER III

Unit Cell and Space Group

The lattice constants, the cell constant and the space group determined by Frondel and Strunz were checked by taking precession photographs and cone-axis pictures with MoK radiation. The selection of the material for x-ray work is not easy because of its great hardness, but it is possible to cause fractures by taking advantage of the incomplete cleavage parallel to (111). Therefore one usually gets little plates instead of cubes as specimens for mounting on the goniometer head. A crystal plate (diameter 0.2 mm and thickness 0.08 mm) was chosen for the work described here. Previous investigation with the polarizing microscope proved the symmetry to be isometric. A rough determination of the refractive index (*n* = 1.694 ± 0.009) confirmed former results.

The crystal was mounted so that its [110] direction was parallel to the dial of the precession camera. The shortest translation period noted on the films (representing the zeroth, first and second level of the reciprocal lattice) was parallel to the four-fold axis as judged by the intensity distribution of the reflections on the film. This translation was taken as a_1^*. The vectors a_2^* and a_3^* were perpendicular to a_1^* and to each other, had the same length as a_1^*, and were also parallel to other four-fold axes. Cone-axis photographs taken along the four-fold axes confirmed the cell and symmetry found from precession photographs.

As there was no systematically extinct group of reflections, the cell was proven to be a primitive cell. The symmetry of the intensity distribution of the reflections on the films shows that the diffraction symbol of rhodizite is $\underline{m}3\underline{mP}$ ---. This, together with the positive piezoelectric and pyroelectric response and the presence of tetrahedral faces on the crystal, establishes the space group as $\underline{P}\bar{4}3\underline{m}$. Table lists some characteristics of the equipoints of this space group.

The refinement of the lattice constant was based upon a back-reflection Weissenberg photograph taken with the original back-reflection camera developed by Buerger (4). The separations of the resolved $\alpha_1 - \alpha_2$ doublets for a few reflections were measured. The measurements were treated by a method developed by Main and Woolfson (18); in order to use this method, the program ALP for the IBM 7090/94 computer, written by Lippard (17), was employed. The values of sin θ for the reflections were determined from these measurements. The determination depends only upon the wavelength of the x-radiation; Cu*K* radiation was used. The reciprocal-lattice parameters, the indices of the reflection, and sin θ are related in the following way:

$$h^2a^{*2} + k^2b^{*2} + \ell^2c^{*2} + 2k\ell b^*c^* \cos\alpha^* + 2\ell hc^*a^* \cos\beta^*$$
$$+ 2hka^*b^* \cos\gamma^* = 4 \sin^2 \theta/\lambda^2 \equiv s^2$$

Differentiation of this formula gives the deviations in the lattice parameters as a function of changes in $s \equiv 2 \sin \vartheta/\lambda$; s was estimated using approximate lattice parameters

TABLE 3

Coordinates of the points in the sets of equivalent position (13)

Symbol of the set of equivalent position	24j	12f	12h	6g	6f	4e	3d	3c	1b	1a
Symmetry	1	m	2	mm	mm	3m	$\bar{4}2m$	$\bar{4}2m$	$\bar{4}3m$	$\bar{4}3m$
	xyz	xxz	$x\frac{1}{2}0$	$x\frac{1}{2}\frac{1}{2}$	$x00$	xxx	$\frac{1}{2}00$	$0\frac{1}{2}\frac{1}{2}$	$\frac{1}{2}\frac{1}{2}\frac{1}{2}$	000
	zxy	zxx	$0x\frac{1}{2}$	$\frac{1}{2}x\frac{1}{2}$	$0x0$	$x\bar{x}\bar{x}$	$0\frac{1}{2}0$	$\frac{1}{2}0\frac{1}{2}$		
	yzx	xzx	$\frac{1}{2}0x$	$\frac{1}{2}\frac{1}{2}x$	$00x$	$\bar{x}\bar{x}x$	$00\frac{1}{2}$	$\frac{1}{2}\frac{1}{2}0$		
	xzy	$\bar{x}x\bar{z}$	$\bar{x}\frac{1}{2}0$	$\bar{x}\frac{1}{2}\frac{1}{2}$	$\bar{x}00$	$\bar{x}x\bar{x}$				
	yxz	$\bar{z}x\bar{x}$	$0\bar{x}\frac{1}{2}$	$\frac{1}{2}\bar{x}\frac{1}{2}$	$0\bar{x}0$					
	zyx	$\bar{x}z\bar{x}$	$\frac{1}{2}0\bar{x}$	$\frac{1}{2}\frac{1}{2}\bar{x}$	$00\bar{x}$					
	$x\bar{y}\bar{z}$	$x\bar{x}\bar{z}$	$x0\frac{1}{2}$							
	$z\bar{x}\bar{y}$	$z\bar{x}\bar{x}$	$\frac{1}{2}x0$							
	$y\bar{z}\bar{x}$	$x\bar{z}\bar{x}$	$0\frac{1}{2}x$							
	$x\bar{z}\bar{y}$	$\bar{x}\bar{x}z$	$\bar{x}0\frac{1}{2}$							
	$y\bar{x}\bar{z}$	$\bar{z}\bar{x}x$	$\frac{1}{2}\bar{x}0$							
	$z\bar{y}\bar{x}$	$\bar{x}\bar{z}x$	$0\frac{1}{2}\bar{x}$							
	$\bar{x}y\bar{z}$									
	$\bar{z}x\bar{y}$									
	$\bar{y}z\bar{x}$									
	$\bar{x}z\bar{y}$									
	$\bar{y}x\bar{z}$									
	$\bar{z}y\bar{x}$									
	$\bar{x}\bar{y}z$									
	$\bar{z}\bar{x}y$									
	$\bar{y}\bar{z}x$									
	$\bar{x}\bar{z}y$									
	$\bar{y}\bar{x}z$									
	$\bar{z}\bar{y}x$									

obtained from the precession photographs. Thus, for each reflection, an equation was set up, and the whole set solved simultaneously by the least-squares technique. The results were

$$a = 7.319 \pm 0.001 \text{ Å}$$

$$a^* = 1/a = 0.13662 \pm 0.00003 \text{ Å}^{-1}$$

$$V = 392.1 \pm 0.5 \text{ Å}^3$$

This determination of the space group and cell thus confirmed the data of Strunz as well as those of Frondel and Ito.

CHAPTER IV

Intensity Measurements for Rhodizite

a. Selection of the material for intensity measurements

As rhodizite does not show good polyhedra or well-formed faces, it seemed desirable to prepare a sphere. This was done by C.T. Prewitt of the Du Pont Research Laboratory using a diamond-impregnated sphere grinder. The radius of the sphere used for the intensity measurements was 0.097 ± 0.002 mm.

b. Measurements

The intensities were measured using a single-crystal diffractometer employing equi-inclination geometry. $MoK\alpha$ radiation filtered through Zr and a scintillation detector were used. The crystal settings, φ , and the settings of the scintillation counter, Υ, were computed for each reflection by the program DIFSET 4 written by Prewitt (26). The rotation axis was parallel to the $[110]$ axis, so that tetragonal lattice geometry had to be applied. The asymmetric Friedel unit in the Mo$\underline{K}\alpha$ sphere contains about 760 reciprocal lattice points; of these, 504 reflections had measurable intensities.

The sphere was initially adjusted using precession photographs (5). The final, highly refined adjustment was accomplished by the Fankuchen method (12). The voltage on the x-ray tube was set at 34.5 kV and the current at 15 mA. The detector voltage and the pulse height analyzer were adjusted to appropriate settings described in the Norelco Radiation Detector Instruction Manual published by Philips Electronic Instruments.

Filtered Mo$\underline{K}$ radiation was used for three reasons:

1. Due to the small inear absorption coefficient of molybdenum radiation, errors in the absorption correction due to deviations of the radius of the sphere and errors in the determination of the composition are minimized.

2. The number of independent reflections in the Mo$\underline{K}\alpha$ sphere was sufficiently large to allow accurate refinement of the structural parameters.

3. The anomalous dispersion correction for Mo*K*α radiation is relatively small compared with that for Cu*K*α radiation.

c. Computation of the intensities and the data reduction

The intensities were computed from the diffractometer measurements by means of the program FINTE 2 written by Onken (20,22). The Lorentz-polarization-correction factor, 1/*Lp*, and the relative error, σ_r, in the structure factor were also calculated with this program.

The spherical absorption correction ($\mu r = 0.2$) was calculated using another program, GAMP, written by Onken (21), and with the subroutines ABSRP1 and ABSRP2 written by Prewitt. The intensities were corrected by multiplying them by the Lorentz-polarization-correction factor, and the structure factors were obtained by computing the square root of the corrected intensities.

The output was a deck of IBM computer cards containing the indices, the structure factors and their computed standard deviations. All reflections *hk*_ were transformed into one sector with $h > k > l$. This sector has 1/48 the size of all reciprocal space.

CHAPTER V

The Patterson Function

The initial step in finding the structure was to prepare a three-dimensional Patterson function P(xyz) from the F_{obs}^2's. This was done with the IBM 7094 computer with the program MIFR 2 written by Sly and Shoemaker (31). This program required a data deck in which all reflections hkℓ in the positive quadrant would appear, since the program was prepared for all symmetry groups lower than or equal to the orthorhombic ones. This meant that reflection cards had to be produced which contained all symmetrically equivalent reflections in the five other equally-sized sections of the positive quadrant. Thus the deck contained six asymmetric units and was called the six-fold deck. Since Pmmm is a subgroup of Pm$\bar{3}$m, the Patterson function was computed for the symmetry group Pmmm, thus obtaining the desired symmetry of Pm$\bar{3}$m. The interval for which the Patterson function was sampled was 1/30 of the cell edge in every direction. The asymmetric unit was contoured.

Before the Patterson synthesis could be interpreted and a structure proposed, some preliminary work was still necessary. This involved:

1. The calculation of the scale factor which brings the Patterson map onto an absolute scale. P(000) is the maximum of a peak, and can be determined by the sum S of the squared number of the electrons of all the atoms in the cell (i.e., $S = \sum M_i Z_i^2$, where M_i is the number of atoms i and Z_i is the number of electrons of atom i). The scale factor is found by dividing the calculated P(000) in the Patterson map by the sum S. The Patterson map must be referred to the true zero level. To find this, the highest negative number in the computed Patterson map was added to every value of the Patterson function (see Tables 4a and 5a).

2. The calculation of the expected peak heights. A vector between two atoms in crystal space is represented by one maximum in the Patterson map, the magnitude of which is equal to the product of the numbers of the electrons of the two atoms (6) (see Tables 4b and 5b).

TABLE 4a

Calculation of the scale factor and of the peak heights based on Frondel's idealized formula $Cs\ B_{11}(OH)_4Al_4Be_4O_{25}$, assuming atoms not all ionized

atom	M (number of atoms per unit cell)	Z (number of electrons)	Z^2	MZ^2
Cs	1	36	1296	1296
Al	4	13	169	696
Be	4	4	16	64
B	11	5	25	275
O	25	8	64	1600
OH	4	9	81	324
			ΣMZ^2 =	4235

$$P\ (000)_{comp} = 1005$$

$$P\ (min)_{comp} = -74$$

$$\text{Scale factor} = \frac{1079}{4235} = 0.255$$

TABLE 4b

Calculation of the expected peak height
(single peaks only)

vector from a	to b	Z_a	Z_b	absolute peak height $Z_a \cdot Z_b = Z(a,b)$	weight $k \cdot Z(a,b)$	expected weight in the computed Patterson map $k \cdot Z(a,b) - P_{(min)}$
Cs	Cs	36	36	1296	330.5	256.5
Cs	Al	36	13	468	119.3	45.3
Cs	B	36	5	180	45.9	-28.1
Cs	Be	36	4	144	36.7	-37.3
Cs	O	36	8	288	73.4	-0.6
Cs	H	36	1	36	1.2	-72.8
Al	Al	13	13	169	43.1	-30.9
Al	B	13	5	65	16.6	-57.4
Al	Be	13	4	52	13.3	-63.7
Al	O	13	8	104	26.5	-47.5
Al	H	13	1	13	3.3	-70.7
B	B	5	5	25	6.4	-67.6
B	Be	5	4	20	5.1	-68.9
B	O	5	8	40	10.2	-63.8
B	H	5	1	5	1.3	-72.7
Be	Be	4	4	16	4.1	-69.9
Be	O	4	8	32	8.2	-65.8
Be	H	4	1	4	1.0	-73.0
O	O	8	8	64	16.3	-57.7
O	H	8	1	8	2.0	-72.0
H	H	9	9	1	0.255	-73.7
Cs	OH	36	9	324	82.6	8.6
Al	OH	13	9	117	29.8	-44.2
Be	OH	5	9	45	11.5	-62.5
B	OH	4	9	36	9.2	-64.8
O	OH	8	9	72	18.4	-55.6
OH	OH	9	9	81	20.7	-53.3

TABLE 5a

Calculation of the scale factor and of the peak heights based on Frondel's idealized formula $Cs\ B_{11}(OH)_4Al_4Be_4O_{25}$, assuming atoms half ionized

atom	M	Z	Z^2	MZ^2
Cs	1	35.5	1260.25	1260.25
Al	4	11.5	132.25	529.00
Be	4	3	9.00	27.00
B	11	3.5	12.25	134.75
O	25	9.0	81.00	2025.00
OH	4	8.5	72.25	289.00
				$\Sigma MZ^2 = 4265.00$

$$k = \frac{1079}{4265.00} = 0.253$$

TABLE 5b

Calculation of the expected peak height (single peaks only)

vector from a	to b	Z_a	Z_b	absolute peak height $Z_a \cdot Z_b = Z(a,b)$	weight $k \cdot Z(a,b)$	expected weight in the computed Patterson map $k \cdot Z(a,b) - P_{(min)}$
Cs	Cs	35.5	35.5	1258.45	318.4	234.4
Cs	Al	35.5	11.5	408.25	103.3	29.3
Cs	B	35.5	3.5	124.25	31.4	-32.6
Cs	Be	35.5	3.0	106.5	26.9	-47.1
Cs	O	35.5	9.0	319.5	80.8	6.8
Cs	OH	35.5	8.5	301.75	76.3	2.3
Al	Al	11.5	11.5	122.25	30.9	-33.1
Al	B	11.5	3.5	40.25	10.2	-63.8
Al	Be	11.5	3.0	34.5	8.7	-65.3
Al	O	11.5	9.0	103.5	26.2	-47.8
Al	OH	11.5	8.5	97.75	24.7	-49.3
B	B	3.5	3.5	12.25	3.1	-70.9
B	Be	3.5	3.0	10.5	2.7	-71.3
B	O	3.5	9.0	31.5	8.0	-66.0
B	OH	3.5	8.5	29.75	7.5	-66.5
Be	Be	3.0	3.0	9.0	2.3	-71.7
Be	O	3.0	9.0	27.0	6.8	-67.2
Be	OH	3.0	8.5	25.5	6.5	-67.5
O	O	9.0	9.0	81.0	20.5	-53.5
O	OH	9.0	8.5	76.5	19.4	-54.6
OH	OH	8.5	8.5	72.25	18.3	-55.7

TABLE 6

Possible distribution of the atoms in rhodizite on equivalent positions of space group $P\bar{4}3m$ for formula $CsAl_4Be_4B_{11}O_{25}(OH)_4$

		The atoms can be distributed on					
Atom	Number in cell	1a or 1b or both	3c or 3d or both	4e	6f or 6g or both	12h or 12i or both	24j
Cs	1	1					
Al	4	1	3				
				4			
Be	4	1	3				
				4			
OH	4	1	3				
				4			
B	11	1		4	6		
		1	33	4			
		11	3		6		
			3	44			
O	25	1		444444			
		11	3	44444			
			3	4444	6		
		1		444		12	
		1	33	444	6		
		1		444	66		
		11	3	44		12	
		11	3	44	66		
			3	4	6	12	
			3	4	666		
		1			6666		
		1	33		666		
		1			66	12	
		1	33		6	12	
		1				12 12	
		1					24

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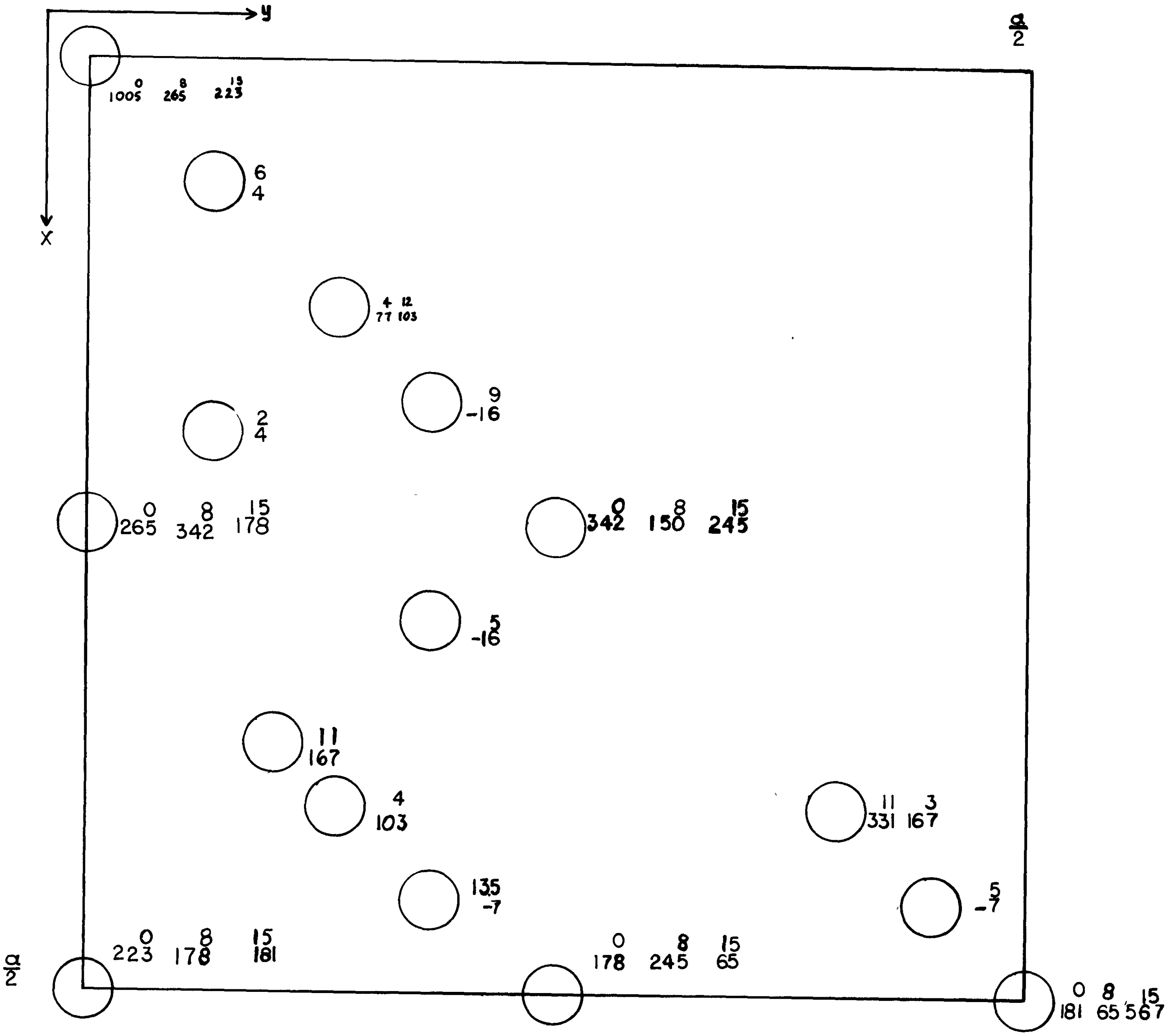
Figure 1

Projection of the maxima of the Patterson function onto the xy0 plane

Legend: The first number is the z coordinate in 30ths of the cell edge. The second number (underneath the first) is the height of the maximum.


y
x
a/2
a/2
0 8 15
1005 265 223
6
4
4 12
77 103
9
-16
2
4
0 8 15
265 342 178
0 8 15
342 150 245
5
-16
11
167
4
103
11 3
331 167
13.5
-7
5
-7
0 8 15
223 178 181
0 8 15
178 245 65
0 8 15
181 65 567

3. Making a plot on which the maxima of the Patterson function are projected onto the plane xy0 (see Figure 1).

4. Finding all possible distributions of the atoms on the atomic positions of the space group (see Table 6).

CHAPTER VI

The First Trial Structure

a. General procedure

The composition of the Manjaka rhodizite deduced by Frondel and Ito implies that there is one atom of alkali, of average atomic number 36 and average atomic weight 90.5, per cell. Because of the large size of this alkali, it is apparently not involved in substitution for the smaller non-alkali atoms, so it is natural to assign the one alkali atom to an equipoint of multiplicity one. Two of these are available in space group $P\bar{4}3m$, namely 1*a* at 000 and 1*b* at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The steps in solving the structure are unaffected by which is chosen; we chose 1*a*. In this case we are dealing with a heavy-atom problem with the heavy atom at the origin. The peaks of the Patterson function might then be expected to be dominated by an image of the structure as seen from the origin.

The most reasonable procedure seemed to be first to find peaks in the Patterson function which corresponded to the oxygen atoms which immediately coordinated with the alkali at the origin, to calculate a trial electron density whose phases were based upon the alkali and these surrounding oxygen atoms, to seek to interpret new peaks appearing in the electron-density function, and then to continue this iterative process until all atoms were located (3).

The trial density function was computed from the observed structure factors, to which were assigned signs which were taken from the calculated structure factors based upon a proposed structure called the model.

b. Calculation of the structure factor

The structure factors were computed using the program SFLSQ 3 written, partly in FORTRAN and partly in FAP, by C.T. Prewitt (25) for the IBM 7090/94 computer. The scattering curves for the atoms were taken from International Tables for X-Ray Crystallography (13). At first all atoms were considered to be half-ionized, since no direct information was available about the status of the electronic shell. The atomic parameters came from a proposed model;

the isotropic temperature factors for each atom were assumed to be 0.5 $\mathring{A}^2$. The scale factor, which puts F_{cal} on the same scale as F_{obs}, was first assumed to be 1.

c. Early stages of refinement

The SFLSQ 3 programs made it possible to refine the positional space parameters, the temperature factors, the scale factor and the occupancy by the least-squares technique. Successive refinement computations were made partly at the same time as the preparation of successive Fourier maps (3). Changes in some subroutines (SPGRP, TEST) were necessary because of the crystal system to which rhodizite belongs. Subroutine WEIGHT was prepared so that each structure factor had a weight of 1 while the structure was being analyzed. This is the safest weighting scheme for the initial stage of a structure analysis, because nothing is known about the correct weighting scheme.

The contributions from the several atoms to the calculated structure factors for weak reflections are nearly in balance, and a small change in coordinates of even one atom could cause a change of sign in the calculated structure factors. Furthermore, the inclusion of an observed structure factor of incorrect sign can give rise to twice the electron-density error that would have occurred had the doubtful term been entirely omitted. Accordingly, the deck containing the structure factors was reduced to approximately 400 reflections in the early stages of refinement by excluding the weak reflections.

An electron-density and electron-density difference function were also computed with the Fourier program MIFR 2 written by W.G. Sly and D.P. Shoemaker (32). After the structure factors were calculated with the program SFLSQ 3 the output data were written on a tape which became the input to the program ADIAG (33). In the program ADIAG a tape deck was then prepared which contained all symmetrically equivalent reflections in the positive quadrant. This tape was used to give the required input data to the program MIFR 2 by which the electron-density, the electron-density difference function, was computed. The interval for which the electron-density function was sampled was 1/30 of the cell edge in every direction. The asymmetric unit was contoured.

d. Derivation of model I

The first model, labeled model zero, contained only the alkali atom at the origin which dominated the phases. The trial electron density was therefore computed with positive signs for all structure factors. The imaginary part was zero. This map showed the heavy atom at 000, as well as other peaks which helped to locate the oxygen atoms surrounding the alkali.

Patterson peaks of fairly great weight at a reasonable distance from the origin were sought which could be interpreted as oxygen locations. These were found at $\underline{xxz}$, $\underline{x} = 1/4$ and $\underline{z} = 0$. Accordingly, the next model, model A, had, in addition to one alkali atom at the origin, an oxygen, O(1), in $12\underline{i}$ at $\frac{1}{4}\,\frac{1}{4}\,0$. The electron-density function for model A was still centrosymmetrical; i.e., the imaginary part of the structure factor was zero because the model contained only atoms which were centrosymmetrical.

The Patterson map agreed with the Fourier density map. It suggested that, in addition to Cs (which hereinafter stands for the averaged alkali, Cs, Rb, K and Na) and O(1), there were four aluminum atoms at position 4<u>e</u>. It also suggested that, since O(1) and O(2) formed an octahedron with Al in the center, 12 atoms O(2) were in equipoint 12<u>i</u> with <u>x</u> = 1/4 and <u>z</u> = 1/2. The distance from the corner to the center ($\underline{d}_{Al-O(2)}$ = 1.83 Å) agreed fairly well with the distances found for an Al-O bond. The exact values were obtained by finding the position of the maximum from the two preceding electron-density maps.

From the electron-density function of models A, B and C, (see Table 7) it seemed very likely that an oxygen atom O(3) should be placed in 1<u>b</u> at $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$. A heavy peak in 4<u>e</u> with <u>x</u> = 3/4 suggested that 4 oxygens O(4) were at the position complementary to that of Al. The electron-density map based on this model made it seem very likely that four beryllium atoms were in position 4<u>e</u> with <u>x</u> = 5/8. All the previous electron-density maps and the Patterson function supported this hypothesis. Beryllium would then form a tetrahedron with a Be-O distance of $\underline{d}_{Be-O} \approx 1.65$ Å. This has been found in bis-acetylacetone-beryllium where $\underline{d}_{Be-O} =$ 1.68 Å (Shangdar *et al.*, 18), in bertrandite, where $\underline{d}_{Be-O} =$ 1.70 Å (Ito and West, 14) and in euclase, where $\underline{d}_{Be-O} = 1.37$ to 1.91 Å (Biscoe and Warren, 2).

The model now represented the formula presented by Frondel fairly well. It was especially encouraging in that it contained 29 oxygen atoms, a feature which had at first made the analytical result appear dubious.

Now only the boron atoms needed to be accounted for. The electron-density and electron-density difference maps suggested that they were located at 6*f*, x00 with x = 1/4 and at 6g, $x\frac{1}{2}\frac{1}{2}$ with x = 1/4. If this were the case, however, there would be twelve boron atoms instead of eleven. This would mean either that Frondel's formula contains too few borons or that it was necessary to use, in the last stage of refinement, an occupancy differing slightly from unity. The Fourier maps showed all expected

TABLE 7

Series of models I, listing the idealized space parameters

Equipoint		1*a*	12*i*	12*i*	1*b*	4*e*	4*e*	4*e*	6*f*	6*g*	*R*,%
Symmetry		$\bar{4}3m$	4m	m	$\bar{4}3m$	$\bar{3}m$	$\bar{3}m$	$\bar{3}m$	mm	mm	
Coordinates	x	0	0.25	0.25	½	0.25	0.625	0.75	0.25	0.125	
	y	0	x	x	½	x	x	x	0	½	
	z	0	00	½	½	x	x	x	0	½	
Atoms in model A		Cs	O(1)								41.0
Atoms in model B		Cs	O(1)								38.5
Atoms in model C		Cs	O(1)	O(2)	O(3)	Al	Be				36.3
Atoms in model D		Cs	O(1)	O(2)	O(3)	Al	Be	O(4)			32.0
Atoms in model E first cycle		Cs	O(1)	O(2)	O(3)	Al	Be	O(4)	B(1)	B(2)	30.5
Atoms in model E second cycle		Cs	O(1)	O(2)	O(3)	Al	Be	O(4)	B(1)	B(2)	30.0

TABLE 8

Series of models I, listing the actual parameters

atom		Cs	O(1)	O(2)	O(3)	Al	O(4)	Be	B(1)	B(2)	
equipoint		1*a*	12*i*	12*i*	1*b*	4*e*	4*e*	4*e*	6*f*	6*g*	*R* (%)
parameters	x	0	0.25								41.0
of model A	y	0	x								
	z	0	0.0								
	B (Å^2)	0.5	0.5								
parameters	x	0	0.264			0.25					38.5
of model B	y	0	x			x					
	z	0	-0.009			x					
	B(Å^2)	0.5	0.5			0.5					
parameters	x	0	0.270	0.261	½	0.274		0.632			36.0
of model C	y	0	x	x	½	x		x			
	z	0	0.009	0.509	½	x		x			
	B (Å^2)	0.5	0.5	0.5	0.5	0.5		0.5			
parameters	x	0	0.261	0.253	½	0.284	0.775	0.626			32.0
of model D	y	0	x	x	½	x	x	x			
	z	0	0.002	0.471	½	x	x	x			
	B (Å^2)	0.44	2.1	3.7	0.01	4.12	1.80	0.01			
parameters	x	0	0.264	0.252	½	0.272	0.774	0.626	0.256	0.099	30.5
of model E	y	0	x	x	½	x	x	x	0	½	
(first	z	0	-0.001	0.526	½	x	x	x	0	½	
cycle)	B (Å^2)	0.30	2.0	2.1	0.2	2.1	0.6	0.01	2.8	5.0	

TABLE 8 (continued)

atom		Cs	O(1)	O(2)	O(3)	Al	O(4)	Be	B(1)	B(2)	
equipoint		1*a*	12*i*	12*i*	1*b*	4*e*	4*e*	4*e*	6*f*	6g	*R*(%)
parameters	x	0	0.261	0.258	$\frac{1}{2}$	0.278	0.776	0.626	0.259	0.071	30.0
of model E	y	0	x	x	$\frac{1}{2}$	x	x	x	x	x	
(second	z	0	0.003	0.472	$\frac{1}{2}$	x	x	x	x	x	
cycle)	B (Å^2)	0.49	1.7	5.9	0.01	5.7	1.3	0.01	2.5	28	

peaks with volumes which were proportional to the number of electrons of the atoms, and it therefore appeared that the model did indeed represent the structure of rhodizite. When attempt was made to refine this model by the least-squares technique, however, it failed.

After computation of the scale factor $\underline{k}$ in order to adjust the average magnitude of $\underline{F}_{cal}$ to $\underline{F}_{obs}$ by the formula

$$\underline{k} = \frac{\sum F_{obs}}{F_{cal}} ,$$

the disagreement between $\underline{F}_{obs}$ and $\underline{F}_{cal}$ was measured by means of the residual,

$$R = \frac{\sum \| F_{cal}| - |F_{obs}\|}{\sum |F_{obs}|}$$

The value of this for model A was 0.41. $\underline{R}$ for model D was only 0.30. Table 7 shows the models and Table 8 contains the results after their refinement. The improvement in $\underline{R}$ from $\underline{R}$ = 41.0% to $\underline{R}$ = 32% and later to 30% is not enough to suggest that the structure is correct. Furthermore, the temperature factor for the boron atoms B(2) increased to 28 Å^2, showing that B(2) had been placed in the wrong position. The temperature factors for Al and O(2) were also too high (see Table 8); their magnitudes did not compare well with those usually found in inorganic structures.

These facts required the conclusion that this model was wrong. Since it had looked reasonable from the electron-density maps, however, perhaps these maps could be interpreted in other ways. The oxygen atoms O(1) and O(2) appeared to occupy the right sites. Therefore several attempts were made at exchanging the positions of O(4), O(3) and various cations. The following models (here idealized) were considered:

Model 1

Cs at 1a	their former position
O(1) at 12i with x = 1/4, z = 0	
O(2) at 12i with x = 1/4, z = 1/2	
O(3) at 1b	
Al at 4e with x = 3/4	the former O(4) position
O(4) at 4e with x = 5/8	the former Be position

R = 31.1%

Model 2

Cs at 1*a*	their former positions
O(1) at 12*i* with x = 1/4, z = 0	
O(2) at 12*i* with x = 1/4, z = 1/2	
B(3) at 1*b*	the former O(3) position
Be at 4*e* with x = 3/8	complementary to the former Be position
Al at 4*e* with x = 3/4	complementary to the former Al position
O(4) at 4*e* with x = 5/8	the former Be position
B(1) at 4*e* with x = 1/4	the former Al position
B(2) at 6*f* with x = 1/4	the former position

R = 26.2%

This model contains 28 oxygen atoms and 11 boron atoms; the former position of the B(2) atom was discarded as being incorrect.

Model 3

Cs at 1*a*	
O(1) at 12*i* with x = 1/4, z = 0	their former position
O(2) at 12*i* with x = 1/4, z = 1/2	
O(3) at 1*b*	
O(4) at 4*e* with x = 5/8	the former Be position
Al at 4*e* with x = 3/4	the former O(4) position
Be at 4*e* with x = 1/4	complementary to the former O(4) position

B(1) at 4*e* with x = 1/4	the former Al position
B(2) at 6*f* with x = 1/4	the former position

R = 25.5%

All these results show that, while the proposed models may have some properties of the actual structure, they do not represent the correct structure.

CHAPTER VII

The Second Trial Structure

A new approach to discovering the right structure was made by taking into account the following points:

1. The relation with pharmacosiderite
2. Interpretation of an apparent substructure
3. A clue to the true structure should be indicated in the results of the computations for the first trial structure.

Pharmacosiderite has the same space group as rhodizite. The cell parameter, a = 7.91 Å, is very close to that of rhodizite. It has four iron atoms in octahedral coordination (34); this coordination was also found for the aluminum atoms in model 1 for rhodizite, although the arrangement of the four octahedra was different. In pharmacosiderite the four octahedra of oxygen atoms around the four iron atoms form a group in the center of the cell; four oxygens in 4e with $x = 5/8$ occupy the tetrahedral position complementary to Fe. The other twelve oxygen atoms are located in equipoint 12i

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Figure 2

The Al_4O_{16} group

Legend: small black circles: Al at z = 3/8

small white circles: Al at z = 5/8

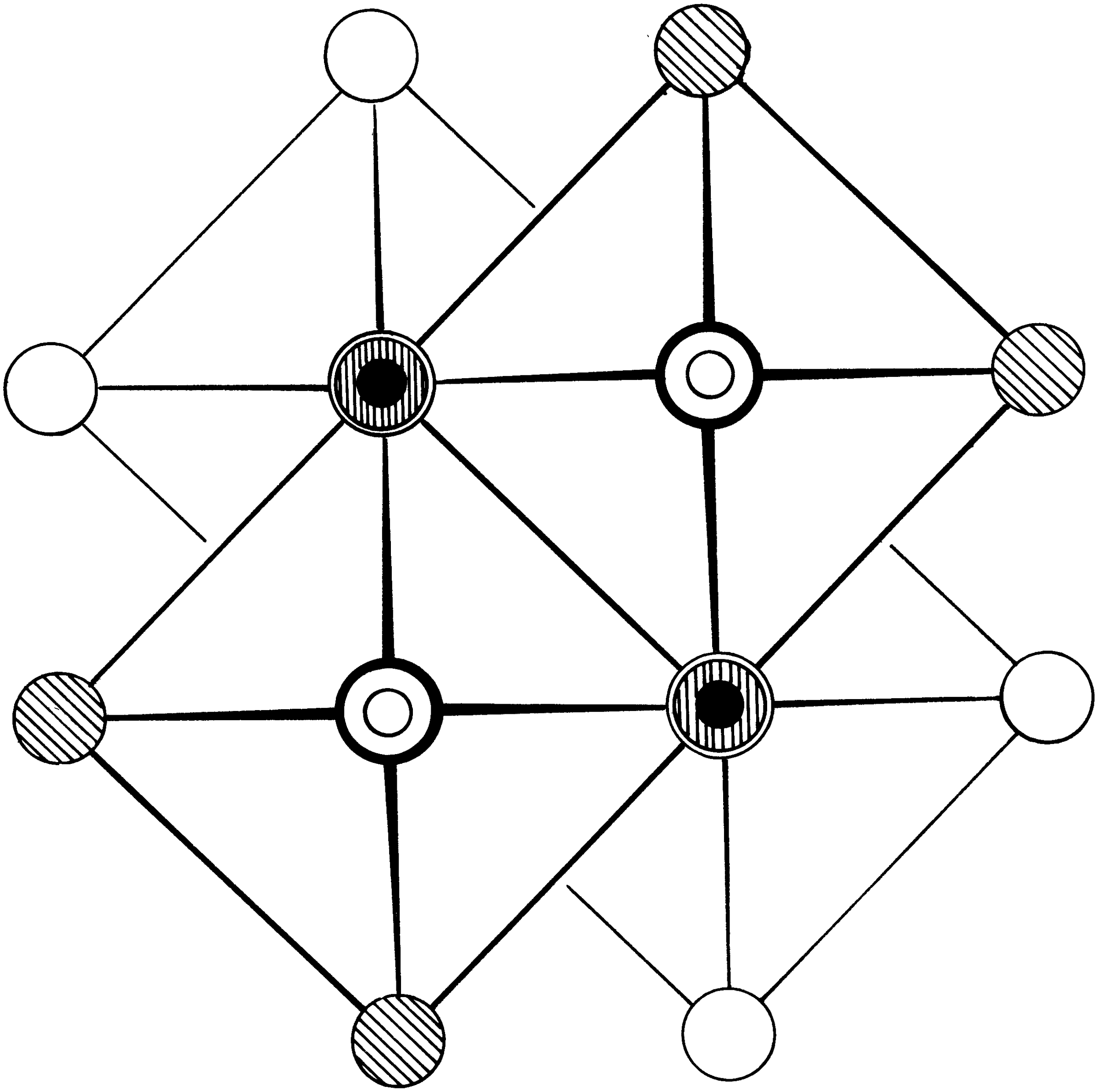
medium white circles: O at z = 3/8

medium striped circles: O at z = 5/8

large white circles: O at z = 1/8*

large black circles: O at z = 7/8*

*appearing as rings



with xxz, x = 3/8 and z = 1/8. Each octahedron shares an edge with the three other octahedra, thus forming a tight cluster ~~arrangement~~ in the center of the cell.

It seemed very likely that a similar group of octahedra, but in this case around aluminum atoms, might replace the other arrangement of octahedra around the four aluminum atoms in rhodizite. In the first trial structure of rhodizite each octahedron around an Al atom shared only a vertex with each of three other octahedra.

By looking at a precession photograph of rhodizite in which the four-fold symmetry axis is normal to the picture, one may observe an arrangement of intensities which may be assumed to be a substructure in rhodizite. From the weights of the reciprocal-lattice points (Figure 3) one can derive a law relating the subcell to the true cell in the reciprocal lattice. This is:

$l = 4n$	Reflections with $h = 4n$, $k = 4n$ only contribute to the reciprocal lattice which is related to the substructure

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Figure 3

Plot of part of the reciprocal lattice

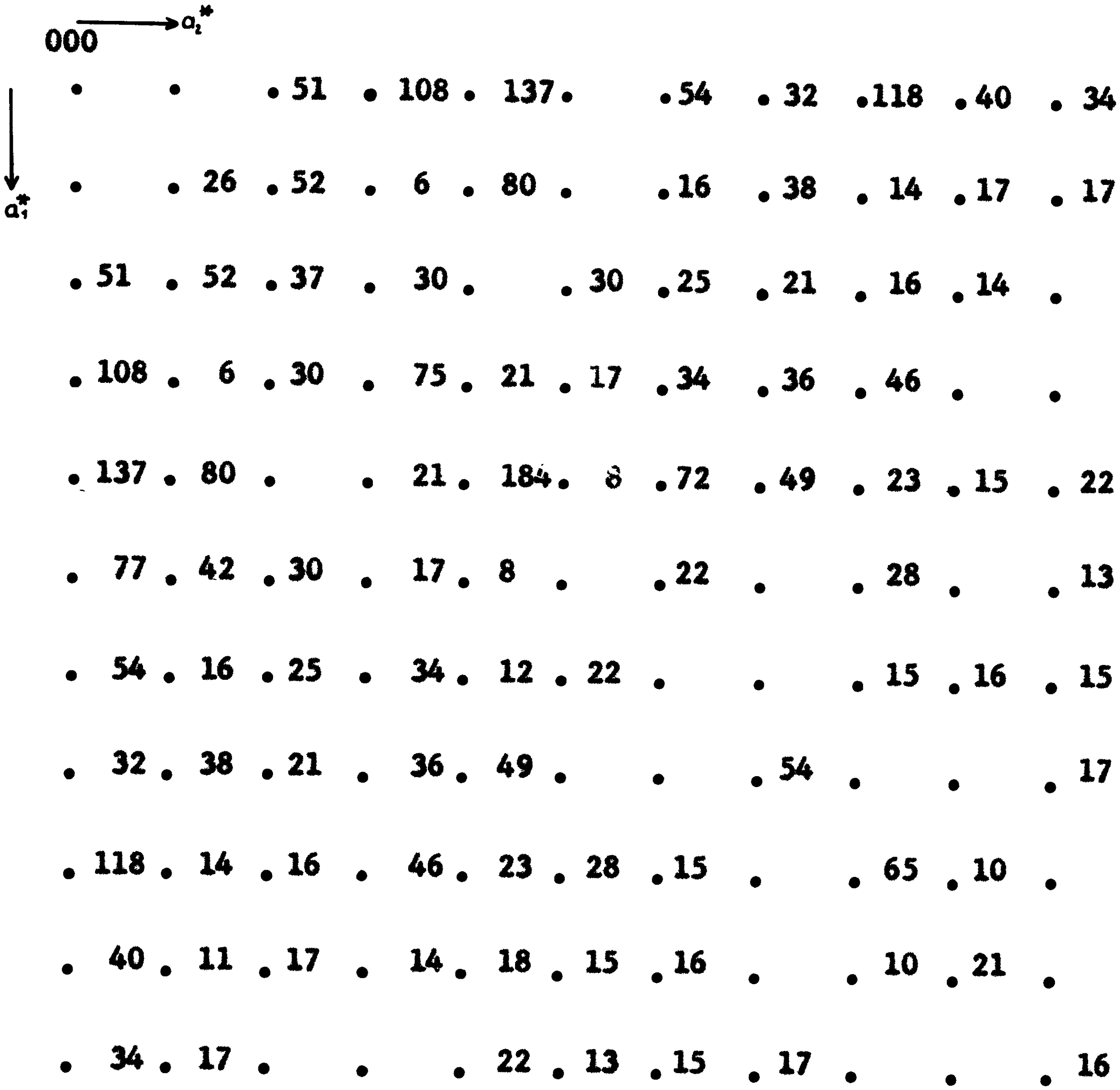
showing F_{obs} as weight of a reciprocal lattice point

(a) page 45: 0th level

(b) page 46: 1st level

(c) page 47: 2nd level

(d) page 48: 3rd level



		51	108	137		54	32	118	40	34
	26	52	6	80		16	38	14	17	17
51	52	37	30		30	25	21	16	14	
108	6	30	75	21	17	34	36	46		
137	80		21	184	8	72	49	23	15	22
77	42	30	17	8		22		28		13
54	16	25	34	12	22			15	16	15
32	38	21	36	49			54			17
118	14	16	46	23	28	15		65	10	
40	11	17	14	18	15	16		10	21	
34	17			22	13	15	17			16

$\longrightarrow a_2^*$

001

$\downarrow a_1^*$

•	• 26	• 52	•	• 80	• 42	• 16	• 38	• 14	• 11	• 17
• 26	•	• 88	•	•	• 48	• 39	•	• 35	• 13	• 31
• 52	• 88	• 38	• 54	• 38	• 36	• 27	• 34	• 28	• 22	• 11
•	•	• 54	• 11	• 46	• 13	• 47	• 38	• 23	• 22	• 15
• 80	•	• 38	• 46	• 9	• 26	• 29	• 8	• 33	• 19	•
• 42	• 48	• 36	• 13	• 26	• 17	• 40	• 21	• 30	• 23	• 15
• 16	• 39	• 27	• 47	• 29	• 40	•	• 13	• 12	• 12	• 15
• 38	•	• 34	• 38	• 8	• 21	• 13	•	• 20	• 10	• 20
• 14	• 35	• 28	• 23	• 33	• 30	• 12	• 20	•	• 20	• 12
• 11	• 13	• 22	• 22	• 19	• 23	• 12	• 10	• 20	•	• 15
• 17	• 31	• 11	• 15	•	• 15	• 15	• 20	• 12	• 15	•

$\xrightarrow{} a_2^*$

002

$\downarrow a_1^*$

51	52	38	30	38	30	25	21	16	17	8
52	88	38	54	31		27		28	22	11
38	38	148	23		32	48	20	21		23
30	54	23	54	32	47	20	26	16	22	12
38	31		32	25	28	20	10	21	19	11
30		32	47	28	30	22	20	18	23	
25	27	48	20	20	22	32	17	20	12	20
21		20	26	10	20	17	11	12	10	8
16	28	21	16	21	18	20	12	19	20	
17	22		22	19	23	12	10	20		8
8	11	23	12	11		20	8	10	8	

$\longrightarrow a_2^*$

003

$\downarrow a_1^*$

	6	30	75	21	17	34	36	46	14	
6		11	11	46	13	47	38	23	22	15
30			54	32	47	20	26	16	18	12
75	11	54	66	29	35	30	12	30	21	22
21	46	32	29	58	23	11	46	6	13	18
17	13	47	35	23	31	21	9	26	8	26
34	47	20	30	11	21	21	22	15	23	
36	38	26	12	46	9	22	18	17		10
46	23	16	30	6	26	15	17	21	15	
14	22	18	21	13	8	23		15	15	
	15	12	22	18	26		10			8

$l = 4n + 1$	These reflections do not contribute to the reciprocal lattice which is related to the substructure
$l = 4n + 2$	Reflections with $h = 4n + 2$, $k = 4n + 2$ only contribute to the reciprocal lattice which is related to the substructure
$l = 4n + 3$	These reflections do not contribute to the reciprocal lattice which is related to the substructure

That is, the lattice of the substructure is face-centered and has the period $\frac{1}{4}a$; its reciprocal is body-centered and has the geometrical lattice period of $4a^*$. The substructure can be interpreted as a lattice array of oxygen atoms in rhodizite in a cubicclose packing.

Actually, a true substructure must have a reciprocal lattice with points whose weight is very strong for the substructure reflections only, and very weak for all the others. As this requirement is not fulfilled, only a large part of the cubic close packing exists, the missing part being occupied by other atoms in a different arrangement.

A key to the correct structure was found in the incorrect one. In that structure the odd oxygen at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ in

1b had been surrounded tetrahedrally by Be atoms in 4e at approximately $\frac{5}{8}\frac{5}{8}\frac{5}{8}$. All Fourier maps, however, showed an additional peak in the complementary tetrahedral position at about $\frac{3}{8}\frac{3}{8}\frac{3}{8}$. This required a set of eight atoms at the vertices of a cube surrounding the center of the cell; the edge of this cube is approximately $1/4a \approx 1.8$ Å. Since this is an acceptable Al-O distance, the set of eight atoms could be interpreted as parts of four octahedra of oxygens surrounding the four Al atoms in equipoint 4e at $\frac{3}{8}\frac{3}{8}\frac{3}{8}$. If this interpretation was correct, there should be 12 oxygen atoms in equipoint 12i at about $\frac{3}{8}\frac{3}{8}\frac{1}{8}$. This central cluster would comprise four octahedra about the four Al atoms, each sharing three edges with its neighboring octahedra and thus forming a tight cluster whose composition would be Al_4O_{16}. Since this provides the correct number of Al atoms for the Strunz as well as for the Frondel and Ito formulae, a new beginning was made by assuming this cluster at the center of the cell, with the alkali at the origin. The expected substructure of cubic close-packed oxygen atoms would become more complete if another oxygen atom at 12*i*, x = 1/8 and z = 5/8 were added. The position of this atom is consistent with the distribution of the maxima of the Patterson function and would have to be consistent also with the electron-density maps based upon models containing only Cs in 1*a* and the cluster at the center of the cell. Approximation of the sites occupied by the boron and beryllium atoms was not attempted at this point, since this information should come out of the electron-density and electron-density difference maps when calculated with the phases determined by the models described above.

The calculation of a series of successive electron-density and electron-density difference maps was now begun. The first model, PL 1, contained Cs in position 1*a* at 000 and Al in position 4*e*, x = 3/8. This led to model PL 2, which had in addition 12 O(2) in position 12*i* with x = 3/8 and z = 1/8; model PL 3 contained O(1) in position 4*e* with x = 5/8 and O(3) in position 12*i* with x = 1/8 and z = 5/8 in addition to the atoms in model PL 2. The discrepancy factor, R, was computed for each structure factor calculation. A refinement of the scale factor was necessary for each new model. For model PL 3 the scale factor, the coordinates and the temperature factors were refined by the least-squares method. The R factor for PL 1 was initially 41%, but dropped to 33% in PL 2. The agreement between F_{cal} and F_{obs} for model PL 3 increased after four refinement cycles and showed a discrepancy factor of only 19.1%.

Now an electron-density function was again computed; the peak at the former Al position in 4e, x = 1/4 almost vanished, and the electron density showed a maximum in the complementary tetrahedral position 4e, x = 3/4; it seemed very likely that the four beryllium atoms could fit in the centers of these four tetrahedra. After another refinement the R factor first increased to 20% and then decreased to 19.4%; it always remained above the former value of 19.1%.

The electron-density map, and especially the electron-density difference map, were again investigated and an additional peak of medium height was discovered in position 12h, x = 1/4. It seemed possible that this might be the

TABLE 9

Series of models II (PLi, i = 1,2,...9), listing the idealized coordinates

equipoint		1*a*	12*h*	12*i*	12*i*	4*e*	4*e*	4*e*	1*b*	3*d*	*R* (%)
symmetry		$\bar{4}3m$	2	m	m	3m	3m	3m	$\bar{4}3m$	$\bar{4}2m$	
idealized coordinates	x	0	1/4	3/8	1/8	3/8	5/8	3/4	1/2	1/2	
	y	0	1/2	x	x	x	x	x	1/2	0	
	z	0	0	1/8	3/8	x	x	x	1/2	0	
Atoms in PL 1		Cs	-	-	-	Al	-	-	-	-	41.2
Atoms in PL 2		Cs	-	O(2)	-	Al	O(1)	-	-	-	33.4
Atoms in PL 3 (R factor only)		Cs	-	O(2)	O(3)	Al	O(1)	-	-	-	27.1
Atoms in PL 3 (first cycle)		Cs	-	O(2)	O(3)	Al	O(1)	-	-	-	23.6
Atoms in PL 3 (second cycle)		Cs	-	O(2)	O(3)	Al	O(1)	-	-	-	21.5
Atoms in PL 3 (third cycle)		Cs	-	O(2)	O(3)	Al	O(1)	-	-	-	19.6
Atoms in PL 3 (fourth cycle)		Cs	-	O(2)	O(3)	Al	O(1)	-	-	-	19.1
Atoms in PL 4 (R factor only)		Cs	-	O(2)	O(3)	Al	O(1)	Be	-	-	20.0
Atoms in PL 4 (first cycle)		Cs	-	O(2)	O(3)	Al	O(1)	Be	-	-	19.4

TABLE 9 (continued)

	1*a*	12*h*	12*i*	12*i*	4*e*	4*e*	4*e*	1*b*	3*d*	*R* (%)
Atoms in PL 5	Cs	B	O(2)	O(3)	Al	O(1)	Be	-	-	19.9
Atoms in PL 6	Cs	B	O(2)	O(3)	Al	O(1)	-	-	-	14.6
Atoms in PL 7	Cs	B	O(2)	O(3)	Al	O(1)	Be	-	-	13.7
Atoms in PL 8	Cs	B	O(2)	O(3)	Al	O(1)	Be	O(4)	-	15.7
Atoms in PL 9	Cs	B	O(2)	O(3)	Al	O(1)	Be	-	O(4)	15.2

TABLE 10

Series of models II (PLi, i = 1,2,...9) listing the actual parameters

atom		Cs	B	O(2)	O(3)	Al	O(1)	Be	R factor based on listed parameters
equipoint		1*a*	12*h*	12*i*	12*i*	4*e*	4*e*	4*e*	
parameters of model PL1	x	0				0.375			
	y	0				x			41.0%
	z	0				x			
	B (Å^2)	0.5				0.4			
parameters of model PL2	x	0		0.375		0.375			
	y	0		x		x			33.0%
	z	0		0.125		x			
	B (Å^2)	0.5		0.6		0.4			
parameters of model PL3 (fourth cycle)	x	0		0.364	0.131	0.3619	0.6164		
	y	0		x	x	x	x		19.1%
	z	0		0.1015	0.604	x	x		
	B (Å^2)	0.8		0.18	0.5	0.22	0.21		
parameters of model PL4	x	0		0.363	0.135	0.3619	0.6185	0.750	
	y	0		x	x	x	x		19.4%
	z	0		0.102	0.604	x	x		
	B (Å^2)	0.81		0.18	0.56	0.17	0.15	0.2	
parameters of model PL5	x	0	0.2389	0.3635	0.1319	0.3603	0.6180	0.749	
	y	0	$\frac{1}{2}$	x	x	x	x	x	19.9%
	z	0	0	0.1027	0.5992	x	x	x	
	B (Å^2)	1.12	1.08	0.17	0.64	0.28	0.01	1.69	

TABLE 10 (continued)

atom		Cs	B	O(2)	O(3)	Al	O(1)	Be	R factor based on listed parameters
equipoint		1*a*	12*h*	12*i*	12*i*	4*e*	4*e*	4*e*	
parameters	x	0	0.245	0.3627	0.1320	0.3604	0.6168		
of model PL6	y	0	½			x		-	14.6%
	z	0	0	0.1022	0.6003	x			
B (Å^2)		1.09	0.93	0.19	0.67	0.20	0.01		
parameters	x	0	0.2397	0.2397	0.1322	0.3602	0.6177	0.7492	
of model PL7	y	0	½	x		x	x	x	13.7%
	z	0	0	0.1023	0.5994	x	x	x	
B (Å^2)		1.12	1.00	0.16	0.65	0.27	0.01	1.03	

location of the boron atoms, especially since their occurrence in a tetrahedral coordination of oxygen atoms is common. The discrepancy factor, R, however, showed an increase to 19.9%. The beryllium atom was therefore taken out of the last model and the discrepancy factor, R, was recalculated. It decreased to 15.5%, and to 14.6% after one cycle of refinement. It seemed unlikely that the discrepancy factor would decrease further. Hence the beryllium atoms were put in again, and after one cycle of refinement the value of R, 13.7%, showed that the right structure had been found. Now an electron-density map was prepared. It still showed a peak at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. Geometrical and crystal chemical considerations preclude the placing of an atom in this very small hole and in the immediate environment of negatively and positively ionized atoms. This was proved by showing that the R factor increased to 15.7% when computed for a model containing an additional oxygen atom at 1b. Then a model with three oxygen atoms at $\frac{1}{2}$ 0 0 in 3d was tried. R increased to 16.0% and then decreased slightly to 15.1% after two refinement cycles.

It was thus established that the unit cell of Rhodizite contains one alkali atom at the origin, twelve atoms O(2) in 12*i* at $x \approx 3/8$, $z \approx 1/8$, four O(1) in 4*e* with $x \approx 5/8$, twelve O(3) in 12*i* at $x \approx 1/8$, $z \approx 5/8$, four Al atoms, four Be atoms and twelve B atoms. Tables 9 and 10 show the series of models II (PLi, i = 1,2,...9).

CHAPTER VIII

The Final Stage of Refinement

The final stage of refinement (Cruickshank, 8) of the structure of rhodizite was now possible and, for several reasons, necessary.

1. The reflection deck had to be thoroughly checked for heavy systematic errors due to the overlapping of reflections by general-radiation streaks. These streaks belonged to reflections which were lying on the same central reciprocal-lattice line but nearer the origin.

2. Adjustment of the subroutine WEIGHT of SFLSQ3(25) to reflect the accuracy of the various data was very important in order to avoid drastic effects on the scale factor and vibration parameters. A good weighting scheme is one which gives refined parameters with the smallest standard deviations (Cruickshank, 7, 8).

3. The alkalies Cs, Rb, K and Na have absorption edges with frequencies ν_{alkali} lying within the range of the frequency, $\nu_{Mo\underline{K}}$, of the Mo$\underline{K}$ radiation ($\nu_{Mo\underline{K}} \lesssim \nu_{alkali}$). This means that corrections for anomalous

dispersion are necessary. The average corrections of the alkali scattering factor are:

$$f' = -0.3\ e; \qquad f'' = 1.9e$$

A section of the subroutine SPGRP of program SFLSQ 3 takes care of this correction.

4. The occupancy of the alkali atom had been assumed to be 1, although the result of the chemical analysis gave a value of 0.94. Refinement of the occupancy was therefore desirable.

The final stage of refinement consisted of six cycles of least-squares refinement. The variations mentioned above for attaining better agreement between F_{obs} and F_{cal} were tried.

All reflections on the same reciprocal-lattice line directly beyond very strong reflections were removed from the deck. These were: 500, 550, 660, 900 and 10 00. For the refinement the full deck of cards was used.

The subroutine WEIGHT was changed as suggested in (3) above. For $\underline{F}_{obs} = 0$, the standard deviation was computed as $\sigma = 100/\underline{F}_{obs}$. The weight for a reflection was calculated according to the formula

$$w = 1/\sigma^2 \quad = \underline{F}_{obs}/10{,}000$$

Some criteria for the right choice of a weighting scheme are:

A. The weighted

$$R = \frac{\sum W(\|F_{obs}| - |F_{cal}\|)}{\sum W|F_{obs}|}$$

should be minimized. It decreased in the computations from 18.4% to 6.6% after the first refinement cycle and to 5.4% after the second.

B. The variance of the refined parameters should become very small. The refined parameters in the first and second refinement cycles were the scale factor, the space parameters and the isotropic temperature factors;

the refined scale factor, $s_n = 1.445$, had a standard deviation of 0.006. In the second refinement cycle for model PL 7 the standard deviation was 0.02. The standard deviations of the space parameters increased slightly in the first cycle and somewhat in the second, but did not go below their values in the second cycle of PL 7.

C. An incorrect weighting scheme also has very drastic effects on the temperature factors. The temperature factors of the beryllium atom increased from 1.7 Å^2 to 8.6 Å^2 in the first cycle, to 24 Å^2 in the second cycle, and to 25 Å^2 in the third cycle of the final stage of refinement. This could have been incorrectly interpreted to mean that Be does not belong at the location at which it had been put. It was found, however, that the weighting scheme was chosen properly but that for two very strong reflections, 400 and 550, the value of $(|F_{obs}| - |F_{cal}|)/\sigma$ had been computed to be abnormally high, although for both reflections F_{cal} and F_{obs} showed very good agreement. These reflections were therefore assigned a weight of zero, since the weighting scheme did not hold for them. After the sixth refinement cycle the temperature factor for Be had a very reasonable value (atomic B for B after the sixth cycle = 1.8 ± 0.5 Å^2).

The presence of an anomalous scatterer separates the symmetrically equivalent Friedel reflections into two groups which are no longer equivalent. Table 11 shows the two groups of reflections for the space group $\underline{P\bar{4}3m}$ derived by Pepinski and Okaya (19). The difference, ΔI, of the intensities $cF^2(hkl)$ and $cF^2(\bar{h}\bar{k}\bar{l})$, where c is the reciprocal of the intensity correction factor, can be computed in the following way:

$$\Delta I = I(hkl) - I(\bar{h}\bar{k}\bar{l}) = (cF^2(hkl) - cF^2(\bar{h}\bar{k}\bar{l}))$$

$$F^2(hkl) = F^*(hkl) \cdot F(hkl), \text{ where}$$

$$F(hkl) = \sum_j f_j e^{i\phi_i} \quad \text{, or}$$

$$F(hkl) = (\Delta f'Cs + i\Delta f''Cs)(\cos\phi Cs + i\sin\phi Cs) + |R|\cos\phi + i|R|\sin\phi, \text{ where}$$

TABLE 11

The two equivalent groups due to anomalous dispersion

equivalent reflections of group 1 (right-handed)	equivalent reflections of group 2 (left-handed)
hkl	$\bar{h}\bar{k}\bar{l}$
khl	$\bar{k}\bar{h}\bar{l}$
$\bar{k}h\bar{l}$	$k\bar{h}l$
$\bar{h}\bar{k}l$	$hk\bar{l}$
$k\bar{h}\bar{l}$	$\bar{k}hl$
$h\bar{k}\bar{l}$	$\bar{h}kl$
$\bar{k}\bar{h}l$	$kh\bar{l}$
$\bar{h}k\bar{l}$	$h\bar{k}l$
lhk	$\bar{l}\bar{h}\bar{k}$
klh	$\bar{k}\bar{l}\bar{h}$
hlk	$\bar{h}\bar{l}\bar{k}$
$\bar{h}l\bar{k}$	$h\bar{l}k$
$\bar{l}\bar{h}k$	$lh\bar{k}$
$h\bar{l}\bar{k}$	$\bar{h}lk$
$l\bar{h}\bar{k}$	$\bar{l}hk$
$\bar{h}\bar{l}k$	$hl\bar{k}$
$\bar{l}h\bar{k}$	$l\bar{h}k$
lkh	$\bar{l}\bar{k}\bar{h}$
$\bar{l}k\bar{h}$	$l\bar{k}h$
$\bar{k}\bar{l}h$	$kl\bar{h}$
$l\bar{k}\bar{h}$	$\bar{l}kh$
$k\bar{l}\bar{h}$	$\bar{k}lh$
$\bar{l}\bar{k}h$	$lk\bar{h}$
$\bar{k}l\bar{h}$	$k\bar{l}h$

$$|R| \cos\phi = \Sigma fj \cos\phi j \quad \text{and} \quad |R| \sin\phi = \Sigma fj \sin\phi j$$

As $\phi cs = 0$, it follows that

$$F(hkl) = \Delta f' \, cs + i \Delta f'' \, cs + |R| \cos\phi + |R| \sin\phi$$

$$cF^2(hkl) = c \cdot \left(|R| \cos\phi + \Delta f' \, cs \right)^2 + \left(\Delta f' \, cs + |R| \sin\phi \right)^2$$

As $\cos\phi = \cos(-\phi)$ and $\sin\phi = -\sin -\phi$, we get

$$cF^2(\bar{h}\bar{k}\bar{l}) = c \cdot \left(R \cos\phi + \Delta f' \, cs \right)^2 + \left(\Delta f' \, cs - |R| \sin\phi \right)^2$$

Therefore, the difference, ΔI, is

$$\Delta I = 4c \, |R| \, \Delta f'' \, cs \sin\phi$$

If the correction factors are not equal and $c_1 = c_2 = c$ does not hold, then

$$I(hkl) - I(\bar{h}\bar{k}\bar{l}) = 2(c_1 - c_2) \, |R| \, \Delta f'' \sin\phi$$

The difference of the corresponding structure factors is:

$$F(hkl) - F(\bar{h}\bar{k}\bar{l}) = \sqrt{F^2(hkl)} - \sqrt{F^2(\bar{h}\bar{k}\bar{l})}$$

$$= \sqrt{(|R| \cos\phi + \Delta f' \, cs)^2 + (\Delta f'' \, cs + R \sin\phi)^2} - \sqrt{(|R| \cos\phi + \Delta f' \, cs)^2 + (\Delta f'' \, cs - |R| \sin\phi)^2}$$

It was not known to which group of reflections the measured intensities should be assigned. It was, however, certain that all these reflections belonged to one group only and not to both. In the first and second refinement cycle they were assumed to be right-handed; as the R factor went up to 17%, it was concluded that they belonged to the other (left-handed) group. After four cycles of refinement the unweighted R factor went down to 12.7%. This was the best agreement between the calculated and observed structure factors. The occupancy of the alkali, which was also refined, did not change significantly. In the fourth cycle the product of the multiplicity factor (1/24) and the occupancy was refined to 0.0407. This means that the occupancy was refined to 0.97. From the correlation matrix it is surprising that the temperature factor of cesium is not very highly dependent on the occupancy, c, of cesium ($\rho(c_{Cs}$, atomic B

TABLE 12

Coordinates and temperature factors of the rhodizite structure

(Space group $P\bar{4}3m$, a = 7.319 Å)

Atom	Equipoint	Coordinates of representative point	Parameters Ideal	 R=12.7% unweighted, 7.1% weighted	Temperature factors, $Å^2$
Cs	1*a*	000			1.33±0.06
B	12*h*	$x\frac{1}{2}0$	$x = \frac{1}{4}$	0.2448±0.0013	0.88±0.09
Be	4*e*	xxx	$x = \frac{3}{4}$	0.755±0.003	1.7±0.5
Al	4*e*	xxx	$x = \frac{3}{8}$	0.3575±0.0005	0.29±0.08
O(1)	4*e*	xxx	$x = \frac{5}{8}$	0.6195±0.0009	0.01±0.09
O(2)	12*i*	xxz	$x = \frac{3}{8}$	0.3635±0.0006	0.13±0.05
			$z = \frac{1}{8}$	0.1017±0.0006	
O(3)	12*i*	xxz	$x = \frac{1}{8}$	0.1339±0.0008	0.68±0.07
			$z = \frac{5}{8}$	0.6019±0.0008	

TABLE 13

Structure Factors

h	k	l	F_{obs}	F_{cal}
1	1	0	26.18	23.10
2	0	0	51.35	44.91
2	1	0	52.29	52.16
2	1	1	88.23	86.49
2	2	0	37.58	37.35
2	2	1	37.90	44.93
2	2	2	147.86	146.34
3	0	0	108.48	108.17
1	0	3	6.04	4.98
3	2	0	29.53	29.00
3	2	1	53.56	50.93
3	2	2	22.62	34.65
3	3	0	75.31	75.14
3	3	1	10.90	12.68
3	3	2	53.60	52.49
3	3	3	65.62	64.57
4	1	0	79.80	79.46
4	1	1	46.86	49.43
4	2	0	37.53	40.30
4	2	1	31.27	31.79
4	2	2	37.30	38.06
4	3	0	21.39	20.15
4	3	1	46.14	44.68
4	3	2	32.07	35.19
4	3	3	28.57	27.58
4	4	1	9.07	10.15
4	4	2	25.47	26.42
4	4	3	58.27	60.32
4	4	4	50.35	51.10
5	1	0	41.65	30.44
5	1	1	48.31	47.62
5	2	0	30.07	28.53
5	2	1	35.73	36.29
5	2	2	32.44	35.18
5	3	0	16.94	14.75
5	3	1	13.32	14.49
5	3	2	46.80	45.10
5	3	3	34.67	33.92
5	4	0	8.43	8.60
5	4	1	25.66	25.57
5	4	2	28.24	28.93
5	4	3	23.30	25.15
5	4	4	33.65	36.41
5	5	1	16.78	20.75
5	5	2	30.40	32.23
5	5	3	31.29	29.91
5	5	4	26.93	29.43
5	5	5	34.82	30.70
6	0	0	54.32	46.47
6	1	0	15.74	15.21
6	1	1	38.59	30.42
6	2	0	22.70	22.48
6	2	1	27.45	27.49
6	2	2	48.27	55.21
6	3	0	33.93	38.77
6	3	1	47.06	46.92
6	3	2	19.59	17.66
6	3	3	30.42	28.38
6	4	0	11.97	10.51
6	4	1	28.91	30.78
6	4	2	20.41	21.67
6	4	3	11.21	10.26
6	4	4	9.17	30.15
6	5	0	22.34	20.15
6	5	1	39.72	40.03
6	5	2	22.41	23.11
6	5	3	21.44	16.17
6	5	4	15.95	17.68
6	6	2	31.71	37.15
6	6	3	20.50	20.01

h	k	l	F_{obs}	F_{cal}
6	6	4	17.96	16.59
6	6	5	13.77	15.06
6	6	6	26.45	25.63
7	0	0	31.82	24.82
7	1	0	38.19	39.69
7	1	1	12.03	14.52
7	2	0	21.32	26.46
7	2	1	33.58	32.04
7	2	2	20.27	18.70
7	3	0	35.61	33.01
7	3	1	37.84	38.94
7	3	2	26.00	26.31
7	3	3	11.89	13.05
7	4	0	49.34	50.55
7	4	1	8.44	10.47
7	4	2	9.80	12.35
7	4	3	45.69	45.40
7	5	1	21.47	22.12
7	5	2	20.31	18.59
7	5	3	9.23	11.39
7	5	4	14.00	12.78
7	5	5	8.27	9.54
7	6	1	12.89	15.54
7	6	2	17.37	15.03
7	6	3	22.01	18.86
7	6	4	18.75	21.78
7	6	5	25.86	25.48
7	6	6	9.25	8.49
7	7	0	54.28	53.41
7	7	2	11.17	16.16
7	7	3	17.77	33.22
7	7	4	32.33	31.21
7	7	5	16.06	15.25
7	7	6	14.06	14.40
7	7	7	15.56	10.92
8	0	0	118.03	118.11
8	1	0	13.87	2.25
8	1	1	35.04	33.40
8	2	0	15.83	18.56
8	2	1	28.20	27.71
8	2	2	20.60	23.73
8	3	0	46.15	38.45
8	3	1	23.06	26.58
8	3	2	16.15	18.89
8	3	3	30.40	27.96
8	4	0	23.09	25.41
8	4	1	32.66	32.31
8	4	2	20.86	23.25
8	4	3	6.24	6.47
8	4	4	85.49	80.96
8	5	0	28.43	25.60
8	5	1	29.86	34.94
8	5	2	18.38	21.11
8	5	3	26.28	24.13
8	5	4	6.99	10.14
8	5	5	22.80	24.72
8	6	0	15.18	17.67
8	6	1	11.53	14.87
8	6	2	20.04	19.88
8	6	3	15.18	17.25
8	6	4	15.01	14.96
8	6	5	17.04	16.09
4	0	0	136.95	126.90
4	4	0	183.60	195.64
8	6	6	11.74	12.01
8	7	1	19.85	18.48
8	7	2	11.54	12.24
8	7	3	16.68	15.55
8	7	4	25.69	24.80
8	7	5	9.68	12.76
8	7	7	23.14	24.77
8	8	0	64.92	59.13
8	8	2	18.52	20.92
8	8	3	20.89	21.42
8	8	4	13.16	15.18
8	8	5	17.39	18.50

h	k	l	F_{obs}	F_{cal}
8	8	6	12.41	16.54
8	8	8	38.86	42.65
9	1	0	10.61	2.73
9	1	1	12.81	14.57
9	2	0	16.69	13.55
9	2	1	22.13	23.50
9	2	2	20.29	20.71
9	3	0	14.40	17.67
9	3	1	21.68	17.70
9	3	2	17.82	15.69
9	3	3	21.08	13.25
9	4	0	18.19	17.04
9	4	1	18.83	21.57
9	4	2	16.73	16.37
9	4	3	12.72	12.73
9	5	0	14.60	9.04
9	5	1	22.54	20.12
9	5	2	15.10	14.06
9	5	3	7.94	6.65
9	5	4	14.82	12.44
9	5	5	11.67	12.08
9	6	0	16.29	16.36
9	6	1	12.01	7.60
9	6	2	13.37	11.83
9	6	3	22.66	24.18
9	6	4	9.96	8.87
9	6	5	17.07	18.25
9	6	6	9.37	10.49
9	7	1	9.69	9.49
9	7	2	16.39	16.86
9	7	4	7.41	12.37
9	7	5	10.20	9.43
9	8	0	9.67	6.29
9	8	1	20.07	18.56
9	8	2	14.59	14.13
9	8	3	14.70	18.26
9	8	4	12.53	12.98
9	8	5	16.88	19.06
9	8	6	10.45	12.27
9	8	7	12.17	10.58
9	9	0	21.48	7.61
9	9	2	17.02	18.51
9	9	3	14.81	12.48
9	9	4	8.16	9.46
9	9	5	14.83	10.71
9	9	8	8.23	12.01
9	9	9	12.51	4.67
10	1	0	17.43	19.49
10	1	1	30.63	31.49
10	2	0	8.38	10.32
10	2	1	10.93	10.84
10	2	2	22.88	28.85
10	3	1	15.03	10.34
10	3	2	12.03	12.54
10	3	3	21.84	20.61
10	4	0	21.56	26.54
10	4	2	11.31	12.26
10	4	3	18.45	18.80
10	5	0	13.10	11.60
10	5	1	14.63	8.61
10	5	3	26.39	27.04
10	5	4	15.46	8.86
10	5	5	29.54	22.21
10	6	0	14.78	6.75
10	6	1	14.55	11.72
10	6	2	20.37	20.65
10	6	4	10.33	7.28
10	6	6	11.75	17.98
10	7	0	17.07	18.79
10	7	1	19.93	18.77
10	7	2	7.81	8.20
10	7	3	10.09	9.48
10	7	5	9.36	3.54
10	7	6	12.95	9.03
10	8	1	12.03	10.67
10	8	2	9.72	9.74
10	8	4	12.89	12.52
10	8	6	12.36	11.04

h	k	l	F_{obs}	F_{cal}
10	8	7	8.80	7.97
10	8	8	11.61	11.72
10	9	1	14.68	19.55
10	9	2	8.06	7.93
10	9	4	9.80	12.50
10	9	7	17.27	16.06
10	9	9	11.58	10.77
10	10	0	15.68	2.00
10	10	3	7.98	7.79
10	10	6	13.74	11.79
10	10	8	7.57	7.25
10	10	9	7.46	5.82
10	10	10	9.00	8.60
11	0	0	38.51	33.86
11	1	0	13.04	11.68
11	1	1	20.87	18.22
11	2	1	11.51	13.17
11	2	2	10.70	12.49
11	3	0	27.26	36.92
11	3	2	11.75	13.85
11	3	3	21.53	23.45
11	4	0	12.29	15.25
11	4	1	17.81	18.89
11	4	2	9.29	10.43
11	4	3	22.63	21.36
11	4	4	23.81	25.31
11	5	0	8.61	7.32
11	5	1	10.45	11.37
11	5	2	14.11	13.77
11	5	3	14.18	12.15
11	5	5	10.55	8.81
11	6	0	17.71	14.11
11	6	1	17.18	14.53
11	6	2	10.61	10.87
11	6	3	10.77	9.07
11	6	6	9.00	8.51
11	7	0	35.17	32.90
11	7	1	15.44	16.69
11	7	2	10.45	9.93
11	7	3	10.97	8.39
11	7	4	34.97	32.73
11	7	7	16.22	19.73
11	8	0	18.68	18.43
11	8	3	17.24	14.89
11	8	7	18.82	17.25
11	8	8	10.48	11.82
11	9	2	9.00	5.96
11	9	3	8.12	8.16
11	9	6	14.52	11.43
11	10	2	9.44	6.99
11	10	3	10.17	7.18
11	10	4	9.09	9.70
11	10	5	14.13	12.83
11	10	6	8.24	6.51
11	10	7	10.57	7.15
11	11	0	38.30	35.21
11	11	2	9.29	6.63
11	11	3	12.90	15.07
11	11	4	28.67	27.43
11	11	6	8.45	6.99
11	11	7	16.75	10.13
11	11	8	19.58	19.90
12	0	0	20.11	8.80
12	1	0	16.20	16.09
12	1	1	22.97	29.99
12	2	0	7.51	8.28
12	2	1	12.44	15.60
12	2	2	11.53	13.59
12	3	0	9.81	1.54
12	3	1	24.20	22.29
12	4	0	47.12	42.36
12	4	2	14.56	14.19
12	4	3	14.74	14.62
12	5	2	15.14	15.55
12	5	3	18.06	20.95
12	5	5	20.37	22.60

h	k	l	F_{obs}	F_{cal}
12	6	0	11.63	12.48
12	6	1	12.17	12.86
12	6	4	10.15	10.53
12	6	5	10.76	11.95
12	6	6	17.43	11.45
12	7	0	14.90	11.70
12	7	1	11.32	12.08
12	7	3	11.06	10.51
12	7	5	14.30	12.19
12	7	6	7.92	5.37
12	8	0	9.75	3.07
12	8	1	10.67	13.87
12	8	2	16.26	16.50
12	8	4	28.10	26.20
12	8	6	14.78	15.31
12	8	7	7.61	8.32
12	8	8	13.85	14.23
12	9	0	8.63	9.24
12	9	1	16.52	18.41
12	9	2	9.27	9.62
12	9	3	16.92	15.71
12	9	5	12.23	13.97
12	9	6	9.87	7.65
12	9	7	9.86	9.85
12	9	8	8.80	10.90
12	9	9	8.69	9.63
12	10	2	11.06	9.32
12	10	3	7.84	5.89
12	10	4	14.30	10.38
12	10	5	9.58	7.13
12	10	6	10.65	7.71
12	10	8	10.31	9.67
12	11	7	7.88	8.45
12	12	0	17.74	14.78
12	12	1	9.70	10.65
12	12	2	14.60	13.87
12	12	4	9.79	9.30
12	12	6	10.29	12.19
12	12	8	15.49	16.46
12	12	9	7.81	8.52
13	0	0	16.94	4.51
13	1	0	9.96	6.19
13	1	1	9.95	9.34
13	2	0	9.13	9.48
13	2	2	9.14	7.95
13	3	2	11.07	11.92
13	4	3	9.00	8.23
13	4	4	8.92	5.99
13	5	0	9.43	3.48
13	5	2	14.68	16.30
13	5	3	8.52	8.45
13	5	5	11.25	9.27
13	6	1	10.91	12.51
13	6	2	10.47	6.95
13	6	3	9.41	1.56
13	6	5	8.10	9.26
13	7	0	7.73	9.92
13	7	3	8.99	7.58
13	7	6	12.56	10.16
13	8	0	7.79	5.66
13	8	1	8.56	12.36
13	8	2	8.66	6.99
13	8	3	13.21	10.82
13	8	5	10.75	10.38
13	8	6	9.04	4.41
13	8	7	7.63	7.49
13	9	0	9.94	5.40
13	9	1	9.09	8.56
13	9	2	15.07	17.52
13	9	9	8.12	6.26
13	10	0	13.88	10.61
13	10	3	9.90	10.59
13	10	5	9.48	8.29
13	10	8	6.36	6.99
13	11	2	8.42	5.17
13	12	1	9.37	10.48

h	k	l	F_{obs}	F_{cal}
13	12	2	8.28	4.56
13	12	3	8.38	9.62
13	12	5	8.11	8.77
13	12	6	6.19	4.50
13	12	7	6.11	7.05
13	13	0	10.89	9.79
13	13	2	15.46	18.55
13	13	3	6.62	7.45
13	13	4	7.75	8.15
13	13	6	7.30	7.40
14	0	0	24.69	24.98
14	1	1	11.70	7.18
14	3	0	11.42	10.85
14	3	1	15.60	18.33
14	3	3	12.60	4.85
14	4	4	18.46	14.83
14	5	1	19.93	18.57
14	5	3	9.22	7.19
14	5	4	10.22	7.82
14	5	5	9.51	6.23
14	6	3	8.69	5.89
14	6	5	9.38	4.24
14	6	6	11.57	9.67
14	7	4	12.54	8.94
14	7	5	14.97	14.10
14	7	7	12.72	5.62
14	8	0	10.91	8.60
14	8	3	9.55	4.37
14	8	6	9.28	6.02
14	8	8	10.68	5.66
14	9	0	13.29	10.13
14	9	3	12.19	14.25
14	9	5	13.44	10.29
14	10	3	8.58	4.08
14	10	7	6.94	4.39
14	10	8	7.76	7.10
14	11	0	8.21	8.82
14	11	1	8.80	7.08
14	11	3	6.64	3.40
14	12	0	6.10	5.36
14	12	2	6.09	6.04
14	12	4	18.67	3.80
14	13	1	6.89	6.67
15	0	0	9.61	13.53
15	1	0	10.60	12.87
15	1	1	9.61	10.65
15	2	1	12.89	10.83
15	2	2	8.67	10.90
15	3	0	19.12	18.10
15	3	1	12.51	11.53
15	3	2	11.40	9.22
15	4	0	14.36	17.39
15	4	3	18.98	18.98
15	5	1	9.27	8.39
15	6	3	11.62	9.89
15	6	5	12.43	9.80
15	6	6	8.73	7.99
15	7	0	25.84	26.68
15	7	1	9.53	5.28
15	7	2	8.49	8.38
15	7	3	9.47	11.93
15	7	4	20.94	20.69
15	7	6	8.11	7.07
15	8	3	10.89	9.11
15	8	4	7.25	11.39
15	8	7	14.93	14.99
15	10	0	8.82	6.31
15	10	1	9.06	8.57
15	10	2	6.85	7.02
15	10	3	8.40	6.12
15	10	5	7.16	5.72
15	11	0	22.59	24.07
15	11	4	18.98	22.50
16	0	0	21.69	15.32
16	1	1	20.14	17.90
16	2	1	9.52	10.64
16	3	1	14.68	17.35
16	3	2	8.58	10.02

h	k	l	F_{obs}	F_{cal}
16	3	3	14.23	14.10
16	4	0	9.18	.71
16	4	4	17.88	12.72
16	5	1	13.32	17.08
16	5	3	17.06	15.16
16	6	1	7.42	9.44
16	6	4	8.62	10.22
16	6	5	9.64	7.50
16	7	1	12.56	11.36
16	7	7	7.51	6.88
16	8	0	12.07	9.71
16	8	2	9.44	10.46
16	8	6	9.92	9.39
16	9	1	11.39	11.13
16	9	3	8.74	11.01
16	10	0	9.64	9.55
17	0	0	7.52	6.67
17	2	1	7.67	7.54
17	3	2	7.55	3.29
17	5	2	8.00	11.57
17	5	4	6.28	7.69
17	6	0	9.30	6.33
17	6	5	8.12	9.19
17	7	4	5.78	4.63
17	8	1	5.66	7.40
17	9	0	4.98	7.14
17	9	2	8.94	8.06
18	0	0	11.45	10.25
18	1	1	12.18	12.34
18	3	1	6.74	5.17
18	3	3	10.00	6.26
18	4	0	14.43	13.25
18	4	4	5.86	6.25
18	5	1	9.05	7.88
18	5	3	8.91	11.36
18	5	5	6.82	6.78
18	6	2	6.00	4.76
18	7	0	5.33	6.56
19	1	0	6.18	4.53
19	2	1	9.10	9.82
19	2	2	5.92	7.26
19	3	0	9.00	8.62

of Cs) = .59). Usually the correlation between these two parameters is very high. Table 12 contains the final space parameters and temperature factors of the rhodizite structure. In Table 13 the observed structure factors and final calculated structure factors are listed.

CHAPTER IX

The Final Structure

In the rhodizite structure the oxygen atoms are arranged in cubic close-packing whose period parallel to a is 1/4a. If all close-packed sites were occupied, 32 oxygen atoms would be required; however, four sites are unoccupied, in the manner described below, and the cell contains only 28 oxygen atoms, namely 4 O(1) + 12 O(2) + 12 O(3).

The metal atoms occupy octahedral and tetrahedral voids between oxygen atoms. Each Al atom is surrounded by six oxygen atoms in octahedral coordination, namely 3 O(1) + 3 O(2). Each of the four octahedra shares three edges with the other octahedra to form a tight central cluster of composition $Al_4O_{16}{}^{-20}$.

Each of the Be atoms is surrounded by four oxygen atoms in tetrahedral coordination, namely O(1) and 3 O(3). The four Be atoms thus augment the central cluster to form a larger cluster of composition $Be_4Al_4O_{28}{}^{-36}$. This cluster is bordered by 24 oxygen atoms, namely 12 O(2) + 12 O(3), and all atoms of this cluster are entirely within the cell boundaries.

Each of the B atoms is surrounded by four oxygen atoms in tetrahedral coordination, namely 2 O(3) + 2 O(2). The Be atoms lie in the cell faces, four to a face, and connect the enlarged clusters with one another. In this way the entire structure, except for the alkali atoms, comprises a connected network of composition $(B_{12}Be_4Al_4O_{28})^0$ per cell.

The oxygen atoms of the connected network are in cubic close-packing which would be complete except for four missing oxygen atoms which would tetrahedrally surround the origin. The resulting hole at the origin is occupied by an alkali atom whose immediate environment consists of 12 O(3) atoms, each at a distance of about 3.24 Å. These oxygen atoms do not surround the alkali uniformly, but occur as four tetrahedrally located clusters of three, each three outlining a face of a tetrahedron of oxygen atoms surrounding Be.

Figures 4 and 5 illustrate the arrangement of atoms in the mineral rhodizite. Figure 4 shows the atom locations in the lower half of the ideal structure, and some of the symmetry elements of space group $\underline{P}\bar{4}3\underline{m}$ which repeat the labelled atoms. Figure 5 shows the network in the upper half of the cell represented as coordination polyhedra. The tetrahedra in the heavily shaded diagonal bands have their centers on level $z \approx 3/4$. In these tetrahedra the metal is alternately B and Be, with the Be on the mirror in the middle of the band. The more lightly shaded tetrahedra have their centers at $z = 1/2$ and contain B only. The central pair of heavily shaded octahedra contain Al at level $z \approx 5/8$. The circles represent the alkali atoms at level $z = 1$.

The structure reported here has the idealized formula $CsB_{12}Al_4Be_4O_{28}$, which differs from the Frondel and Ito formula in that (a) it has 12 B instead of 11, (b) it has 28 O instead of 29, and (c) it does not appear to need any hydrogen atoms, as suggested by the following argument: All oxygen atoms of rhodizite are exactly satisfied by electrostatic valency bonds provided that the alkali atom is ignored and no oxygen atoms are regarded as hydroxyls. The electrostatic valency summations are as follows:

Figure 4

Atom locations in the lower half

of the ideal structure

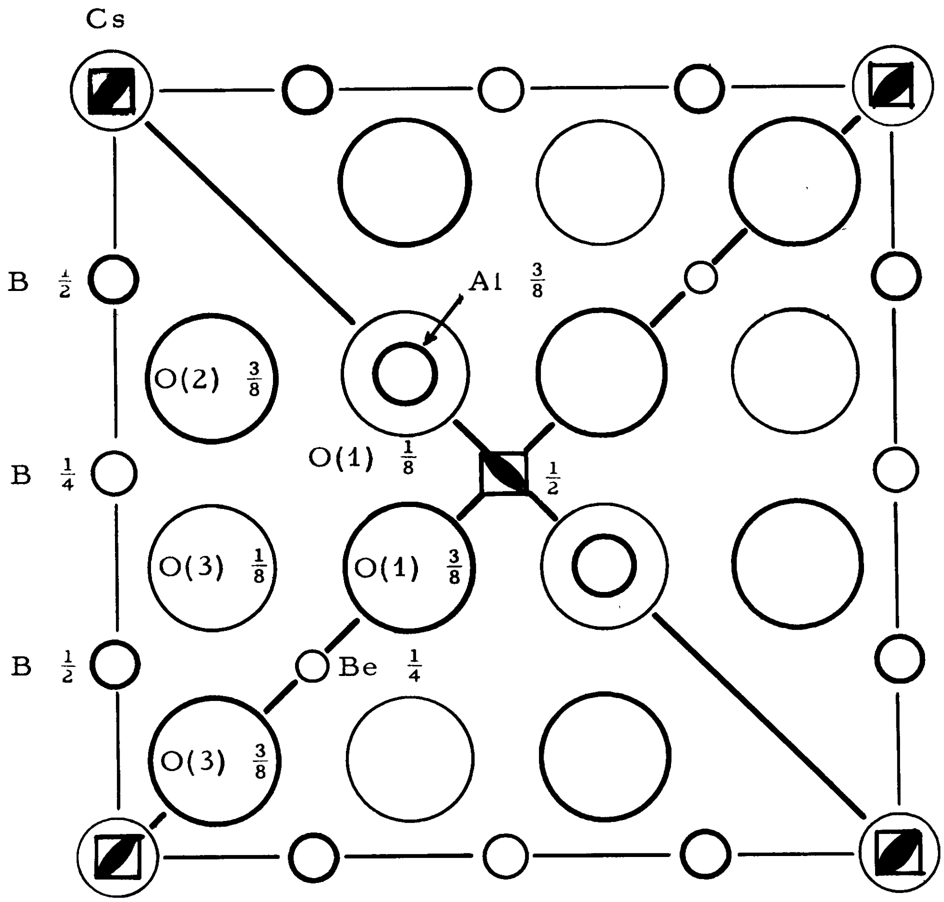
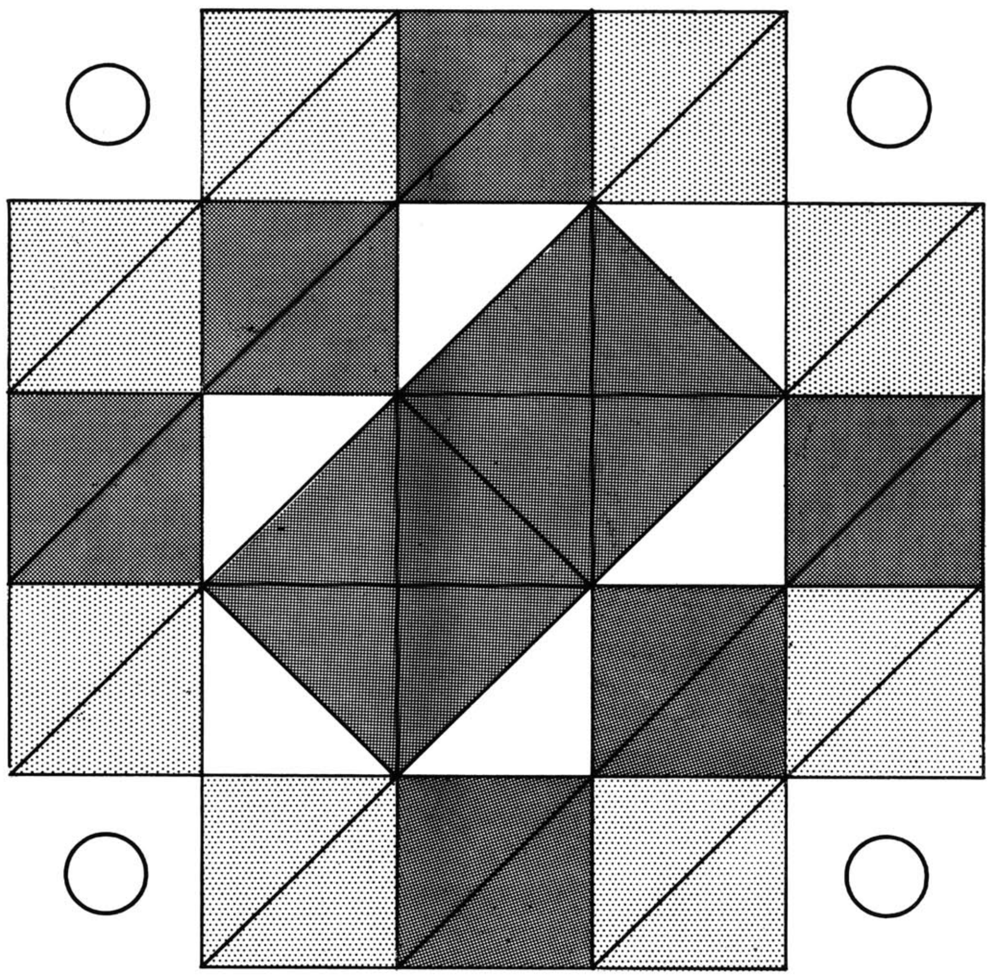

Cs
B 1/2
B 1/4
B 1/2
Al 3/8
O(2) 3/8
O(1) 1/8
1/2
O(3) 1/8
O(1) 3/8
Be 1/4
O(3) 3/8

Figure 5

Network in the upper half of the cell
represented as coordination polyhedra



$$O(1): \quad 3\cdot\frac{1}{2}\,(\mathrm{Al}) + \frac{1}{2}\,(\mathrm{Be}) = 2$$

$$O(2): \quad \frac{1}{2}\,(\mathrm{Al}) + 2\cdot\frac{3}{4}\,(\mathrm{B}) = 2$$

$$O(3): \quad \frac{1}{2}\,(\mathrm{Be}) + 2\cdot\frac{3}{4}\,(\mathrm{B}) = 2$$

Because of this, it seems reasonable to suppose that the hydrogen atoms reported in Frondel and Ito's analysis are, in fact, absent from the structure, and that in the recorded analysis the loss on ignition was due rather to a loss of some of the other constituents, especially B and alkali. The density computed for the ideal formula, $CsB_{12}Be_4Al_4O_{28}$ (except that the alkali mixture found by Frondel and Ito was used instead of pure Cs), in an isometric cell of edge $\underline{a}$ = 7.319 Å, is 3.478 g/cc. This is essentially the same as that of Frondel and Ito's preferred formula, which requires 3.47, as compared with a measured density of 3.44. The small excess in calculated density could readily be attributed to a small error in determination of the proportions of the several alkalies making up the alkali site.

The ideal formula $CsB_{12}Be_4Al_4O_{28}$ appears to be unbalanced in the amount of one excess positive charge. In other

TABLE 14

Bond distances

Bond	distance, Å	standard deviation, Å
Al - O(1)	1.932	0.005
Al - O(2)	1.873	0.005
Al - Al	2.950	0.007
Be - O(1)	1.72	0.02
Be - O(3)	1.606	0.010
B - O(2)	1.519	0.006
B - O(3)	1.475	0.006
Cs - O(3)	3.227	0.010

TABLE 15

Bond angles

	bond angle (degrees)	standard deviation (degrees)
Al - O(1) - Al	99.5	0.4
Al - O(2) - B	119.5	0.3
Al - Al - O(1)	40.2	0.2
Al - Al - O(2)	88.1	0.2
O(1) - Al - O(2)	93.5	0.2
Be - O(1) - Al	118.2	0.8
Be - O(3) - B	114.2	0.9
B - O(2) - B	120.8	0.6
B - O(2) - Al	119.5	0.4
B - O(3) - Cs	114.9	0.4
B - O(3) - B	118.4	0.4
O(1) - Be - O(3)	100.5	1.2
O(2) - B - O(3)	108.8	0.4
O(2) - B - O(2)	110.2	0.4
O(3) - B - O(3)	113.2	0.8

words, the alkali appears to behave formally as a neutral atom. It also appears to be held, clathrate fashion, within the large hole at the origin. For the Manjaka rhodizite, the composition of the alkali in the hole is $Cs_{.47}Rb_{.17}K_{.33}Na_{.03}$. It is evident that these various atoms, whose radii vary from about 1.7 Å down to 1 Å for ionic radii, or about 2.4 Å to 1.6 Å for metallic radii, cannot all fit the same void. The occurrence of neutral Na in the clathrate structure Na_8Si_{46} and Na_xSi_{136} has just been discovered and discussed by Kasper et al. (15) Rhodizite appears to offer another example of a neutral alkali in a cage. This is anomalous, however, because Cs is one of the most easily ionized atoms. An explanation may be that it contributes its electron to a bond between the four close Al atoms, thus permitting the network to have a valence of -1. Each of the four AlO_6 tetrahedra shares three edges with the other three, giving rise to a tight cluster whose composition is Al_4O_{16}, with a formal valence of -20. The distance between Al atoms of this cluster (2.95 Å) is only a little larger than in metallic Al, and a bond between them thus appears possible. The same cluster is found in the spinel and pharmacosiderite structures.

In Tables 14 and 15 the inter-atomic distances and bond angles, with their standard deviations, are listed.

Bibliography

1. Behier, J. Contribution a la mineralogie de Madagascar. Ann. Geol. de Madagascar 29 (1960) 56.

2. Biscoe, J. and Warren, B.E. The structure of euclase, $HBeAlSiO_5$. Z. Krist. A 86 (1933) 292-297.

3. Buerger, M.J. Crystal-structure analysis. John Wiley & Sons, Inc., New York (1958).

4. Buerger, M.J. X-ray crystallography. John Wiley & Sons, Inc., New York (1942).

5. Buerger, M.J. The precession method. John Wiley & Sons, Inc., New York (1964).

6. Buerger, M.J. Vector space and its application in crystal-structure analysis. John Wiley & Sons, Inc., New York (1959).

7. Cruickshanck, D.W.J. The required precision of intensity measurements for single-crystal analysis. Acta Cryst. 13 (1960) 774.

8. Cruickshanck, D.W.J. Errors in least-squares methods, in Computing methods in crystallography (ed. J.S. Rollet), Pergamon Press, Oxford (1965) 112.

9. Damour, A. Sur la rhodizite. Bull. soc. min. franc. 5 (1882), 98-103.

10. Duparo, W.L., Wunder, M. and Sabot, R. Contribution a la connaissance des mineraux des pegmatites. Bull. soc. min. franc. 34 (1911) 136-139.

11. Frondel, C. and Ito, J. Composition of rhodizite. Tschermaks min. u. potr. Mitt. 10 (3) (1965) 409.

12. Fankuchen, I. Fine angle adjustments. A new use of the Weissenberg goniometer. Acta Cryst. 16 (1963) 930.

13. International tables for x-ray crystallography, volumes I, II and III. The Kynoch Press, Oxford (1955).

14. Ito, J. and West, J. The structure of bertrandite $H_2Be_4Si_2O_9$. Z. Krist. 83 (1932) 384-393.

15. Kasper, J.S., Hagemuller, P., Pouchard, M. and Cros, C. Clathrate structure of silicon Na_8Si_{46} and Na_xSi_{136} (x 11). Science 150 (1965) 1713.

16. Lacroix, A. Mineralogie de Madagascar 1 (1922) 340-342.

17. Lippard, S.J. ALP program for accurate lattice parameters (private communication).

18. Main, P. and Woolfson, M.M. Accurate lattice parameters from Weissenberg photographs. Acta Cryst. 16 (1963) 731.

19. Okaya, Y. and Pepinsky, R. New developments in the anomalous dispersion method for structure analysis: paper 28 in Computing methods and the phase problem in x-ray analysis (report of a conference held at Glasgow) (ed. R. Pepinsky, J.M. Robertson and K. Speakman). Pergamon Press, New York (1961) 273.

20. Onken, H.H. Manual for some computer programs for x-ray analysis. Massachusetts Institute of Technology, Cambridge, Massachusetts (1964).

21. Onken, H.H. GAMP: Program for computing absorption correction.

22. Onken, H.H. FINTE 2: Program for computing integrated intensities.

23. Palache, C., Berman, H. and Frondel, C. Dana's System of mineralogy, Vol. II. John Wiley & Sons, Inc., New York (1951), 329.

24. Pisani, Bull. soc. min. 33 (1910) 37.

25. Prewitt, C.T. SFLSQ 3: Program for structure factor calculation and least squares refinement.

26. Prewitt, C.T. DFSET: Program for computing diffractometer settings.

27. Rose, G. Über den Rhodizit, eine neue Mineral gattung. Ann. Phys. 33 (1834) 253-256.

28. Shankar, J. Amirthalingam, V. and Padmanabhan, V.M. The crystal structure of bis-acetylacetone-beryllium. Acta Cryst. 13 (1960) 201.

29. Strunz, H. Gitterkonstante und Raumgruppe von Rhodizit. Naturwiss. 26 (1938) 217.

30. Strunz, H. Die Struktur von Rhodizit. Naturwiss. 31 (1943) 68.

31. Strunz, H. Mineralogische Tabellen. Akademische Verlagsgesellschaft Geest & Portig K.-G., Leipzig (1957).

32. Sly, W.G. and Shoemaker, D.P. MIFR 2: Crystallographic Fourier summation program for the IBM 7090/94.

33. Trojer, F.J. and Dollase, W.D. ADIAG: Program to generate a six-fold deck for MIFR 2.

34. Zeman, J. Formel und Strukturtyp des Pharmacosiderits. Tschermaks min. u. petr. Mitt. 1 (1) (1948).