



## A rietveld analysis of the crystal structure of ammonioleucite

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### Abstract

The crystal structure of ammonioleucite was refined by a Rietveld analysis using X-ray diffraction data of the type specimen. The refinement with a space group  $I4_1/a$  was converged at  $R_{wp} = 12.12$ ,  $R_p = 9.39$ ,  $R_F = 4.86$ ,  $R_B = 7.71$ , and  $R_e = 2.55\%$  with lattice parameters of  $a = 13.2106(6)$  and  $c = 13.7210(7)$  Å. Ammonioleucite is isostructural with leucite. The (Si, Al)O<sub>4</sub> tetrahedra form 4-, 6-, and 8-membered rings by sharing their apical oxygen atoms. The crystal structure consists of the three-dimensional framework of the rings of the tetrahedra. Ammonium ions are located in cavities in the framework. The (NH<sub>4</sub>)<sup>+</sup> ions in these cavities are larger than the corresponding K<sup>+</sup> ions in leucite, causing the cavities to be enlarged relative to those in leucite. Among the 4-, 6-, and 8-membered rings of (Si,Al)O<sub>4</sub> tetrahedra, only the 8-membered rings have diameters large enough to allow the migration of exchangeable K<sup>+</sup>, (NH<sub>4</sub>)<sup>+</sup> and Na<sup>+</sup> ions.

### Introduction

Ammonioleucite, (NH<sub>4</sub>)AlSi<sub>2</sub>O<sub>6</sub>, is an (NH<sub>4</sub>)-analogue of leucite, and was described as a new mineral found in Fujioka, Japan (Hori *et al.*, 1986). It occurs as fine crystals which replace the surface layers of analcime. Twinning was observed in all eighteen samples investigated for the single crystal study on ammonioleucite. Both 'merohedric' and 'pseudomerohedric' twins, which were reported for leucite (Mazzi *et al.*, 1976), were also observed

for ammonioleucite. Such complex twinning makes it difficult to obtain the correct intensity data on individual reflections in an X-ray diffraction examination. Therefore, the present authors conducted the crystal structure analysis of ammonioleucite by using a Rietveld refinement technique, which is free from the problem of twinning.

### Data Collection

The sample of ammonioleucite is a part of the type specimen from Tatarazawa, Fujioka, Japan (Hori *et al.*, 1986). The sample was carefully separated from the associated minerals such as analcime and dolomite under a binocular microscope. The sample was ground in an agate mortar, and the powdered sample was placed on an X-ray non-reflection specimen holder made of a quartz plate. The powder X-ray diffraction data were collected on a RIGAKU RAD-II B diffractometer, with graphite monochromatized  $\text{CuK}\alpha$  radiation from a conventional X-ray tube operated at 40kV - 20mA. The intensity data were collected by  $\theta$ - $2\theta$  step scanning (40 s per step and  $0.02^\circ$  step width) in the range of  $5 \leq 2\theta \leq 90^\circ$ . The slits used in the measurement were: divergence slit =  $1/2^\circ$ , Receiving slit = 0.15 mm, and anti-scatter slit =  $1/2^\circ$ .

### Rietveld Analysis

The Rietveld analysis was carried out on the basis of the experimental chemical formula of ammonioleucite:  $(\text{NH}_4, \text{K})_{0.869}\text{Al}_{0.89}\text{Si}_{2.115}\text{O}_6$  (Hori *et al.*, 1986). A Rietveld refinement program "RIETAN, ver. 2.5" (Izumi, 1983) was used in the analysis. The atomic parameters of leucite (Mazzi *et al.*, 1976) were used as the initial parameters for refinement. The distribution of aluminum and silicon atoms in the tetrahedral (T) site was assumed to be disordered, and the Al/Si ratio was fixed at 0.892/2.115, which is in accordance with the above chemical formula. The scattering factor for the T sites was represented by a virtual scatter with the Al/Si ratio. The scattering factor of nitrogen was used for the ammonium ion. The relative  $\text{NH}_4/\text{K}$  ratio was refined with the following constraint:  $\text{NH}_4 + \text{K} = 0.869$ . The thermal parameter of the K atom was assumed to be equal to the N atom. The occupancy factors of the  $\text{NH}_4$  and K ions and their thermal parameters were refined through a consecutive analysis. The zero-point shift of the counter was also refined. Preferred orientation correction was made, but no significant improvement of the  $R$  factors was observed, and hence the correction was neglected. During the refinement, the (Si,Al)-O interatomic distance was constrained to be  $1.65 \pm 0.1 \text{ \AA}$ , which is the expected (Si,Al)-O distance calculated for the Al/Si ratio by the method of Jones (1968). In the first step of refinement, all isotropic thermal parameters and occupancy parameters were fixed at the initial values, and atomic coordinates were refined. After the convergence of the atomic coordinates, the thermal and occupancy parameters for the ammonium (N) site were refined.

The refinement was converged at  $R_{wp} = 12.12$ ,  $R_p = 9.39$ ,  $R_F = 4.86$ ,  $R_B = 7.71$ , and  $R_e =$

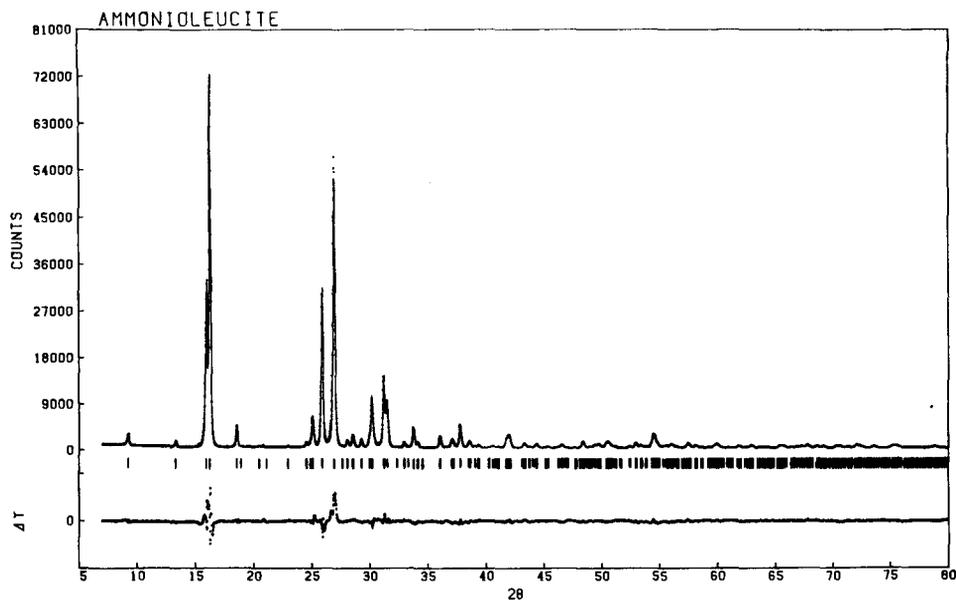


FIG. 1. Result of Rietveld analysis for ammonioleucite. Observed and calculated diffraction profiles are shown as dots and as a line, respectively. Short bars indicate Bragg angles, and  $\Delta Y$  indicates the difference between the observed and calculated intensities.

TABLE 1. Atomic coordinates and thermal parameters for Ammonioleucite.

Atom	x	y	z	B eq.(Å <sup>2</sup> )
N	0.358(2)	0.368(1)	0.112(2)	6.5(1)
T(1)	0.0632(8)	0.395(1)	0.1672(9)	0.960
T(2)	0.1668(8)	0.6115(8)	0.125(1)	0.89
T(3)	0.390(1)	0.6418(9)	0.0872(8)	0.97
O(1)	0.124(2)	0.304(2)	0.111(2)	2.37
O(2)	0.106(1)	0.507(1)	0.126(2)	2.32
O(3)	0.130(2)	0.663(1)	0.2246(9)	1.82
O(4)	0.125(1)	0.670(1)	0.0310(7)	1.88
O(5)	0.2921(8)	0.583(1)	0.124(2)	1.99
O(6)	0.482(1)	0.627(1)	0.162(1)	1.87

\* Thermal parameters except for N were not refined and values reported for leucite were used in the calculation.

2.55 % with lattice parameters of  $a = 13.2106(6)$  and  $c = 13.7210(7)$ Å. The fitting result is shown in Figure 1. The final atomic parameters are given in Table 1.

### Description and Discussion of Structure

The final occupancy parameter at the ammonium site is  $0.53(2)\text{[NH}_4\text{]} + 0.34(2)\text{K}$ . In the mineralogical description of ammonioleucite (Hori *et al.*, 1986), we found that accurate analysis of the  $\text{NH}_4$  ion in the mineral was difficult given the limited amount of the sample available and the unavoidable contamination by the associate minerals. Because the possibility of contamination of the  $\text{NH}_4$  ion could not be fully precluded by a bulk chemical analysis, the present analysis has been undertaken to provide further experimental evidence of the existence of the  $\text{NH}_4$  ion in this new mineral. This is another reason why a structure analysis was performed.

Figure 2 illustrates the crystal structure of ammonioleucite (*ORTEP II*, Johnson, 1976). Interatomic distances and bond angles were calculated by a computer program known as *UMBADTEA* (Finger, 1968), and are listed in Table 2. It was confirmed that ammonioleucite is isostructural with leucite (tetragonal low temperature phase). The crystal structure of ammonioleucite consists of a three-dimensional framework made of the  $(\text{Si,Al})\text{O}_4$  tetrahedra. The  $(\text{Si,Al})\text{O}_4$  tetrahedra share their apical oxygen atoms to form 4-, 6-, and 8-membered rings. Average  $(\text{Si,Al})\text{-O}$  distances at the tetrahedral sites are 1.64, 1.63, and 1.62 Å for the T1, T2, and T3 sites, respectively. They are slightly shorter than the expected value of 1.65 Å, whereas those distances for leucite (1.643, 1.656 and 1.656 Å) are in a good agreement with the expected value of 1.656 Å (Mazzi *et al.*, 1976). The ammonium ion is located in a cavity of the framework. It is surrounded by 6 oxygen atoms at distances of 2.98–3.25 Å and the other three oxygen atoms located at 3.55 Å. The coordination number of the potassium atom in leucite (Mazzi *et al.*, 1976) was described as 6 + 6, and inner and outer K-O distances were in the ranges of 2.956 - 3.004 and 3.506 - 3.759 Å, respectively. In the same manner, the coordination number of the ammonium ion in ammonioleucite can be expressed as 6 + 7 or 6 + 3 + 4, with four additional oxygen atoms located between 3.81 and 3.93 Å from the ammonium ion (Table 2). However, the interatomic distance exceeding 3.8 Å is too long for the  $(\text{NH}_4)\text{-O}$  bond. The mean  $(\text{NH}_4)\text{-O}$  distance of 3.17 Å for the six closest oxygen atoms is longer than the corresponding mean K-O distance of 3.014 Å in

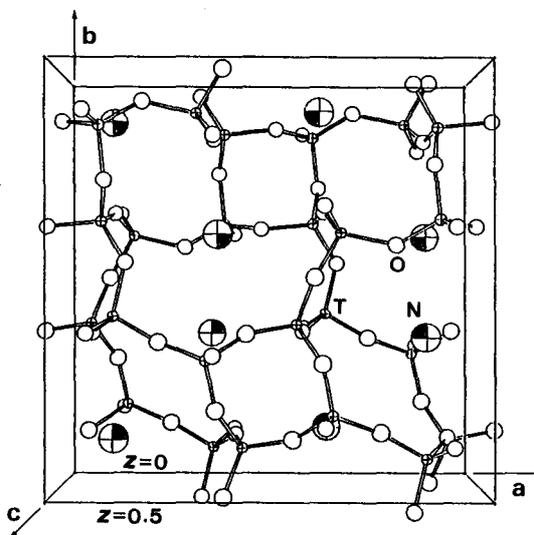


FIG. 2. The crystal structure of ammonioleucite. A view of a half of the unit cell ( $0 < z < 0.5$ ) along the  $c$  axis.

TABLE 2. Interatomic distances (Å) and angles (°) for Ammonioleucite

<u>N-polyhedron</u>			
N <sub>i</sub> -O(1) <sub>i</sub>	3.20(4)	N <sub>i</sub> -O(1) <sub>iii</sub>	3.61(4)
-O(2) <sub>vi</sub>	3.25(2)	-O(3) <sub>vi</sub>	3.56(3)
-O(3) <sub>vii</sub>	3.25(3)	-O(5) <sub>iv</sub>	3.49(4)
-O(4) <sub>vii</sub>	3.28(3)	mean	3.55 <sub>3</sub>
-O(5) <sub>i</sub>	2.98(2)		
-O(6) <sub>iv</sub>	3.06(3)		
mean	3.17		
<u>T(1)-tetrahedron</u>			
T(1) <sub>i</sub> -O(1) <sub>i</sub>	1.64(3)	O(1) <sub>i</sub> -T(1) <sub>i</sub> -O(1) <sub>ii</sub>	103(2)
-O(1) <sub>ii</sub>	1.62(3)		-O(2) <sub>i</sub> 109(1)
-O(2) <sub>i</sub>	1.68(2)		-O(4) <sub>iii</sub> 106(1)
-O(4) <sub>iii</sub>	1.60(2)	O(1) <sub>ii</sub> -T(1) <sub>i</sub> -O(2) <sub>i</sub>	113(1)
mean	1.63 <sub>5</sub>		-O(4) <sub>iii</sub> 110(1)
		O(2) <sub>i</sub> -T(1) <sub>i</sub> -O(4) <sub>iii</sub>	115(1)
<u>T(2)-tetrahedron</u>			
T(2) <sub>i</sub> -O(2) <sub>i</sub>	1.60(2)	O(2) <sub>i</sub> -T(2) <sub>i</sub> -O(3) <sub>i</sub>	102(1)
-O(3) <sub>i</sub>	1.60(2)		-O(4) <sub>i</sub> 105(1)
-O(4) <sub>i</sub>	1.60(2)		-O(5) <sub>i</sub> 107.4(9)
-O(5) <sub>i</sub>	1.70(2)	O(3) <sub>i</sub> -T(2) <sub>i</sub> -O(4) <sub>i</sub>	112(1)
mean	1.62 <sub>5</sub>		-O(5) <sub>i</sub> 113(1)
		O(4) <sub>i</sub> -T(2) <sub>i</sub> -O(5) <sub>i</sub>	116(1)
<u>T(3)-tetrahedron</u>			
T(3) <sub>i</sub> -O(3) <sub>iv</sub>	1.60(2)	O(3) <sub>iv</sub> -T(3) <sub>i</sub> -O(5) <sub>i</sub>	112(1)
-O(5) <sub>i</sub>	1.59(2)		-O(6) <sub>i</sub> 117(1)
-O(6) <sub>i</sub>	1.60(2)		-O(6) <sub>v</sub> 102(1)
-O(6) <sub>v</sub>	1.68(2)	O(5) <sub>iv</sub> -T(3) <sub>i</sub> -O(6) <sub>i</sub>	111(1)
mean	1.61 <sub>8</sub>		-O(6) <sub>v</sub> 114(1)
		O(6) <sub>i</sub> -T(3) <sub>i</sub> -O(6) <sub>v</sub>	101(1)
Subscript number refer to the following positions			
i)	x	y	z
ii)	1/4-y	1/4+x	1/4-z
iii)	3/4-y	1/4+x	1/4+z
iv)	3/4+y-1	3/4-x	3/4+z-1
v)	3/4+y-1	1/4-x+1	1/4-z
vi)	3/4+y-1	1/4-x	1/4-z
vii)	1/4-y+1	1/4+x	1/4-z

leucite (Mazzi *et al.*, 1976). This elongation indicates an enlargement of the cavity for the ammonium (potassium) site, and is a result of the cavity's being occupied by the relatively larger ammonium ion instead of the smaller potassium ion.

The mean (NH<sub>4</sub>)-O distance (3.17 Å) is apparently longer than those reported for (NH<sub>4</sub>)<sub>3</sub>Be<sub>2</sub>O<sub>10</sub> (3.016 Å) (Averbuch-Pouchot *et al.*, 1977) and (NH<sub>4</sub>)<sub>2</sub>SiP<sub>4</sub>O<sub>13</sub> (2.957 Å). Similarly, the mean K-O distance for leucite (3.014 Å) (Mazzi *et al.*, 1976) is longer than the distance of 2.78 Å that was calculated from their effective ionic radii by adding 1.38(K<sup>+</sup>) and 1.40 (O<sup>2-</sup>) Å (Shannon and Prewitt, 1969). In the crystal structures of both ammonioleucite and leucite, the observed (NH<sub>4</sub>)-O and K-O distances are longer than the expected values. This means that the size of the cavity where the (NH<sub>4</sub>) and K ions reside, which is surrounded by the tight (Si,Al)O<sub>4</sub> framework, is much larger than the ideal size for (NH<sub>4</sub>) and K ions. The relatively large thermal parameters, namely (6.5 Å<sup>2</sup>) for (NH<sub>4</sub>) in ammonioleucite and 4.21 Å<sup>2</sup> for K in leucite, suggest that these cations are loosely trapped at the cation sites in the large cavities.

The (Si,Al)O<sub>4</sub> framework structure of ammonioleucite, as well as that of leucite, is virtually identical with that of analcime (Ferraris *et al.*, 1972). Hori *et al.* (1986) suggested that ammonioleucite is a resultant product of the (NH<sub>4</sub>,K) ion-exchange for the Na ion in analcime. The crystallographic site corresponding to the K and (NH<sub>4</sub>) sites in leucite and ammonioleucite, respectively, is occupied by a water molecule in the analcime structure. A passageway is required in the framework structure for the migration of water molecules and exchangeable ions, such as K<sup>+</sup>, (NH<sub>4</sub>)<sup>+</sup>, and Na<sup>+</sup>.

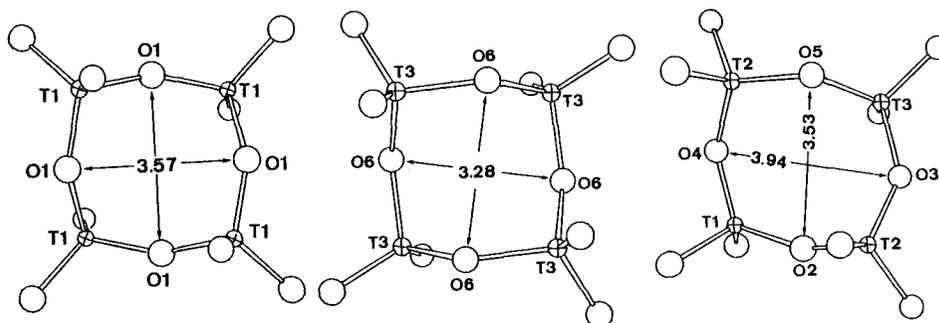


FIG. 3. The 4-membered rings of the  $(\text{Si,Al})\text{O}_4$  tetrahedra in the crystal structure of ammonioleucite. The values in the arrows are interatomic distances (in  $\text{\AA}$ ) between the oxygen atoms, which define the inside diameter of the ring.

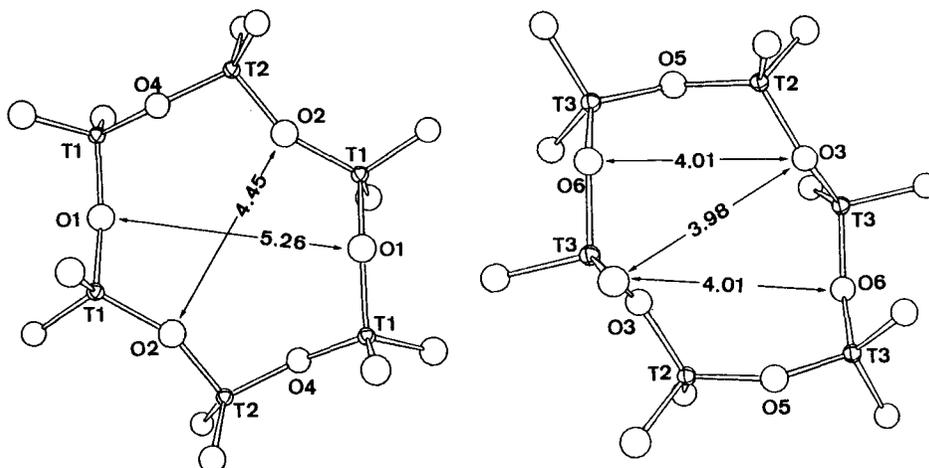
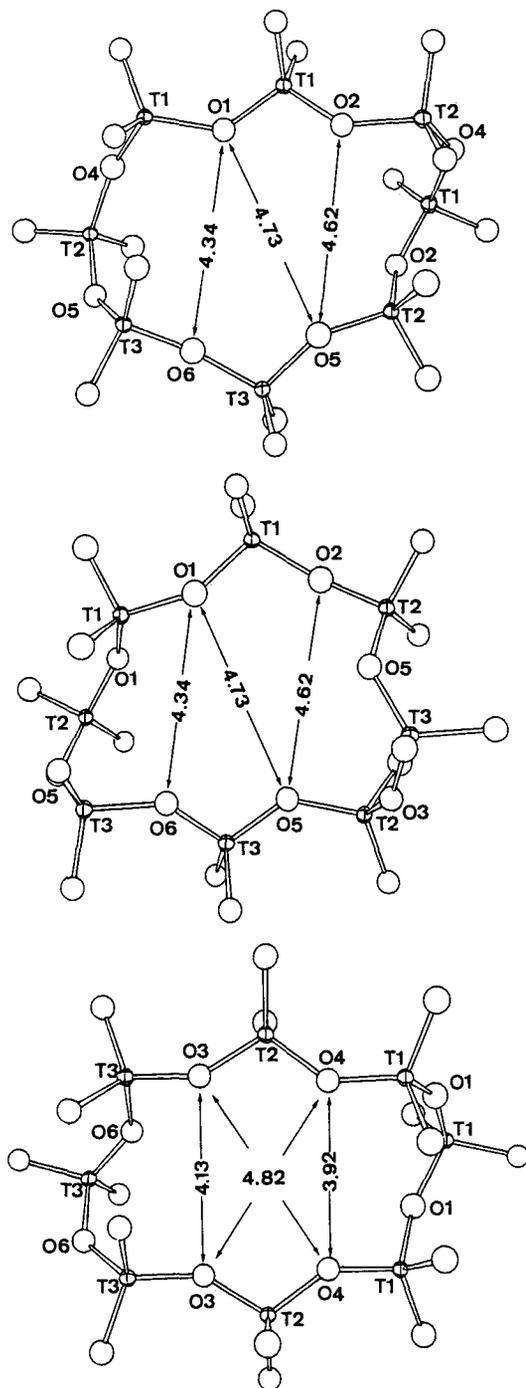


FIG. 4. The 6-membered rings of the  $(\text{Si,Al})\text{O}_4$  tetrahedra in the crystal structure of ammonioleucite. The values in the arrows are interatomic distances (in  $\text{\AA}$ ) between the oxygen atoms, which define the inside diameter of the ring.

As described above, the framework structure consists of the 4-, 6-, and 8-membered rings of  $(\text{Si,Al})\text{O}_4$  tetrahedra (Figs. 3, 4, 5). The 4-membered rings (Fig. 3) and the 6-membered rings (Fig. 4) are too small to allow the passage of water molecules and exchangeable cations. All three types of 8-membered rings in the crystal structure of ammonioleucite (Fig. 5) are bent to form 'chair' type shapes. The effective inside diameters of the 8-membered rings were estimated from the O-O distances (4.73 - 4.82  $\text{\AA}$ ) using the ionic radius of oxygen (1.40  $\text{\AA}$ ), and they were found to be in the range from 1.93 to 2.02  $\text{\AA}$ . These diameters are large enough for the  $\text{Na}^+$  ion (0.98  $\text{\AA}$  in radius) to be transferred through the ring, but not for the  $\text{K}^+$  (1.33



Å) and  $(\text{NH}_4)^+$  (1.43 Å) ions to be transferred at a room temperature. However, the effective inside diameter would be enlarged by increasing lattice vibration at a higher temperature. The dimensions of 8-membered rings are too narrow to allow much larger cations, *e.g.*,  $\text{Cs}^+$ , to pass through. The existence of this structural feature that limits the size of exchangeable cations was confirmed by the ion exchange experiments performed under hydrothermal conditions (Barrer, 1950; Yamada, 1985); *i.e.*,  $\text{Na}^+$ ,  $\text{K}^+$ , and  $(\text{NH}_4)^+$  are exchangeable in the analcime-leucite framework, whereas  $\text{Cs}^+$  is not.

**Acknowledgments**—The authors are grateful to Prof. Hajime Asano of the University of Tsukuba for his help in the X-ray measurement for Rietveld analysis. They wish to express their thanks to Dr. Hidemichi Hori for his suggestions and encouragement.

#### References

- AVERBUCH-POUCHOT, M. T., DURIF, A., CONIG-BOYAT, J. and GUITER, J. C. (1977) Le phosphobéryllate d'ammonium. *Acta Crystallographica*, **B33**, 203–205.

FIG. 5. The 8-membered rings of the  $(\text{Si,Al})\text{O}_4$  tetrahedra in the crystal structure of ammonioleucite. The values in the arrows are interatomic distances (in Å) between the oxygen atoms, which define the inside diameter of the ring.

- BARRER, R. M. (1950) Ion-exchange and ion-sieve process in crystalline zeolites. *Journal of the Chemical Society*, **1950**, 2342–2350.
- FERRARIS, G., JONES, D. W. and YERKES, J. (1972) A neutron-diffraction study of the crystal structure of analcime,  $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ . *Zeitschrift für Kristallographie*, **135**, 240–252.
- FINGER, L. W. (1968) *UMBADTEA*, Program for computing bond angles and distances, and thermal ellipsoids with error analysis. *Univ. of Minnesota, USA*.
- HORI, H., NAGASHIMA, K., YAMADA, M., MIYAWAKI, R. and MARUBASHI, T. (1986) Ammonioleucite, a new mineral from Tatarazawa, Fujioka, Japan. *American Mineralogist*, **71**, 1022–1027.
- IZUMI, F. (1983) Rietveld analysis and simulation of X-ray powder diffraction patterns. In *Advances in X-ray chemical analysis, Japan, No.14*, Ed. by the Discussion Group of X-ray Analysis, the Japan Society for Analytical Chemistry, Agne Gijutsu Center, Tokyo, pp.43–56 (in Japanese with English abstract).
- JOHNSON, C. K. (1976) *ORTEP II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee*.
- JONES, J. B. (1968) Al-O and Si-O tetrahedral distances in aluminosilicate framework structures. *Acta Crystallographica*, **B24**, 355–358.
- MAZZI, F., GALLI, E. and GOTTARDI, G. (1976) The crystal structure of tetragonal leucite. *American Mineralogist*, **61**, 108–115.
- SHANNON, R. D. and PREWITT, C. T. (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallographica*, **B25**, 925–946.
- YAMADA, M. (1985) Mineral chemistry of ammonium-bearing aluminosilicates. *Thesis for master of science, Department of Chemistry, the University of Tsukuba, Tsukuba, Ibaraki 305, Japan*.

*Received December 15, 1997; accepted June 30, 1998*