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A SINGLE-CRYSTAL NEUTRON-DIFFRACTION INVESTIGATION OF SPODUMENE AT 54 K

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Abstract

A single-crystal investigation of spodumene from a granitic pegmatite in Minas Gerais, Brazil, was undertaken using neutron (54 K) and X-ray diffraction (room temperature) (R_{all} = 2.8% and 1.9%, respectively). In both refinements, space group $C2/c$ was assigned; the presence of several reflections violating the *c* glide plane in the low-temperature neutron-diffraction data set is attributed to multiple scattering. An asymmetric density of scattering at the Li site was observed in both refinements, and is related to dynamic disorder. In spodumene, a $C2/c$ fully relaxed low-temperature structure is therefore present, in contrast to $LiCrSi_2O_6$, $LiFeSi_2O_6$, and $LiGaSi_2O_6$ pyroxenes, for which it is $P2_1/c$. The main geometrical difference between spodumene and $LiFeSi_2O_6$ is the flexibility with temperature of the chain of S-rotated tetrahedra in spodumene. It enables spodumene to cope with the variation in octahedron size, in comparison with the stiffness of the completely extended chain of tetrahedra in $LiFeSi_2O_6$.

Keywords: spodumene, X-ray diffraction, neutron diffraction, Li pyroxene, multiple scattering.

Sommaire

Nous décrivons les résultats d'une étude sur cristal unique de spodumène provenant d'une pegmatite granitique de Minas Gerais, au Brésil, par diffraction de neutrons à 54 K et par diffraction X à température ambiante (R_{all} = 2.8% et 1.9%, respectivement). Dans les deux cas, nous adoptons le groupe spatial $C2/c$; la présence de plusieurs réflexions en violation du plan de glissement *c* dans les données provenant de la diffraction de neutrons à basse température est attribuable à la dispersion multiple. Une répartition asymétrique de la dispersion associée au site Li a été observée dans les deux affinements, et serait due à un désordre dynamique. Dans le spodumène, une structure $C2/c$ pleinement décontractée est donc présente à basse température, contrairement aux cas des pyroxènes $LiCrSi_2O_6$, $LiFeSi_2O_6$, et $LiGaSi_2O_6$, dans lesquels il s'agit d'une structure $P2_1/c$. La différence géométrique principale entre le spodumène et $LiFeSi_2O_6$ porte sur la flexibilité selon la température de la chaîne de tétraèdres à rotation S dans le spodumène. C'est ce qui permet au spodumène de se conformer aux variations dans la taille des octaèdres, par rapport à l'inflexibilité dans les chaînes de tétraèdres complètement distendues dans le composé $LiFeSi_2O_6$.

(Traduit par la Rédaction)

Mots-clés: spodumène, diffraction X, diffraction de neutrons, pyroxène lithinique, dispersion multiple.

Introduction

Several investigations have been undertaken to clarify the structural behavior and the phase transitions of Li-bearing pyroxenes. In the pyroxene structure, Li occupies the *M*2 site *via* a coupled substitution with a trivalent cation at *M*1. In natural pyroxenes, the substituting trivalent cation is Al, forming the mineral spodumene (Clark *et al.* 1969, Sasaki *et al.* 1980, Kuntzinger & Ghermani 1999). However, pyroxenes with trivalent Fe, Cr, Ni, In, V, Sc, Ti and Ga at the *M*1 site have also been synthesized (Hawthorne & Grundy 1977, Grotepaß *et al.* 1983, Behruzi *et al.* 1984, Baum *et al.* 1988, Ohashi & Osawa 1988, Sato *et al.* 1994, 1995, Satto *et al.*1997, Lottermoser *et al.* 1998, Redhammer *et al.* 2001). Structure refinements of the end members containing the above trivalent cations were performed at ambient conditions and at high tem-

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perature (Cameron *et al.* 1973, Redhammer *et al.* 2001) and high pressure (Arlt & Angel 2000). In general, a structure in space group $C2/c$ with a chain arrangement similar to that of high-T (temperature) pigeonite is stable at high temperature. A phase transition from $C2/c$ to a $P2_1/c$ structure, similar to that of high-T to low-T pigeonite (Smyth 1974, Brown *et al.* 1972, Tribaudino *et al.* 2002), occurs in the Cr^{3+} (Behruzi *et al.* 1984), Fe^{3+} (Lottermoser *et al.* 1998, Redhammer *et al.* 2001) and Ga end-members (Sato *et al.* 1994, 1995), at 343, 228 and 285 K, respectively. At high pressure, a phase transition to a $P2_1/c$ structure was observed in spodumene and $LiScSi_2O_6$ at P = 3.6 and 0.6 GPa, respectively (Arlt & Angel 2000). For all Li-bearing pyroxenes, and by analogy with $ZnSiO_3$, Arlt & Angel (2002) predicted a second phase-transition to a high-pressure $C2/c$ structure, similar to the high-pressure $C2/c$ structure found in clinoenstatite (Angel *et al.* 1992). Arlt & Angel (2000) have shown that smaller cations at the *M*1 site favor the $P2_1/c$ structure at ambient conditions. An exception is spodumene, which displays a $C2/c$ structure at room temperature (Sasaki *et al.* 1980, 1981), despite the fact that Al has the smallest radius of all possible *M*1 cations. They explained this exception by the presence of chains of S-rotated tetrahedra in spodumene, but structural details were not provided.

The behavior of Li within the *M*2 cavity in spodumene is also interesting, as Li has the largest displacement parameters in pyroxenes (Cameron *et al.* 1973). Rietveld analysis of preliminary data from low-T neutron powder-diffraction (Knight & Schofield 2000) has shown evidence for positional disorder of Li off the diad axis and of possible violations of a centric space-group. These violations could originate because of a phase transition below room temperature.

In the present work, data from an investigation of neutron scattering at T = 54 K are reported and compared with a high-resolution X-ray measurement at 298 K. The aim is to verify the low-temperature structure of spodumene and to compare the structural changes occurring with temperature in spodumene to those in other Li-bearing pyroxenes. Moreover, in this work, we document a severe case of multiple diffraction in a neutron-diffraction single-crystal investigation.

This paper focuses on structural features. In a forthcoming paper, the results of quantum mechanical *ab initio* calculations and multipolar refinements will be reported.

EXPERIMENTAL

A transparent and colorless gem-quality crystal of spodumene from Minas Gerais, Brazil, was used for the diffraction studies. The composition was verified by energy-dispersion analysis, using a Cambridge S 360 scanning electron microscope, equipped with Link Analytical QX 2000 energy-dispersion spectrometer (EDS). The analyses were performed using relatively long counting-times (500 s), in order to improve the detection of elements at low concentrations. Apart from Al and Si, only Na and Fe were found in significant concentrations. Assuming Li to be present in stoichiometric amounts, the following formula based on six atoms of oxygen was obtained: $LiNa_{0.012(1)}Fe_{0.004(2)}Al_{0.98(1)}Si_{2.01(1)}O_6$.

Two crystals were separated, one to be used for neutron ($6 \times 4 \times 2$ mm^3) and the other for X-ray diffraction ($300 \times 150 \times 100$ μm^3). Both show sharp extinction and no evidence of twinning upon examination under crossed nicols.

Collection of X-ray and neutron data

X-ray-diffraction intensity data were collected at room temperature using a Siemens P4 four-circle diffractometer, operating at 50 kV and 20 mA, with Mo$K\alpha$ radiation ($\lambda = 0.71069$ Å) monochromatized with a flat graphite crystal. Cell parameters were measured using 25 reflections over the 2θ interval of 15 and 30°. Diffraction intensities were collected in the θ–2θ scan mode; the reciprocal lattice sphere was explored up to $2\theta = 100°$, *i.e.*, at a resolution of 0.46 Å, with a scanning speed of 2°/min. All equivalent reflections were collected in a full sphere. An empirical absorption-correction based on the Ψ-scan method (North *et al.* 1968) was done. A total of 1960 unique reflections were used in the refinement.

The collection of neutron data was performed at NFL (NeutronForskningsLaboratoriet, Studsvik, Sweden) research reactor, using the single-crystal SXD HUBER four-circle goniometer, positioned at H8, one of the radial neutron channels at the R2 reactor. The primary beam was monochromatized by two copper (220) crystals, one of which is focusing, creating the neutron wavelength λ of 1.202 Å. The crystal was mounted with [001] approximately parallel to the ω axis of the instrument and was cooled to 54 K using a close-cycle refrigerator. The diffracted beams were measured with a single ^{3}He detector. The data collection was performed up to a 2θ of 104°, corresponding to a resolution of 0.76 Å. All measurable reflections with indices $\pm h + k \pm l$, constituting half of the reflection sphere, were collected. A set of 455 unique reflections was obtained after merging symmetry-equivalents. The intensities were corrected for absorption ($\mu = 1.07$ mm^{-1}) using a laboratory-supplied routine.

Data refinement

Weighted full-matrix least-squares anisotropic refinements for both neutron and X-ray data were completed using SHELX–97 (Sheldrick 1997), the space group $C2/c$ and starting atom-coordinates of spodumene (Sasaki *et al.* 1980). Atomic scattering curves and neutron scattering lengths were taken from the *International Tables for X-Ray Crystallography* (Ibers & Hamilton

1974). Only the scattering curves of Li and Al were used to refine the atom positions at the *M*2 and *M*1 sites, respectively. The extinction was corrected according to Larson's (1970) model, as implemented in SHELX–97. A fixed weighting scheme was used $[1/\sigma(F_O)^2]$.

Cell parameters, agreement factors, fractional coordinates, polyhedron bond-lengths and mean square-root amplitudes of the atomic displacement ellipsoids (ADP) are reported in Tables 1, 2 , 3 and 4. A table of structure factors is available at the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

TABLE 1. UNIT-CELL PARAMETERS OF SPODUMENE AND DETAILS OF THE REFINEMENTS

	54 K	298 K
a (Å)	9.504(1)	9.479(2)
b (Å)	8.371(2)	8.403(2)
c (Å)	5.204(1)	5.223(1)
β (°)	110.33(1)	110.14(1)
V (Å^3)	388.2(1)	390.6(1)
Total number of reflections	455	1960
Number of reflections with $F_o>4\sigma$	452	1864
R_{int} %	2.3	2.6
$R_{4\sigma}$ %	2.8	1.7
R_{all} %	2.8	1.9
wR^2 %	7.9	6.2
GooF	1.35	0.98
Number of parameters refined	48	48

RESULTS AND DISCUSSION

Space group at room and low temperature

A set of 302 $h + k = 2n + 1$ reflections was collected at 54 K, to check for possible violations of the *C*-centering. None of these reflections was found to have $I > 3\sigma$, and the subsequent full collection of data was performed in the *C*-centered lattice. The collection of neutron data at 54 K and at room temperature revealed instead several $h0l$ reflections with $l = 2n + 1$ (average $I/\sigma = 9.2$) violating the *c* glide plane of the *C*2/*c* space group. In the X-ray data collection, only a few such reflections were significant. Violations of the *c* glide plane were reported in the literature for X-ray data on spodumene (Clark *et al.* 1969), and interpreted as evidence of the acentric space-group *C*2. However, further investigations (Sasaki *et al.* 1981) showed that the *c* glide violations in the intensity data of spodumene are due to multiple diffraction. Multiple diffraction occurs when a strong diffracted beam in the crystal acts as an incident beam for further diffraction by the crystal. In low-temperature neutron diffraction, it was decided to test for the actual presence of these violations, as they could provide evidence of a transition to an acentric space-group.

An indication on the presence of the center of symmetry can be obtained by the distribution of the normalized structure-factors (| E |; Viterbo 1992) and by the related mean value of the | E*E – 1 | function. Such dis-

TABLE 2. ATOM COORDINATES, EQUIVALENT ISOTROPIC AND ANISOTROPIC DISPLACEMENT COEFFICIENTS FOR SPODUMENE AT 54 AND 298 K

	x/a	*y/b*	*z/c*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
					54 K					
Li	0	0.2735(5)	0.25	0.0107(8)	0.012(2)	0.010(2)	0.010(2)	0.0	0.005(1)	0.0
Al	0	0.9070(2)	0.25	0.0031(5)	0.0021(9)	0.0040(9)	0.0031(9)	0.0	0.0009(7)	0.0
Si	0.2939(1)	0.0937(1)	0.2573(2)	0.0027(4)	0.0004(6)	0.0042(6)	0.0037(6)	0.0001(4)	0.0011(5)	-0.0001(4)
O1	0.1097(1)	0.08265(9)	0.1413(2)	0.0036(4)	0.0009(5)	0.0058(6)	0.0043(5)	0.0003(3)	0.0012(4)	0.0003(2)
O2	0.36461(9)	0.2674(1)	0.3001(2)	0.0043(4)	0.0024(5)	0.0054(6)	0.0059(6)	-0.0006(3)	0.0023(4)	-0.0001
O3	0.35656(9)	-0.0146(1)	1.0609(2)	0.0044(4)	0.0017(5)	0.0073(6)	0.0042(6)	0.0001(3)	0.0012(4)	-0.0015(3)
					298 K					
Li	0	0.2741(2)	0.25	0.0164(3)	0.0158(6)	0.0152(6)	0.0181(7)	0.00	0.0055(4)	0.00
Al	0	0.90661(2)	0.25	0.00457(4)	0.00411(7)	0.00444(7)	0.00494(7)	0.00	0.00129(5)	0.00
Si	0.29410(1)	0.09345(1)	0.25609(2)	0.00434(4)	0.00370(5)	0.00473(5)	0.00439(5)	-0.00062(2)	0.00115(3)	-0.00022(2)
O1	0.10972(3)	0.08233(3)	0.14057(6)	0.00532(5)	0.00383(8)	0.00626(9)	0.00536(9)	-0.00037(6)	0.00092(6)	0.00015(6)
O2	0.36476(3)	0.26704(4)	0.30051(7)	0.00812(5)	0.00823(9)	0.00595(9)	0.0107(1)	-0.00288(7)	0.00391(8)	-0.00093(7)
O3	0.35664(3)	-0.01332(4)	1.05854(6)	0.00802(5)	0.00587(9)	0.0118(1)	0.00599(9)	0.00063(7)	0.00150(7)	-0.00316(7)

The exponent of the anisotropic displacement factor takes the form: $-2\pi^2(h^2a^{*2}U_{11} + ... + 2klb^*c^*U_{23})$.

TABLE 3. BOND LENGTHS (Å) AND O3A2–O3A1–O3A2 ANGLE OF CHAIN KINKING (°) IN SPODUMENE

	54K	298 K		54K	298 K		54K	298 K
Li - O1A1, B1 (×2)	2.090(3)	2.101(2)	Al - O1A2, B2 (×2)	1.9407(9)	1.9470(5)	Si - O1	1.644(1)	1.6435(4)
Li - O2C2, D2 (x2)	2.272(1)	2.2808(6)	Al -O1A1, B1 (×2)	1.995(2)	1.9995(4)	Si - O2	1.585(1)	1.5884(4)
Li - O3C1, D1 (x2)	2.245(4)	2.259(2)	Al - O2C1, D1 (×2)	1.822(2)	1.8224(4)	Si - O3A1	1.623(1)	1.6256(4)
< Li - O>	2.202	2.214	< Al - O>	1.919	1.923	Si - O3A2	1.626(1)	1.6295(4)
Li - O3C2, D2 (×2)	3.176(1)	3.161(1)	O3A2-O3A1-O3A2	169.2(1)	170.20(3)	< Si -O>	1.620	1.6218

Atom nomenclature as in Burnham *et al.* (1967).

tribution can be calculated theoretically, independently of the complexity of the structure. The centric distribution yields a higher percentage of reflections with extreme intensity, whereas in the acentric one, there is a maximum corresponding to intermediate values of the intensities. The theoretical values of the average of the | E*E – 1 | distribution are 0.960 in the centrosymmetric case and 0.738 in the non-centrosymmetric case. In this work, the X-ray data confirm the presence of a center of symmetry at room temperature (< | E*E – 1 | > is 0.980), but the low-T neutron-diffraction data give an anomalous value (< | E*E – 1 | > is 0.620).

The possible presence of multiple diffraction inducing glide-plane violations was tested by performing Ψ-scans on selected *h*0*l* reflections with $l = 2n + 1$, with X-rays as well as neutrons. In the X-ray experiment, the intensity of violating reflections was found not to be significant, other than for specific Ψ angles, in agreement with the findings of Sasaki *et al.* (1981). The observed violations were therefore attributed to multiple diffraction. The neutron data, on the other hand, show an intensity of the violating reflections much higher than the observed standard deviation for any Ψ angle also at room temperature. However, the intensities shows sharp changes as a function of Ψ angle. Such changes are not due to experimental fluctuations: the Ψ scan was repeated twice, at steps of 0.2 and 0.5°, and the intensity changes are very similar. Also, these changes cannot be due to absorption, since the crystal has a regular shape, and only minor anisotropic absorption was observed. A likely interpretation is that in the large gem-quality crystal used for neutron diffraction, multiple scattering is so widespread that owing to overlap of multiple diffraction, the intensity does not decrease below significance. This would also explain the anomalous statistics of the intensities: strong multiple diffraction and extinction would increase the intensity of weaker reflections and decrease that of the stronger ones. As a consequence, the presence of violating reflections cannot be used as evidence of the lack of an inversion center at low temperature.

TABLE 4. ROOT MEAN SQUARE AMPLITUDE (Å) OF DISPLACEMENT ELLIPSOIDS IN SPODUMENE

	54 K			298 K		
Li	0.110	0.101	0.098	0.136	0.126	0.123
Al	0.063	0.073	0.056	0.072	0.066	0.064
Si	0.065	0.061	0.010	0.071	0.068	0.058
O1	0.077	0.066	0.026	0.081	0.075	0.061
O2	0.077	0.073	0.040	0.105	0.096	0.062
O3	0.089	0.060	0.039	0.117	0.076	0.068

Refinement with the alternative non-centrosymmetric space-groups *C*2 and *Cc* were attempted on the 54 K neutron data to verify the actual space-group. In both cases, the results yielded worse agreement-factors (R = 3.3%) than those of the *C*2/*c* refinement. In addition, errors associated with the bond lengths increased, and the anisotropic displacement parameters became non-positive definite. Also, no significant decrease of the large displacement parameters for Li, nor of any other atoms, was observed. Therefore a *C*2/*c* model was chosen also for the low-T neutron data.

This result indicates that no phase transition occurs down to 54 K in spodumene, although further investigations at lower T would be useful to finalize the issue.

Displacement parameters and zero-point motion

The displacement parameter observed for Li in spodumene (*e.g.*, Cameron *et al.* 1973) is significantly larger than that at *M*2 in other pyroxenes. Moreover, the possible presence of site splitting was suggested by Knight & Schofield (2000). Dynamic and static disorder can be distinguished by an analysis of the evolution of the displacement parameters with temperature. In the case of negligible positional disorder, the relation between the displacement parameters and temperature should be asymptotically approximated by a straight line passing through the origin at 0 K. Such dependence is no longer linear at low temperature. As previously shown (*e.g.*, Benna *et al.* 1990, Pavese *et al.* 1995, Pilati *et al.* 1996, Prencipe *et al.* 2000), a positive intercept for a linear extrapolation of the high-temperature data at 0 K can provide an indication of the presence of positional disorder. As shown in Figure 1, an extrapolation of the B_{eq} (equivalent to isotropic displacement parameters) from data for spodumene over the interval 298 to 1033 K (this work, Cameron *et al.* 1973) to 0 K shows no significant residual for any atom. The B_{eq} are significant (about 60% of the room-temperature data) also in the neutron datum at 54 K; this value is related to 0 K point motion, but possibly also to extinction effects that are not fully corrected for. The presence of significant zero-point motion is in agreement with previous theoretical (Pilati *et al.* 1996) and experimental findings (Prencipe *et al.* 2000) on the structurally related diopside, for which the zero-point contribution is about 40% of the room-temperature B_{eq}.

Effect of M1 cations on the $P2_1/c$ – $C2/c$ phase transition

As discussed in the introduction, Li-bearing clinopyroxenes have $P2_1/c$ or $C2/c$ symmetry. In Figure 2, the radius of the *M*1 cation is plotted as a function of the temperature of data collection. The transition temperature for $LiCrSi_2O_6$, $LiFeSi_2O_6$, and $LiGaSi_2O_6$ also is shown. As observed by Arlt & Angel (2000), the $C2/c$ structure is present in Li clinopyroxenes hosting a relatively large *M*1 cation (Fig. 2), whereas the $P2_1/c$ structure is adopted in those with a smaller *M*1 cation. This observation is closely followed where the *M*1 cation is a transition metal or Ga. However, from Figure 2, spodumene could be predicted to be $P2_1/c$ up to high temperature, whereas experimental evidence shows that the $C2/c$ structure is retained down to 54 K: in spodumene, a fully relaxed $C2/c$ structure is observed, whereas in $LiCrSi_2O_6$, $LiFeSi_2O_6$ and $LiGaSi_2O_6$ pyroxenes, the ground structure has $P2_1/c$ symmetry. An explanation for this behavior requires additional data on the high- and low-T behavior of Li pyroxenes, at present available only for spodumene and $LiFeSi_2O_6$ (Cameron *et al.* 1973, Redhammer *et al.* 2001). A comparison between the $C2/c$ structures of spodumene and $LiFeSi_2O_6$ at the different temperatures is nevertheless interesting, to outline the geometrical behavior of Li pyroxenes with and without the phase transition. As shown in Figure 3, in spodumene all the *M*2–O bond lengths decrease with temperature continuously and at a similar rate. In $LiFeSi_2O_6$, with decreasing temperature, the *M*2–O1 distances undergo a significant decrease, whereas the *M*2–O3 distances increase (Fig. 3). At the critical temperature, one of the two *M*2–O3 bond lengths is released. At the same time, in the $C2/c$ structure of $LiFeSi_2O_6$, Li moves along the diad axis by as much as 2.6×10^{-4} Å/K, whereas in spodumene it does so by only 0.2×10^{-4} Å/K (Cameron *et al.* 1973, Redhammer *et al.* 2001). Another difference lies in chain rotation among the tetrahedra (Fig. 4). In pyroxenes, the chain angle extends with increasing temperature (Cameron *et al.* 1973, Benna *et al.* 1990, Tribaudino 1996), as a consequence of the stiffness of the tetrahedron with respect to the expansion of the *M*1 octahedra, which are linked to the tetrahedra *via* the common O1 and O2 oxygen atoms (Cameron *et al.* 1973). The extension in the chain of tetrahedra with temperature is not possible in the Fe end-member, which has the chains already fully elongated at room temperature, as shown in Figure 4 for $LiFeSi_2O_6$. In spodumene, by contrast, the chain can extend with temperature, approaching, but not reaching, the fully extended situation at higher temperature.

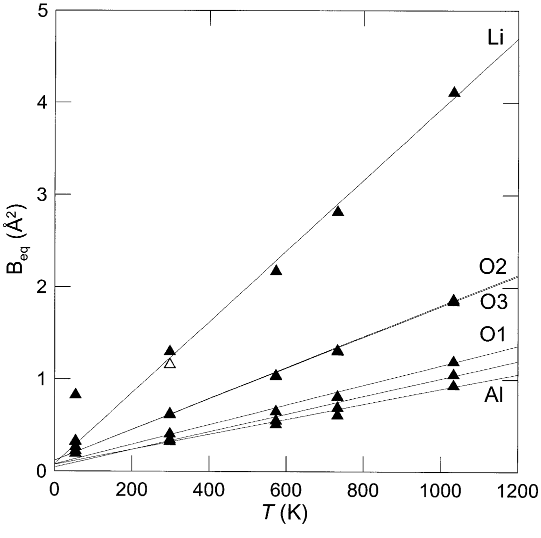

FIG. 1. Equivalent B factors ($B_{eq} = 8\pi^2 U_{eq}$) for spodumene as a function of temperature: data at 54 and 298 K are from this work; data at 573, 733 and 1033 K are taken from Cameron *et al.* (1973). The plot for Si is between those for O1 and Al. The B_{eq} for Li from the refinement by Sasaki *et al.* (1980) is reported as an open triangle. The fit was calculated without the 54 K datum.

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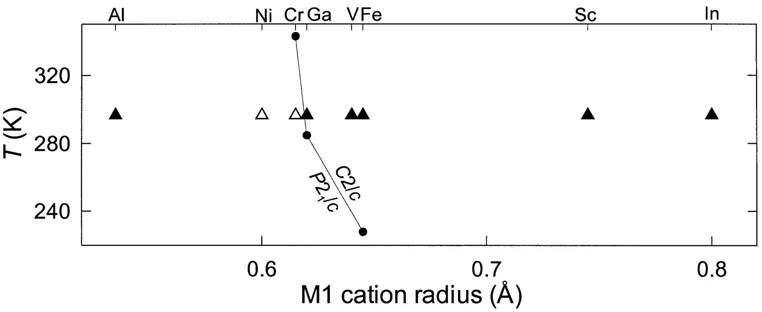

FIG. 2. $P2_1/c$ (open triangles) and $C2/c$ (full triangles) structures for Li*M*1Si_2O_6 clinopyroxenes in a plot of T *versus* *M*1cation radius. The transition temperatures for Cr, Ga and Fe end members are given and linked. Only room-temperature data are reported. The data are taken from this work for $LiAlSi_2O_6$, Ohashi & Osawa (1988) for $LiNiSi_2O_6$, Redhammer *et al.* (2001) for $LiFeSi_2O_6$, Behruzi *et al.* (1984) for $LiCrSi_2O_6$, Sato *et al.* (1994, 1995) for $LiGaSi_2O_6$, Hawthorne & Grundy (1977) for $LiScSi_2O_6$, Grotenpaß *et al.* (1983) for $LiInSi_2O_6$, and Satto *et al.* (1997) for $LiVSi_2O_6$.

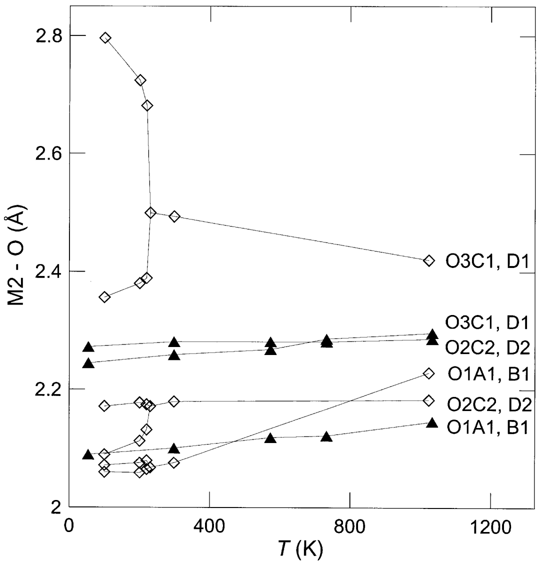

FIG. 3. *M*2–O bond lengths *versus* T in spodumene (full triangles) and $LiFeSi_2O_6$ (diamonds). Data as in Figure 2.

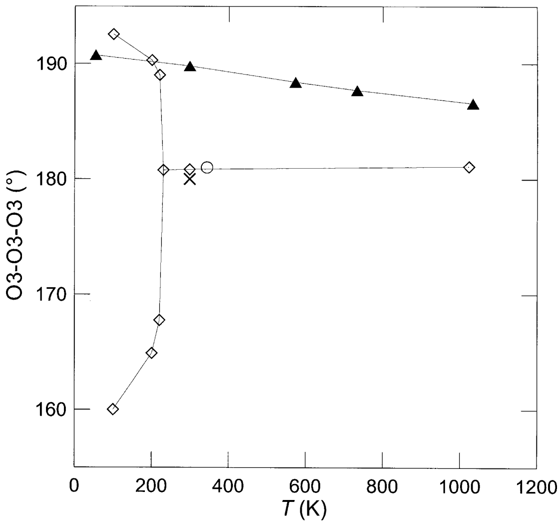

FIG. 4. O3–O3–O3 kinking angle as a function of T in spodumene (full triangles), in $LiFeSi_2O_6$ (diamonds), in $LiGaSi_2O_6$ (cross), and in $LiCrSi_2O_6$ (circle). Data as in Figure 2.

REFERENCES

ANGEL, R.J., CHOPELAS, A. & ROSS, N.L. (1992): Stability of high-density clinoenstatite at upper mantle pressures. *Nature* **358**, 322-324.

ARLT, T. & ANGEL, R.J. (2000): Displacive phase transitions in *C*-centered clinopyroxenes: spodumene, $LiScSi_2O_6$ and $ZnSiO_3$. *Phys. Chem. Minerals* **27**, 719-731.

BAUM, E., TREUTMANN, W., BEHRUZI, M., LOTTERMOSER, W. & AMTHAUER, G. (1988): Structural and magnetic properties of the clinopyroxenes $NaFeSi_2O_6$ and $LiFeSi_2O_6$. *Z. Kristallogr.* **183**, 273-284.

BEHRUZI, M., HAHN, T., PREWITT, C.T. & BALDWIN, K. (1984): Low and high temperature crystal structures of $LiFeGe_2O_6$, $LiFeSi_2O_6$ and $LiCrSi_2O_6$. *Acta Crystallogr.* **A40**, *suppl.* C-247.

BENNA, P., TRIBAUDINO, M., ZANINI, G. & BRUNO, E. (1990): The crystal structure of $Ca_{0.8}Mg_{1.2}Si_2O_6$ clinopyroxene ($Di_{80}En_{20}$) at T = –130°, 25°, 400° and 700°C. *Z. Kristallogr.* **192**, 183-199.

BROWN, G.E., PREWITT, C.T., PAPIKE, J.J. & SUENO, S. (1972): A comparison of the structures of high and low pigeonite. *J. Geophys. Res.* **77**, 5778-5789.

BURNHAM, C.W., CLARK, J.R., PAPIKE, J.J. & PREWITT, C.T. (1967): A proposed crystallographic nomenclature for clinopyroxene structure. *Z. Kristallogr.* **125**, 109-119.

CAMERON, M., SUENO, S., PREWITT, C.T.& PAPIKE, J.J. (1973): High-temperature crystal chemistry of acmite, diopside, hedenbergite, jadeite, spodumene, and ureyite. *Am. Mineral.* **58**, 594-618.

CLARK, J.R., APPLEMAN, D.E.& PAPIKE, J.J. (1969): Crystal chemical characterization of clinopyroxenes based on eight new structure refinements. *Mineral. Soc. Am., Spec. Pap.* **2**, 31-50.

GROTENPAß, M., BEHRUZI, M. & HAHN, T. (1983): Strukturen, Polymorphie und Mischkristallbildung im System $LiScSi_2O_6$ – $LiInSi_2O_6$ – $LiScGe_2O_6$ – $LiInGe_2O_6$. *Z. Kristallogr.* **162**, 90-91.

HAWTHORNE, F.C. & GRUNDY, H.D. (1977): Refinement of the crystal structure of $LiScSi_2O_6$ and structural variations in alkali pyroxenes. *Can. Mineral.* **15**, 50-58.

IBERS, J.A. & HAMILTON, W.C., eds. (1974): International Tables for X-Ray Crystallography IV. Kynoch Press, Birmingham, U.K. (99-101).

KNIGHT, K.S. & SCHOFIELD, P.F. (2000): Structural basis for the negative eigenvalue in the thermal expansion tensor of spodumene. *ISIS Experimental Rep.* **10782**.

KUNTZINGER, S. & GHERMANI, N.E. (1999): Electron density distribution and Madelung potential in α-spodumene, $LiAl(SiO_3)_2$ from two-wavelength high-resolution X-ray diffraction data. *Acta Crystallogr.* **B55**, 273-284.

LARSON, A.C. (1970): The inclusion of secondary extinction in least-squares refinement of crystal structures. *In* Crystallographic Computing (F.R. Ahmed, ed.). Munksgaard, Copenhagen, Denmark (291-294).

LOTTERMOSER, W., REDHAMMER, G., FORCHER, K. & AMTHAUER, G. (1998): Single-crystal Mössbauer and neutron powder diffraction measurements on the synthetic clinopyroxene Li-acmite $LiFeSi_2O_6$. *Z. Kristallogr.* **213**, 101-107.

NORTH, A.C.T., PHILLIPS, D.C. & MATHEWS, F.S. (1968): A semi-empirical method of absorption correction. *Acta Crystalogr.* **A24**, 351-359.

OHASHI, H. & OSAWA, T. (1988): Synthesis of $LiNiSi_2O_6$ and $LiTiSi_2O_6$ spodumenes. *J. Japan. Mineral. Petrogr. Econ. Geol.* **83**, 308-310.

PAVESE, A., ARTIOLI, G. & PRENCIPE, M. (1995): X-ray single crystal diffraction study of pyrope in the temperature range 30–973 K. *Am. Mineral.* **80**, 457-464.

PILATI, T., DEMARTIN, F. & GRAMACCIOLI, C.M. (1996): Lattice-dynamical evaluation of atomic displacement parameters of minerals and its implications: the example of diopside. *Am. Mineral.* **81**, 811-821.

PRENCIPE M., TRIBAUDINO M., PAVESE A., HOSER A. & REEHUIS M. (2000): A single-crystal neutron diffraction investigation on diopside at 10 K. *Can. Mineral.* **38**, 183-189.

REDHAMMER, G.J., ROTH, G., PAULUS, W., ANDRÉ, G., LOTTERMOSER, W., AMTHAUER, G., TREUTMANN, W. & KOPPELHUBER-BITSCHNAU, B. (2001): The crystal and magnetic structure of Li-aegirine $LiFe^{3+}Si_2O_6$: a temperature-dependent study. *Phys. Chem. Minerals* **28**, 337-346.

SASAKI, S., FUJINO, K., TAKÉUCHI, Y. & SADANAGA, R. (1980): On the estimation of atomic charges by the X-ray method for some oxides and silicates. *Acta Crystallogr.* **A36**, 904-915.

________, MATSUMOTO, T. & SAWADA, C. (1981): The influence of multiple diffraction on the space group determination of orthopyroxenes, spodumene, low omphacite and pigeonite. *Phys. Chem. Minerals* **7**, 260-267.

SATO, A., OSAWA, T. & OHASHI, H. (1994): $LiGaSi_2O_6$. *Acta Crystallogr.* **C50**, 487-488.

________, ________ & ________ (1995) Low-temperature form of $LiGaSi_2O_6$. *Acta Crystallogr.* **C51**, 1959-1960.

SATTO, C., MILLET, P. & GALY, J. (1997): Lithium vanadium metasilicate, $LiVSi_2O_6$. *Acta Crystallogr.* **C53**, 1727-1728.

SHELDRICK, G.M. (1997): *SHELXL–97. Program for Crystal Structure Refinement*. University of Göttingen, Göttingen, Germany.

SMYTH, J.R. (1974): The high temperature crystal chemistry of clinohypersthene. *Am. Mineral.* **59**, 1069-1082.

TRIBAUDINO, M. (1996): High-temperature crystal chemistry of $C2/c$ clinopyroxenes along the join $CaMgSi_2O_6$ – $CaAl_2SiO_6$. *Eur. J. Mineral.* **8**, 273-279.

________, NESTOLA, F., CÁMARA, F. & DOMENEGHETTI, M.C. (2002): The high temperature $P2_1/c$ – $C2/c$ phase transition in Fe-free pyroxene ($Ca_{0.15}Mg_{1.85}Si_2O_6$): structural and thermodynamic behavior. *Am. Mineral.* **87**, 648-657.

VITERBO, D. (1992): Solution and refinement of crystal structures. *In* Fundamentals of Crystallography (C. Giacovazzo, ed.). Oxford University Press, Oxford, U.K. (319-401).

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