

The crystal chemistry of rhodizite: a re-examination

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ABSTRACT. The crystal chemistry of rhodizite was re-examined using data from high-resolution electron microscopy (HREM), magic angle spinning nuclear magnetic resonance (MASNMR), a single crystal X-ray structure refinement, and a new chemical analysis. The analysis calculates to the formula: $(K_{0.46}Cs_{0.36}Rb_{0.06}Na_{0.02})_{20.90}Al_{3.99}Be_4(B_{11.35}Be_{0.55}Li_{0.02})O_{28}$. The distribution of alkali cations was shown to be truly random by HREM images and computer image simulations. The distribution of boron and beryllium was monitored by MASNMR, the spectra for both elements gave only single resonances indicating that all beryllium and boron atoms are located in chemically equivalent sites. The structure of rhodizite was refined by single crystal X-ray diffraction techniques. The mineral is cubic $a = 7.318(1)$ Å, space group $P\bar{4}3m$. A full matrix least-squares refinement using 152 unique observed reflections [$F > 3\sigma(F)$] converged to $R = 0.0344$. The refinement confirmed the basic structure as determined by Taxer and Buerger (1967), 4 beryllium atoms of the unit cell were found to occupy a $4e$ special position, the remaining 0.5 being randomly distributed with the 11.35 boron atoms over the $12h$ sites.

KEYWORDS: rhodizite, crystal chemistry, high-resolution electron microscopy, magic angle spinning nuclear magnetic resonance.

THE year 1984—the one hundred and fiftieth anniversary of the description of the mineral rhodizite—offered a timely opportunity to re-examine the crystal chemistry of this unusual mineral. Rhodizite is a relatively rare mineral and one of the few which contains significant amounts of caesium. The exact chemical composition of the mineral has, however, remained problematical since its description by the German mineralogist and chemist, Gustav Rose (Rose, 1834, 1836). Rhodizite was first found as minute crystals on rubellite tourmaline in the lithia-rich pegmatites around the villages of Sarapulsk and Shaitansk, both near Mursinsk, north of Sverdlovsk (then Ekaterinburg), USSR. The mineral has since been found in crystals up to 2

cm on edge at several localities in Madagascar, including Antandrokomby near Mt Bity and at Manjaka and Ampakita in the Sahatany valley (Lacroix, 1922).

Early attempts at chemical analysis of rhodizite were hindered by the small amount of material available (see section 3). Many crystalline specimens were obtained from Madagascar in the early 1960s and using material from this source for analysis, Frondel and Ito (1965) proposed the formula $CsAl_4Be_4B_{11}O_{25}(OH)_4$. A structure determination of rhodizite was subsequently undertaken by Buerger and Taxer, 1966 (see also Taxer and Buerger 1967). They assigned the space group as $P\bar{4}3m$ (as did Strunz, 1938) on the basis of diffraction symmetry, positive pyro- and piezoelectric characteristics and crystal habit. A structure solution was obtained using Patterson methods and the structure was refined to 9.1%; the structure is described in detail in the next section.

From their studies Buerger and Taxer (1966) obtained a structural formula $CsAl_4Be_4B_{12}O_{28}$, which is at variance with their analysis in requiring an additional boron, one less oxygen and no hydrogen atoms. This formula also requires the caesium to be neutral in order to maintain charge balance. However, Donnay *et al.* (1966) showed by electron spin resonance (ESR) and magnetic susceptibility measurements that caesium is present in its unipositive state and proposed the alternative formula $CsAl_4Be_4B_{11}O_{26}(OH)_2$. This formula is consistent with the analytical data of Frondel and Ito—and with the density measurements and a structure of Taxer and Buerger—if a randomly disordered boron vacancy is introduced and two hydroxyl groups are randomly substituted for oxygen. In the light of the findings of Donnay *et al.* (1966) and due to the uncertainties in the interpretation of the chemical analysis, Taxer and Buerger (1967) decided to curtail their refinement at 9.1%, leaving certain aspects of the crystal chemistry unclear. The exact occupation of the

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alkali site remained uncertain. Earlier workers (Fron del and Ito, 1965; Duparc *et al.*, 1911) found that other alkali elements substitute for caesium, the total occupancy from the chemical analyses being slightly less than unity. It was left unclear whether this value should be unity and whether the alkali substitution is random or ordered. Similarly, uncertainties remained as to the locations of the proposed boron vacancy and the two hydroxyl groups suggested by Donnay *et al.* (1966). Since the thermal parameters for boron were not refined, the assignment of boron and beryllium into the $12h$ and $4e$ sites is open to question.

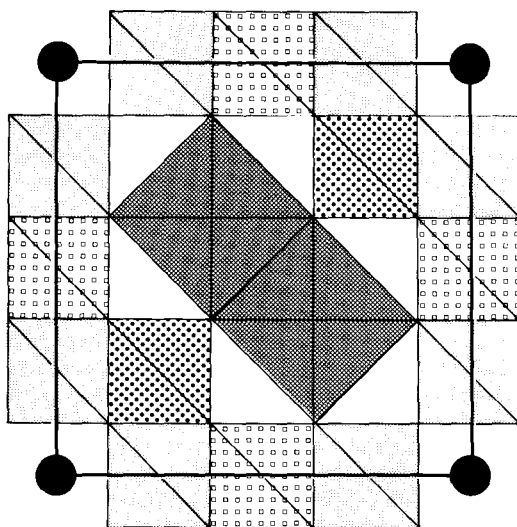


FIG. 1. Schematic diagram showing the upper half of the rhodizite cell. Alkali ions (black circles) are positioned at the cubic cell corners. The edge-sharing pair of AlO_6 octahedra are shown finely crosshatched. The tetrahedra containing beryllium (at $z = \frac{3}{4}$), which lie on the mirror planes, are shaded with large dots and the set of tetrahedra containing boron (also at $z = \frac{3}{4}$) are shaded with squares. The other tetrahedral sites, lightly shaded, contain boron at height $z = \frac{1}{2}$.

We carried out a structural investigation of rhodizite using electron diffraction, HREM and MASNMR. A full chemical analysis of the material studied was also undertaken. The initial results obtained using these techniques raised several new questions regarding the crystal chemistry of rhodizite, in particular the site assignment of boron and beryllium. Therefore, a crystal structure refinement by single crystal X-ray diffraction was carried out in an attempt to clarify these points. In this

paper, accounts of the structural imaging, chemical analysis and the structure refinement are given, together with a brief discussion of the MASNMR data. A preliminary account of the structural imaging has been given elsewhere. (Pring *et al.*, 1983) and a full account of the MASNMR data will be presented later.

The structure of rhodizite

The general structure of rhodizite, as determined by Buerger and Taxer (1966) is shown schematically in fig. 1. It is built around a central tetrahedral cluster of four edge-sharing AlO_6 octahedra, these clusters being linked through the cell faces by BO_4 tetrahedra. Beryllium and boron atoms occupy rows of tetrahedral sites parallel to $\{110\}$, with the four beryllium atoms assigned to a set of $4e$ type special positions which lie on the mirror planes. The alkali ions occupy large 12-coordinate sites, of approximately tetrahedral geometry, at the cell origins. The idealized atomic arrangement is illustrated in fig. 2.

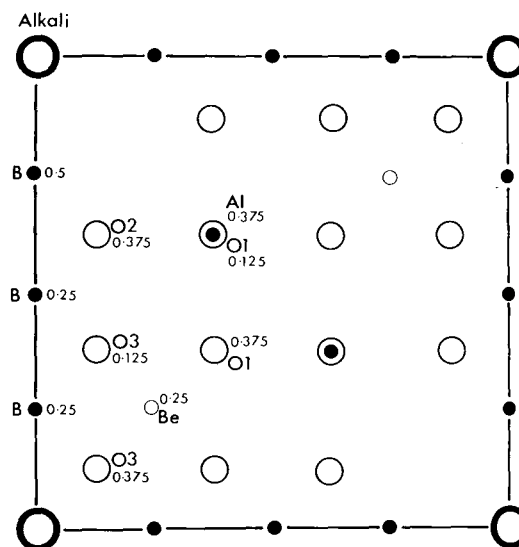


FIG. 2. Idealized atomic arrangement in the lower half of the rhodizite unit cell.

Taxer and Buerger also provide an alternative description of the structure based on an incomplete array of cubic close-packed oxygen atoms. If the close-packed set were complete, the rhodizite cell would contain 32 oxygens; however, 4 atoms about the origin are omitted, resulting in the large tetra-

hedral 12-coordinate alkali site. An oxygen subcell is evident within the structure, its cell edges parallel to those of the rhodizite cell but only half the length. The 4 Al atoms occupy the octahedral intersites between the oxygen atoms nearest to the centre of the rhodizite cell, with the boron and beryllium atoms occupying tetrahedral voids in the close-packed oxygen array.

Chemical analysis

Several rhodizite crystals from Ambatofinandrahana, in the Ankarata Mts, Madagascar (20° 33' S., 46° 49' E.), were obtained from Mr G. Binns of Hastings, England. A preliminary electron microprobe examination of a rhodizite crystal fragment and the X-ray powder pattern of the material prepared for analysis showed quartz to be the only significant impurity. Consequently all Si was assumed to be present as quartz and the analytical results were recalculated accordingly. For the analyses, fragments taken from a single rhodizite crystal were finely powdered in an agate mortar (some additional SiO₂ may have been introduced by this process) and the resultant powder was dried at 110° for 2 hours prior to semi-microanalysis, according to the procedures described. Analytical grade reagents were used except where otherwise specified.

A portion of 49.7 mg of the powdered material was fused with spectrographic grade Li₂CO₃ and the cold fusion product was dissolved in 2 ml of 4M HCl. The solution was made up to volume with deionized water and analysed for Al, Be, Ca, Cs, Fe, K, Na, Rb, and Si by atomic absorption spectrophotometry (AAS). Li was also determined by AAS on a separate aliquot of 132.4 mg of sample fused with NaOH then dissolved in 3M H₂SO₄ and made up to standard volume as before. A separately prepared crystal fragment (4.12 mg) was used for the determination of B by inductively coupled plasma emission spectrometry (ICPES). The powdered sample was fused with NaOH and the fusion product was dissolved in 4M HNO₃ and made up to standard volume for analysis. Si was also determined in this solution in order that the measured B concentration could be corrected for quartz impurity. The AAS and ICPES instruments were calibrated using standards prepared to match closely the analyte solutions. H₂O⁺ and CO₂ were determined on a 27.5 mg sample using a CHN elemental analyser (Din and Jones, 1978).

Our full chemical analysis of the Ambatofinandrahana material is presented in Table I together with the analyses reported by Frondel and Ito (1965) and earlier workers. The cell contents listed in Table I were calculated on the basis of 28

oxygens per cell. There are several differences between our analysis and that of Frondel and Ito. For example, potassium was found to exceed caesium as the principal alkali cation rather than the contrary. However, the two most important differences between the analyses, from a structural viewpoint, are the much lower water and the higher beryllium contents of the material we studied. The formula (K,Cs)_{0.9}Al₄Be_{4.5}B_{11.35}O₂₈ was obtained, compared to CsAl₄Be₄B₁₁O₂₆(OH)₂ as proposed by Donnay *et al.* (1966) on the basis of Frondel and Ito's analysis. The former formula matches the structural formula of Buerger and Taxer with Be + B = 15.85 (Buerger and Taxer, Be + B = 16) and at the same time achieves charge neutrality without the boron deficiency and hydroxyl substitution required by the formula proposed by Donnay *et al.* It is proposed that the additional (0.5 atom) beryllium is randomly disordered over the 12 boron sites and there is 0.15 boron site vacancy.

Three early analyses of rhodizite appear in the literature, but of these only the material analysed by Duparc *et al.* (1911), although contaminated by albite, yields a structurally meaningful composition. Duparc *et al.* (1911) obtained the formula (Li,K,Cs,Rb,Na,H)₄Al₆Be₇B₁₄O₃₉. However, if this analysis is recalculated assuming all silicon present is from the albite impurity (4.63%), the formula obtained is (Na_{0.33}K_{0.25}Rb_{0.20}Cs_{0.20})Al_{4.24}Be_{4.92}Li_{0.37}B_{10.26}H_{1.28}O₂₈. Sodium is the dominant alkali while potassium, rubidium, and caesium are approximately equal. It is also notable that there are 4.92 Be atoms per cell, the excess Be and Al, together with the Li can be assigned to the 12 boron sites. There are 11.79 cations assigned to the boron sites, excluding the protons, and only 0.21 of a boron vacancy is required. The structural ramifications of the higher Be content and the possible role of water or hydroxyl groups are discussed below. The most widely quoted of the early analyses is that of Pisani (Lacroix, 1910), whose sample was heavily contaminated with spodumene (LiAlSi₂O₆). On the basis of this analysis Lacroix (1910, 1922) proposed the formula (Cs,Rb,K,Na,H)₈Be₄Al₆B₁₂O₃₅. Also based on Pisani's analysis and with a knowledge of the cell, Strunz (1938) proposed the stoichiometry NaKLi₄Al₄Be₃B₁₀O₂₇ and later (Strunz, 1943) suggested a structural model for the mineral which was subsequently shown to be incorrect. The earliest rhodizite analysis is that by Damour (1882) of material from the type locality in the Urals. Since he unfortunately overlooked Be and did not determine the alkali elements individually, the type Russian rhodizite is chemically very poorly defined; to rectify this situation a modern analysis on Urals material has been initiated.

Table I. Analytical Data

	% Oxides by weight					Cations per 28 oxygens for analysis 1	
	1	2	3	4	5		
Li ₂ O	0.03		0.68	7.30		Li	0.02
Na ₂ O	0.06	0.12	1.78	3.30	1.62	Na	0.02
K ₂ O	2.77	1.79	1.41	5.90	12.00	K	0.46
Rb ₂ O	0.73	1.83	2.29			Rb	0.06
Cs ₂ O	6.4	7.54	3.47			Cs	0.36
Al ₂ O ₃	25.8	24.41	27.40	30.50	41.40	Al	3.99
BeO	14.3	12.20	14.93	10.10		Be	4.51
B ₂ O ₃	50.2	46.82	[43.33]	40.60	33.93	B	11.35
H ₂ O+	0.32	4.10	1.42	0.45	2.96		
CO ₂	0.15						
Rem	0.28	1.10	3.29	1.36	3.49		
TOTAL	101.0	99.91	100.00	99.51	95.40		

- (1) Ambatofinandrahana, Madagascar. Sample weight for main analysis: 49.7mg contained 6.23% SiO₂. Sample weight for boron determination: 4.12mg (contained 3.75% SiO₂). The data are for material dried at 110°C and are calculated to a SiO₂-free basis. 'Rem' is the sum of FeO (0.09%), CaO (0.18%), and MgO (0.01%). The estimated analytical error is ±5% relative for Cs₂O and oxides < 1% by weight and ±1% relative for other components. Analyst V.K. Din.
- (2) Manjaka, Madagascar. Sample weight 5g. The data are from Frondel and Ito (1965). 'Rem' is SiO₂ (0.45%); Fe₂O₃ (0.12%); Sn (0.1%); H₂O (0.43%). Analysts Ito and Haramura.
- (3) Manjaka, Madagascar. Sample weight 2.5g. Analysis by Duparc *et al.* (1911). 'Rem' is MgO (0.11%) and SiO₂ (3.18%). Contained albite admixed.
- (4) Antandrokomby, Madagascar. Sample weight 1.25g. The data are from Lacroix (1910). 'Rem' is SiO₂ (1.36%). Contained spodumene admixed. Analyst F. Pisani.
- (5) Urals, Russia. Sample weight 0.135g. The data are from Damour (1882), beryllium was overlooked. 'Rem' is CaO (0.74%), MgO (0.82%) and Fe₂O₃ (1.93%).

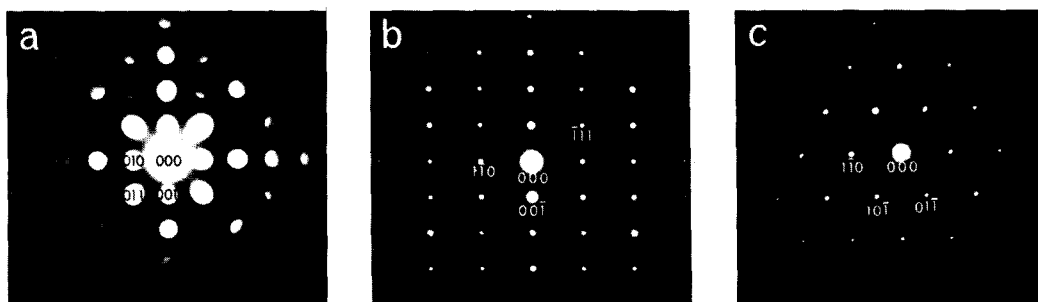


Fig. 3. Electron diffraction of rhodizite: (a) [100]; (b) [110]; (c) [111].

Electron optical studies

Imaging and diffraction. All electron microscopy was performed using a JEOL JEM 200Cx electron microscope operating at 200 kV with a standard tungsten hairpin filament and a beam current of typically $40 \mu\text{A}$. A $\pm 25^\circ$ side-entry eucentric goniometer stage was used and the spherical and chromatic aberration coefficients of the objective lens were $C_s = 2.5 \text{ mm}$ and the nominal $C_c = 2.7 \text{ mm}$, giving an optimum defocus (the so-called Scherzer defocus (Scherzer, 1949) of -950 \AA). The point to point resolution at this defocus was 2.9 \AA .

Thin fracture fragments of rhodizite for EM study, obtained by crushing the mineral under acetone in an agate pestle and mortar, were deposited on to holey carbon support films from suspension. Electron diffraction patterns were recorded with the beam parallel to zone axes $[100]$, $[110]$, and $[111]$ of this cubic mineral (fig. 3*a-c*). They show no evidence of supercell ordering of the alkali ions or of the proposed boron vacancies.

High resolution lattice images of sections perpendicular to these three zones were recorded (fig. 4*a-c*). Images viewed down $[100]$ (fig. 4*a*), show square arrays of bright spots 7.3 \AA apart, corresponding to the cubic cell a repeat. At the centre of these nets are weaker-contrast white dots, the intensities of which increase with crystal thickness. The image is slightly distorted at the crystal edge indicating that the crystal was tilted slightly off the exact zone orientation. Fig. 4*b* is a lattice image viewed down $[110]$, showing a rectangular $7.3 \times 5.2 \text{ \AA}$ motif, while the $[111]$ zone image (fig. 4*c*) shows a repeat pattern of black hexagons, a projection consistent with the threefold symmetry axis along $[111]$. These lattice images show large regions of perfect lattice and neither point defects nor dislocations were observed.

Computer image simulations. Simulations of the high resolution lattice images were generated using computer programs, written by one of us (D.A.J.), based on the multislice method of Goodman and Moodie (1974) (see also Cowley and Moodie, 1957). Calculations were performed using the electron optical parameters of the JEOL 200Cx as described above. The final atomic parameters of Taxer and Buerger (1967) were used in all calculations; image simulations were completed before the new structure refinement was undertaken (the minor changes in atomic coordinates that resulted would not affect these simulations). Images were calculated over a range of defocus (Δf) from 0 to -1600 \AA and for crystal thicknesses (ΔH) 2.5 to 200 \AA . It should be noted that in the course of these image simulations

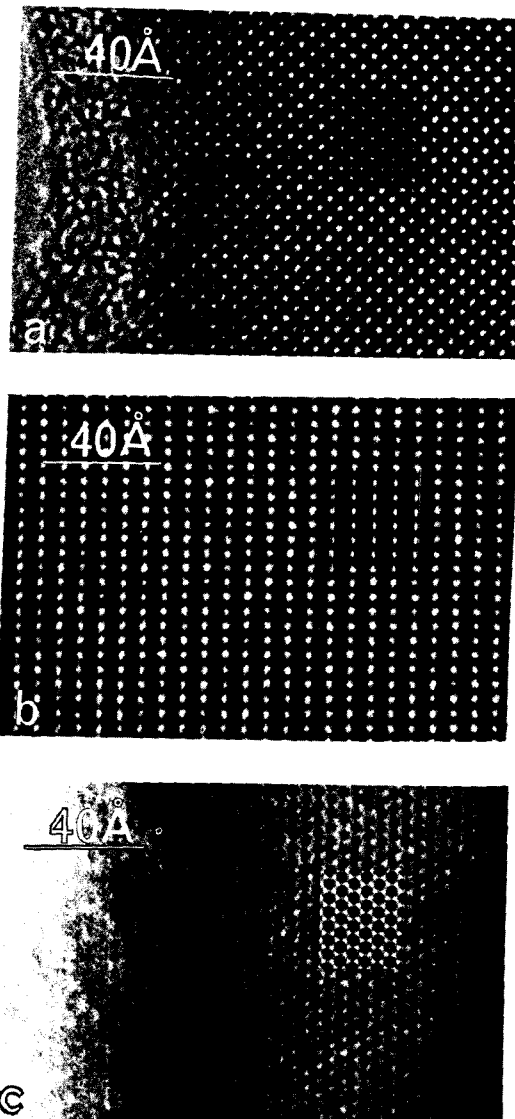


FIG. 4. Lattice projections of rhodizite viewed down: (a) $[100]$, image defocus -700 \AA , crystal thickness approximately 50 \AA . (b) $[110]$, image defocus -450 \AA , crystal thickness approximately 100 \AA . (c) $[111]$, image defocus -500 \AA , crystal thickness approximately 150 \AA . The inserts show matching image simulations for an average alkali (36 electron scatterer).

the effects of beam tilt were not considered. The recent work of Smith, Saxton *et al.* (1983) demonstrated that beam alignment can have a marked effect on image detail, particularly in materials with small unit cells.

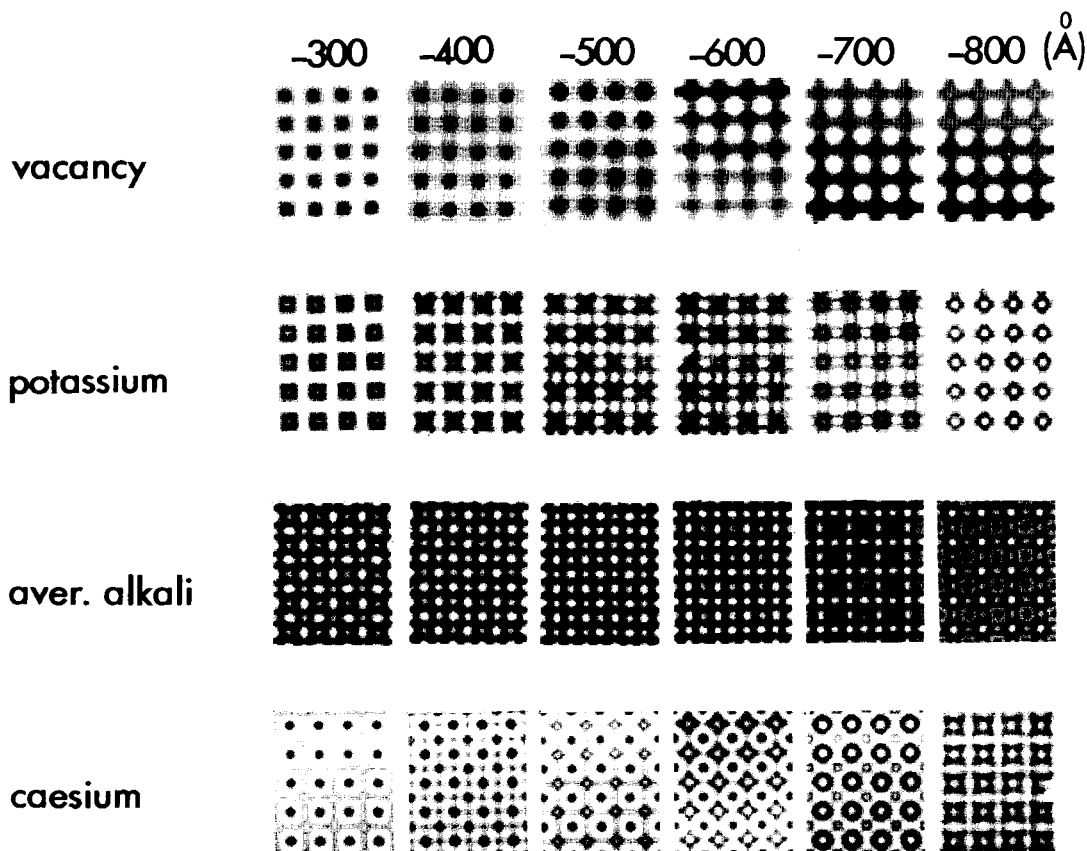


FIG. 5. Series of image simulations for rhodizites, [100] zone, with different alkali site occupancies, viz: vacant, potassium, average alkali, and caesium. The crystal thickness for the calculations is 50 Å.

The alkali ions are the strongest scatterers in the structure (accounting for about 10% of the total electrons) and their effect on the image detail was investigated by simulation of a series of [100] images. Fig. 5 shows a set of through-focus series calculated with four different scatterers occupying the alkali sites, viz: a vacancy, potassium, the 'average alkali' (used by Buerger and Taxer in their refinements), and caesium. The average alkali was calculated from the earlier alkali analysis of Frondel and Ito (1965) and corresponds to an atom with the scattering power of 36 electrons. The images simulated using the average alkali provide the best match for the [100] image shown in fig. 4a. The image match was also sustained in through-thickness calculations (see fig. 6). Matching image simulations for each of the three zones, calculated with the 36 electron scatterer, are shown as inserts in the lattice images (fig. 4a-c).

Overall the agreement between the observed and

calculated image is good and can be taken as confirmation of Buerger and Taxer's structure. The homogeneity of the image detail for a given crystal thickness in the lattice images indicates the absence of any highly ordered domains rich in a particular alkali. However, it was not possible to draw any conclusions regarding the distribution of the lighter boron and beryllium atoms using image simulation techniques owing to the lack of sensitivity of the method to small changes in electron density.

Magic angle spinning NMR

Rhodizite is ideally suited to study using multi-nuclear MASNMR as the principal cations are responsive to the technique by which it is possible to probe the site coordination and distribution of the responsive cations (Fyfe *et al.*, 1982, 1983). A series of MASNMR spectra of rhodizite were kindly recorded by Dr C. A. Fyfe and his colleagues

