

Al,Si order in the crystal structure of α -eucryptite (LiAlSiO_4)

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ABSTRACT

The crystal structure of α -eucryptite, LiAlSiO_4 , is reinvestigated by combining ²⁹Si NMR spectroscopy and single-crystal X-ray diffraction. The silicon coordination in α -eucryptite of three different samples (two of natural, one of synthetic origin) is shown to be identical on a local scale by means of ²⁹Si MAS NMR spectroscopy. This method also suggests a well ordered arrangement of Si and Al within the crystal structure of α -eucryptite and the presence of two symmetrically non-equivalent sites for silicon. The refinement of the structure of a natural crystal using single-crystal X-ray diffraction confirms these observations and demonstrates the presence of long-range Al-Si order and the acentric space group $R\bar{3}$.

INTRODUCTION

In our studies of minerals with four-coordinated lithium and well-determined crystal structures to be used as reference materials for the ⁷Li NMR spectroscopy of newly synthesized microporous lithosilicates (Park et al. 2000), we encountered α -eucryptite (LiAlSiO_4). Its structure had been predicted by Winkler (1953) and determined by Hesse (1985). According to the latter α -eucryptite is isostructural with phenakite (Be_2SiO_4) and willemite (Zn_2SiO_4), with Li occupying the Si positions and Si and Al on the Be positions of the phenakite structure. Each LiO_4^- , SiO_4^- , and AlO_4^- -tetrahedron is connected to eight other tetrahedra via shared vertex oxygen atoms, thus forming channels running parallel to [0001]. These channels appear as six-membered rings in a projection along [0001]. The connection among these channels creates another set of smaller channels appearing as four-membered rings in a projection along [0001]. With X-ray diffraction experiments the distribution of Si and Al over the tetrahedral sites of α -eucryptite has been found to be either completely disordered or ordered only on a microdomain scale that is inaccessible by X-ray diffraction methods. Consequently, Hesse (1985) chose space group $R\bar{3}$ to describe the symmetry of α -eucryptite with three symmetrically non-equivalent tetrahedral sites of which one is solely occupied by Li and the other two are occupied by both Si and Al.

We obtained a ²⁹Si MAS NMR spectrum of a natural sample taken from a lithium-rich pegmatite from Bikita, Zimbabwe (Hurlbut 1957), containing α -eucryptite as the major phase.

This spectrum did not support the presence of Al-Si disorder and suggested a perfectly ordered structure in contrast to earlier assumptions (Hesse 1985). Since Al-Si ordering affects the Gibbs free energy of a phase, the question as to whether there is an ordered or a disordered Al-Si arrangement may be of some importance for thermodynamic investigations in respective petrological systems (Fasshauer et al. 1998). Consequently, we have re-examined the crystal structure of α -eucryptite by using both X-ray diffraction methods and NMR spectroscopy.

SAMPLE DESCRIPTION

Three samples of α -eucryptite were investigated. The first one originated from a pegmatite at Bikita, Zimbabwe, a locality described by Hurlbut (1957). The second natural sample was from a Siberian pegmatite at Vishnjakovskoje described by Lugovskiy et al. (1977). Both these samples were taken from larger pieces of the collection of the institute for mineralogy at Ruhr-University Bochum, Germany. The third α -eucryptite sample was synthesized by Fasshauer (1998) by hydrothermal treatment of a gel of appropriate composition. The chemical compositions of all three samples were assumed to be stoichiometric. The synthetic (Fasshauer 1998) as well as the natural sample from Bikita (Hesse 1985) were previously analyzed by electron microprobe showing that their Al-Si ratios are practically unity. The chemical composition of the Siberian sample as published by Lugovskiy et al. (1977) lies a little further off the ideal values, but the sample analyzed was contaminated by phases other than α -eucryptite.

Besides α -eucryptite, both natural samples contained quartz as the second major component. The Bikita sample additionally contained some spodumene, which disappeared upon heating to 1000 °C; after cooling only β -eucryptite, quartz, and some amorphous material remain. According to X-ray powder

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diffraction, the synthetic sample consisted of only one single phase. However, this does not preclude the possible presence of non-crystalline phases. Because our interest was centered on the crystal structure of α -eucryptite, the chemical compositions of the bulk samples and its components were not further analyzed.

NMR-SPECTROSCOPY

The ^{29}Si solid-state MAS NMR spectra of powders of the three samples (Fig. 1) were obtained using a Bruker ASX 400 spectrometer and tetramethylsilane (TMS) as reference. The spectrum in Figure 1a ($\delta = -80.9, -81.9$ ppm) was collected from the synthetic material consisting of pure α -eucryptite (Fasshauer 1998). Using this spectrum as a guide, the extra signals arising from the additional phases in the natural samples could be identified. A signal with $\delta = -107.5$ ppm observed in both the Siberian (Fig. 1b) and the Bikita (Fig. 1c) sample, is assigned to quartz. A signal at $\delta = -92.0$ ppm, observed only in the Bikita sample, is assigned to spodumene. The synthetic sample is microcrystalline, precluding single crystal diffraction studies, but the data show clearly that suitable single crystals could be selected from the natural materials.

The ^{29}Si MAS NMR spectra also provide important insight into the detailed structures of these samples. Although it is not possible to deduce crystal structures from NMR spectra, they sensitively reflect the local environments of the nuclei. Most important in the present context, the observation of sharp resonances for α -eucryptite in all three samples indicates that the SiO_4 - and AlO_4 -tetrahedra are long-range ordered in the structure. It is known from measurements of zeolites and aluminosilicate materials that such exceptionally sharp resonances ($\Delta\nu_{1/2} \leq 1$ ppm) are only observed when the structures exhibit perfect long-range Al-Si order, as seen in albite and zeolite A with Si-Al = 1 (Fyfe et al. 1984). For zeolites with Si-Al > 1, all of the resonances are broad, as are those of disordered natural aluminosilicates due to disordering of Si and Al in second and further coordination spheres. In contrast, the number of aluminium atoms coordinated to silicon does not significantly affect the linewidths.

From a previous X-ray structural study (Hesse 1985), α -eucryptite has SiO_4 -tetrahedra that are coordinated by eight other tetrahedra (Fig. 2) every vertex O atom of the SiO_4 -tetrahedron is shared with one Li atom and one Al atom, both in tetrahedral coordination. Although the ^{29}Si NMR chemical shifts observed for α -eucryptite are in the range for such materials (Engelhardt and Michel 1987), it is not possible to deduce the number of Al atoms coordinating Si from these data as it can be done with tecto-silicates where only two different cations occupy the tetrahedra and when each tetrahedron is coordinated by only four other tetrahedra. More importantly, any model for the structure must have complete ordering of Al and Si and must possess two sites of equal occupancy in the asymmetric unit because two separate signals can clearly be distinguished in the ^{29}Si NMR spectra of α -eucryptite (Fig. 1). Primarily, this proves the existence of short-range Al-Si order. Because α -eucryptite has an Al-Si ratio of one, any deviation from an existing long-range order would have to lead to Al-O-Al bonds thus destroying the short-range order as well. Hence, Si and Al

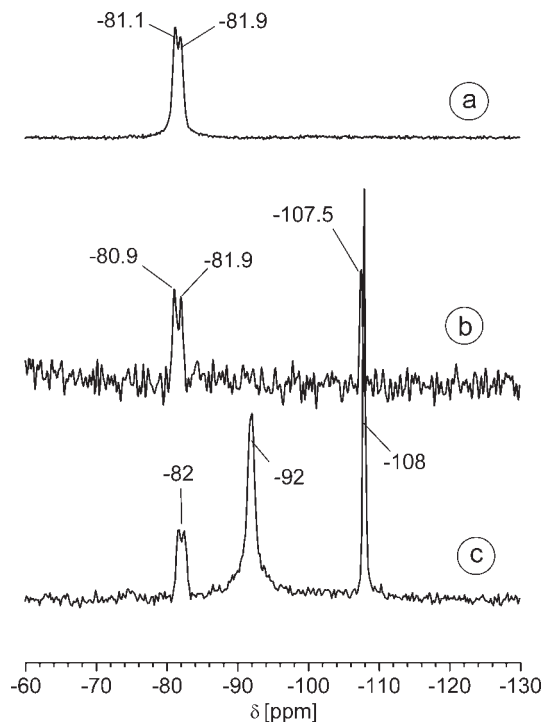


FIGURE 1. ^{29}Si MAS NMR spectra of three different samples consisting of pure α -eucryptite in the synthetic sample (a), of α -eucryptite and quartz in the sample from Vishnjakovskoje, Siberia (b), and of α -eucryptite, spodumene and quartz in the sample from Bikita, Zimbabwe (c). The α -eucryptite signal between -80 and -82 ppm is clearly split into two. The spinning frequency for all three spectra was 4 kHz; the pulse lengths were 3.0 μs for c and 3.3 μs for a and b; the delay between two pulses was 120 s for a and c and 60 s for b. All spectra were obtained by adding several measurements. The number of measurements were 145 for a, 1246 for b, and 1252 for c. In the case of b, high power decoupling was used to enhance the ^{29}Si spectrum.

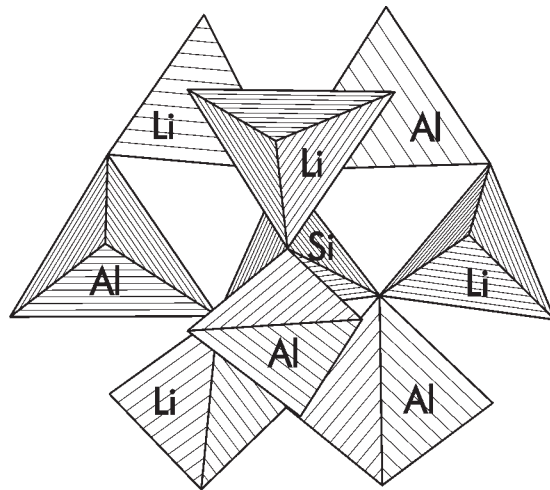


FIGURE 2. The coordination of a SiO_4 -tetrahedron in the crystal structure of α -eucryptite by four LiO_4 - and four AlO_4 -tetrahedra. Every O atom is coordinated by three cations.

must also be ordered on a long-range scale, a fact which must be accounted for in any structural model derived from X-ray diffraction data.

CRYSTAL STRUCTURE

Experimental methods

A single crystal of irregular morphology was selected from the Vishnjakovskoje sample and subsequently ground because its shape was unfavorable for diffraction experiments. The resulting crystal fragment had the shape of an ellipsoidal disc with a thickness of 200 μm and an area of $400 \times 600 \mu\text{m}^2$. Prior to data collection its quality was checked by obtaining a series of precession photographs. The visual inspection of intensities and systematic extinctions also confirmed the symmetry to be rhombohedral.

Diffraction intensities were collected on an automated Siemens P3 four circle diffractometer using graphite monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The angular positions of 25 reflections centered automatically gave the trigonal unit-cell dimensions $a = 13.532(4) \text{ \AA}$ and $c = 9.044(3) \text{ \AA}$. On the basis of this unit cell and considering the reflection conditions for its rhombohedral centering, the intensities of 11702 reflections were measured in a complete sphere of reflection up to $80^\circ 2\theta$. During the measurements the intensities of three check reflections were monitored at regular intervals. Inspection of these revealed a mechanical instability of the diffractometer during the first 500 measurements so that the respective data were omitted from the set, finally leaving 11 232 intensities which were then corrected for Lorentz and polarization effects and for absorption with an empirical method using the intensity data of 390 reflections obtained in a Ψ -scan. With a linear absorption coefficient $\mu = 0.82 \text{ mm}^{-1}$ the minimum and maximum transmissions found were 0.61 and 0.65 respectively. Using the normalized structure amplitudes E it is often possible to obtain information about the presence or ab-

sence of a center of symmetry. For our α -eucryptite we calculated the average $|E^2 - 1| = 0.887$ which, although closer to the value expected for a centric structure (0.968) than to the respective acentric value (0.736), does not allow to draw definite conclusions. These preliminary calculations were performed using programs from the SHELXTL program package (Siemens 1990).

Structure refinements

The refinements of the α -eucryptite crystal structure were all done using the program SHELX93 (Sheldrick 1993). In a first step the structure was refined in space group $R\bar{3}$ as published by Hesse (1985). Merging of symmetry equivalent intensities gave 1978 unique reflections with an internal R -ratio $R_{\text{int}} = 3.21\%$. The refinement converged well, reproducing the positional parameters of Hesse (1985) within 3σ (Table 1) and giving the R -ratios $wR(I) = 13.24\%$ (referring to the intensities) and $R = 5.57\%$ (referring to the structure factor amplitudes) for 64 variable parameters.

The basic structural topology of Hesse (1985) is confirmed: Channels parallel [0001] formed by rings of LiO_4^- , SiO_4^- , and AlO_4^- -tetrahedra are connected in such a way that smaller channels also paralleling [0001] result (Fig. 3). The next step in the refinement process consisted of a reduction of symmetry. Because the observations implied that α -eucryptite must be rhombohedral, only space group $R3$ was an alternative to $R\bar{3}$. With this acentric symmetry it is possible to distribute Si and Al over the tetrahedral sites in an ordered way obeying the Al-O-Al avoidance rule (Loewenstein 1954) (Figs. 2 and 3). Again, symmetry equivalent reflections were merged prior to refinement yielding 3956 unique reflections with $R_{\text{int}} = 3.09\%$. Despite the small difference in scattering factors between Al and Si it was possible to clearly identify the occupants of the tetrahedral sites in difference Fourier syntheses. The choice of tetrahedral cations was strongly supported by the systematic variation of T-O bond lengths (Table 2). With the strictly alternating distribu-

TABLE 1. Refined positional and displacement parameters for the crystal structure of α -eucryptite (LiAlSiO_4)

Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
(a) Space group $R\bar{3}$									
Li	0.0204(4)	0.8132(4)	0.7515(6)	0.022(2)	0.017(2)	0.022(2)	0.002(2)	-0.002(2)	0.007(2)
T1	0.53030(5)	0.88076(5)	0.74951(6)	0.0108(2)	0.0106(2)	0.0094(2)	-0.0003(2)	-0.0002(2)	0.0056(2)
T2	0.87526(5)	0.34430(5)	0.91608(6)	0.0107(2)	0.0097(2)	0.0095(2)	0.0000(2)	-0.0004(2)	0.0050(2)
O1	0.7593(2)	0.2131(1)	0.8944(2)	0.0197(7)	0.0133(6)	0.0108(5)	0.0011(4)	0.0022(5)	0.0076(5)
O2	0.7329(1)	0.1993(1)	0.5846(2)	0.0119(6)	0.0105(5)	0.0179(7)	-0.0001(5)	0.0007(5)	0.0037(5)
O3	0.1005(1)	0.8843(1)	0.9413(2)	0.0145(6)	0.0141(6)	0.0119(6)	-0.0016(5)	-0.0020(4)	0.0059(5)
O4	0.6592(1)	0.0026(1)	0.7495(2)	0.0130(6)	0.0176(6)	0.0148(6)	0.0001(5)	-0.0000(5)	0.0100(5)
(b) Space group $R3$									
Li1	-0.0172(2)	-0.8111(2)	-0.7486(4)	0.0176(9)	0.0197(9)	0.0132(7)	0.0027(7)	0.0012(6)	0.0088(8)
Li2	0.0208(2)	0.8117(2)	0.7535(4)	0.0163(8)	0.0148(8)	0.0150(8)	-0.0013(7)	-0.0011(7)	0.0069(7)
Si1	0.53003(2)	0.87978(2)	0.74976(2)	0.0098(1)	0.0100(1)	0.0092(1)	-0.00025(7)	-0.00023(6)	0.00512(8)
Al1	-0.53033(3)	-0.88160(3)	-0.74912(3)	0.0105(1)	0.0103(1)	0.0091(1)	-0.00008(8)	-0.00011(7)	0.00537(9)
Si2	0.87557(2)	0.34416(2)	0.91628(2)	0.01036(9)	0.0095(1)	0.0091(1)	0.00011(6)	-0.00031(7)	0.00498(8)
Al2	-0.87508(3)	-0.34475(3)	-0.91580(3)	0.0106(1)	0.0098(1)	0.0094(1)	-0.00011(7)	-0.00023(8)	0.00519(9)
O1	-0.75287(6)	-0.20991(6)	-0.89041(9)	0.0118(2)	0.0117(2)	0.0107(2)	-0.0011(2)	-0.0014(2)	0.0035(2)
O2	0.76554(6)	0.21616(6)	0.89841(8)	0.0120(2)	0.0110(2)	0.0111(2)	-0.0009(2)	-0.0016(2)	0.0033(2)
O3	-0.73280(6)	-0.19912(6)	-0.59329(7)	0.0129(2)	0.0120(2)	0.0093(2)	0.0000(2)	-0.0001(2)	0.0047(2)
O4	0.73246(6)	0.19928(6)	0.57644(7)	0.0126(2)	0.0117(2)	0.0087(2)	-0.0002(2)	0.0003(2)	0.0044(2)
O5	-0.10448(6)	-0.88798(6)	-0.93692(8)	0.0118(2)	0.0113(2)	0.0109(2)	0.0013(2)	0.0010(2)	0.0035(2)
O6	0.09633(6)	0.88060(6)	0.94630(8)	0.0126(2)	0.0112(2)	0.0108(2)	0.0008(2)	0.0016(2)	0.0036(2)
O7	-0.66426(5)	-0.00862(6)	-0.74899(9)	0.0108(2)	0.0100(2)	0.0139(2)	0.0000(2)	-0.0001(2)	0.0048(2)
O8	0.65458(7)	-0.00374(5)	0.74982(9)	0.0106(2)	0.0099(2)	0.0137(2)	0.0003(2)	0.0005(2)	0.0044(2)

Notes: Standard deviations given in parentheses refer to the last digit.

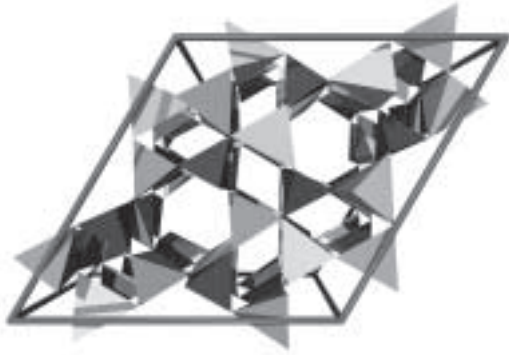


FIGURE 3. The crystal structure of α -eucryptite viewed along [0001]. Light gray tetrahedra represent LiO_4 , medium gray tetrahedra are AlO_4 , and SiO_4 -tetrahedra are drawn in dark gray. The unit cell is outlined with the origin in the lower right corner.

tion of Al and Si the R-ratios converged to $wR(I) = 7.09\%$ and $R = 2.59\%$ for 3956 data and 127 variable parameters. The x parameter of Flack (1983) was calculated to be 0.0074 with an estimated standard deviation of 0.0570 indicating the correct choice of enantiomorph. Usually, when the symmetry restrictions are reduced in a refinement, the number of high correlation coefficients (r^2) increases. In the case of α -eucryptite the highest correlation exists between the z coordinates of Li1 and

Li2 (Table 1b) with $r^2 = 0.88$. All other r^2 values are below 0.67.

DISCUSSION

The ^{29}Si MAS NMR spectra clearly demonstrate the existence of short range Al-Si order in α -eucryptite of all three samples investigated. Even the presence of two symmetrically slightly different Si sites can be detected clearly in the synthetic sample from the splitting of the ^{29}Si signal (Fig. 1a). The presence of long-range order is shown by the structure refinement. The differences in R-ratios [$wR(I)$ and R] are significant on a 0.005 error level according to Hamilton (1965). Moreover, the fact that the Flack x parameter is very close to zero with a small estimated standard deviation is a strong indication of the correctness of the refinement using space group $R\bar{3}$. Nevertheless, these results could also be artefacts due to undetected systematic errors during intensity measurements (Hamilton 1965; Flack 1983), but the geometric measures of the structure are also systematically changed when the symmetry is reduced.

The distances between the tetrahedral sites and their coordinating O neighbors change during the refinement in space group $R\bar{3}$ according to the type of cation on the T-position. This result is independent of the kind of scattering curve (Si or Al) assigned to the respective T-site. The reduction of symmetry particularly allows the O atoms to be moved relative to the

TABLE 2. Bonds lengths and angles as results of the two refinements of the structure of α -eucryptite

Space group $R\bar{3}$			Space group $R\bar{3}$				
Bond lengths (Å)		Bond angles (deg.)		Bond lengths (Å)		Bond angles (deg.)	
Li-O1	1.962(5)	O1-Li-O4	105.0(3)	Li1-O7	1.953(2)	O7-Li1-O1	106.1(2)
Li-O4	1.981(5)	O1-Li-O3	120.4(3)	Li1-O1	1.956(4)	O7-Li1-O4	107.3(1)
Li-O3	2.001(5)	O1-Li-O2	106.8(2)	Li1-O4	1.978(3)	O7-Li1-O5	107.1(2)
Li-O2	2.004(6)	O4-Li-O3	106.2(2)	Li1-O5	2.037(4)	O1-Li1-O4	108.0(2)
		O4-Li-O2	107.7(2)			O1-Li1-O5	119.0(1)
		O3-Li-O2	110.1(3)			O4-Li1-O5	108.7(2)
				Li2-O8	1.970(2)	O8-Li2-O2	104.5(1)
				Li2-O2	1.982(4)	O8-Li2-O6	105.6(2)
				Li2-O6	2.000(4)	O8-Li2-O3	110.1(1)
				Li2-O3	2.024(2)	O2-Li2-O6	119.9(1)
						O2-Li2-O3	105.5(2)
						O6-Li2-O3	110.9(2)
T1-O3	1.695(2)	O3-T1-O3	108.17(9)	Si1-O5	1.631(1)	O5-Si1-O6	109.36(4)
T1-O3	1.697(2)	O3-T1-O4	109.35(8)	Si1-O6	1.631(1)	O5-Si1-O8	108.33(4)
T1-O4	1.697(2)	O3-T1-O2	108.04(8)	Si1-O8	1.633(1)	O5-Si1-O4	107.94(4)
T1-O2	1.709(2)	O3-T1-O4	110.10(8)	Si1-O4	1.641(1)	O6-Si1-O8	110.03(4)
		O3-T1-O2	112.49(8)			O6-Si1-O4	111.67(4)
		O4-T1-O2	108.62(8)	Al1-O5	1.755(1)	O8-Si1-O4	109.42(4)
				Al1-O6	1.765(1)	O5-Al1-O6	107.06(4)
				Al1-O7	1.767(1)	O5-Al1-O7	110.32(4)
				Al1-O3	1.780(1)	O5-Al1-O3	113.47(4)
						O6-Al1-O7	109.91(4)
						O6-Al1-O3	108.04(4)
						O7-Al1-O3	107.99(4)
T2-O1	1.688(2)	O1-T2-O4	111.54(9)	Si2-O1	1.623(1)	O1-Si2-O7	111.38(4)
T2-O4	1.690(2)	O1-T2-O1	107.90(9)	Si2-O7	1.631(1)	O1-Si2-O2	107.78(4)
T2-O1	1.692(2)	O1-T2-O2	112.29(8)	Si2-O2	1.632(1)	O1-Si2-O3	111.68(4)
T2-O2	1.705(2)	O4-T2-O1	106.48(9)	Si2-O3	1.636(1)	O7-Si2-O2	107.06(4)
		O4-T2-O2	109.03(8)			O7-Si2-O3	109.21(4)
		O1-T2-O2	109.41(8)			O2-Si2-O3	109.61(4)
				Al2-O2	1.752(1)	O2-Al2-O8	111.78(4)
				Al2-O8	1.758(1)	O2-Al2-O1	107.96(4)
				Al2-O1	1.760(1)	O2-Al2-O4	113.09(4)
				Al2-O4	1.768(1)	O8-Al2-O1	106.02(4)
						O8-Al2-O4	108.77(4)
						O1-Al2-O4	108.93(4)

Notes: Standard deviations given in parentheses refer to the last digit.

tetrahedral sites in a characteristic way such that the typical Si-O and Al-O distances of relatively undistorted tetrahedra result (Table 2). Whereas the refinement in space group $R\bar{3}$ yields mean T-O distances of 1.700(6) Å and 1.694(8) Å for T1 and T2 respectively, the mean distances calculated from the parameters in space group $R3$ are 1.634(5) Å and 1.631(5) Å for Si1-O and Si2-O and 1.767(10) Å and 1.760(7) Å for Al1-O and Al2-O. Although, assuming the symmetry to be $R\bar{3}$ leads to an averaging over the T-O bond lengths and to values characteristic for a disordered Si-Al occupancy of the tetrahedra, it is improbable that systematic errors obscuring the presence of a centre of symmetry could also result in such changes of distances that are typical for Si-Al order.

Another, perhaps even more sensitive, measure for the correctness of the choice of symmetry is given by the displacement parameters (Table 1). According to Downs et al. (1990), the mean square displacement amplitudes (m.s.a.) of the atoms in a rigid group such as AlO_4^- and SiO_4 -tetrahedra should be highly correlated in such a way that the m.s.a. of the T-site and the m.s.a. of the coordinating O-atoms are identical in the direction of the chemical bond. The m.s.a. values in the bond direction as calculated from the data in Table 1 and from the data given by Hesse (1985) are displayed in Figure 4. Clearly, only the m.s.a. for Si and Al and the O-atoms bonded to them in space group $R3$ correspond to the behavior expected for rigid groups (Downs et al. 1990). All other m.s.a. data, including

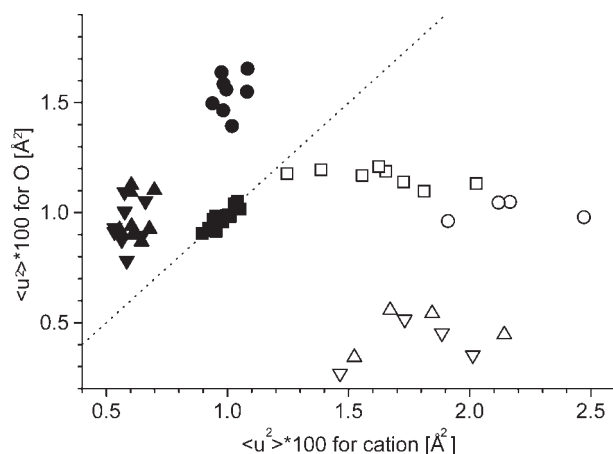


FIGURE 4. The mean square displacement amplitude in bond direction $\langle u^2 \rangle$ of O atoms as a function of $\langle u^2 \rangle$ of the tetrahedrally coordinated cations in the structure of α -eucryptite. Data obtained in this work are represented by circles (space group $R\bar{3}$) and squares (space group $R3$); triangles stand for data derived from Hesse (1985). Solid symbols show the data for Al and Si, open symbols are those for Li. The dashed line is the line of equality of $\langle u^2 \rangle$ for bonded O atoms and cations.

those for refinements in space group $R\bar{3}$ as well as those for the much weaker Li-O bonds, lie far off the line of equality.

These derived values (distances and m.s.a. values) prove that the deviation from the centric symmetry of space group $R\bar{3}$ is not an artefact induced by systematic errors. Taken together, both ^{29}Si MAS NMR-spectroscopy and X-ray diffraction show that Si and Al in the crystal structure of α -eucryptite are well ordered on all scales.

The Si-Al order in the crystal structure of α -eucryptite presented here has an influence on the configurational entropy and thus on stability calculations on the basis of thermodynamic data sets. This proves the importance of such analyses. The fact that the structure of α -eucryptite is well ordered has been found by pure chance. Perhaps there are more examples of crystal structures hidden in the older literature, for which the degree of order could not reliably be analyzed with the methods available then. A reexamination of such structures by combining MAS NMR spectroscopy and X-ray diffraction seems worthwhile.

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