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The Crystal Structure of Beta Eucryptite as a Function of Temperature[1]

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Abstract

Crystals of beta-eucryptite ($LiAlSiO_4$, space group $P6_422$, $a = 10.497$, $c = 11.200$ Å) have been studied as a function of temperature, using a single-crystal diffractometer. Reflections with h or $k = 2n + 1$, which are superstructure reflections arising in part due to distortions of the quartz-structure-type framework, continuously decrease in intensity with increasing temperature and become unobservable at 460°C. The lack of discontinuities in either intensity or lattice parameters as a function of temperature suggests that there is no first-order transition. The crystal structure was refined using data measured at 23, 200, 335, 440, 484, and 647°C. Atom coordinates which are not symmetry-equivalent at temperatures below the transition do not shift toward equality at the transition. In addition, there is strong evidence for atom "splitting" above the transition. The decrease in intensity of reflections with h or $k = 2n + 1$ is therefore not related to displacements of the framework. On the other hand, Li atoms appear to shift to other channel sites which are unoccupied at low temperature. The decrease in intensity of superstructure reflections thus seems to be due to a combination of normal thermal vibration of the framework and order-disorder of the Li atoms.

Introduction

The crystal structure of β-eucryptite has been investigated by Winkler (1948), Buerger (1948), Hornyak (1969), and most recently, Tscherry, Schulz, and Laves (1972a, b). A principal reason for current interest in this structure lies in its unusual thermal expansion properties. Although increasing temperature causes expansion to occur along the a-axis, sufficient contraction occurs along the c-axis to result in a net negative thermal coefficient of volume expansion.

The structure was first investigated by Winkler (1948) and proposed to be β-quartz-like with space group $P6_422$. He determined that the c-axis is double that of the quartz structure, there is ordering of Al and Si in tetrahedral sites, and the Li atoms are coplanar with the Al atoms and tetrahedrally coordinated. Buerger (1948) grew crystals by Winkler's recipe and noted that the a-axis doubled relative to that of the quartz structure. He later (Buerger, 1954) classed β-eucryptite as a stuffed derivative of β-quartz.

Hornyak (1969) was the first to attempt refinement of the atom coordinates. He found both the a- and c-axes to be doubled relative to their values in quartz, with the Li atoms located in framework channels running parallel to c. Only the Li atoms in one of the four channels per unit cell were ordered. These were coplanar with the Si atoms.

A second attempt at refining the atom coordinates was carried out by Tscherry, Schulz, and Laves (1972a, b). Their structure is slightly different from that of Hornyak. The Al, Si and O atoms are all shifted somewhat from the positions of Hornyak. All of the Li positions are fixed by symmetry.

Hummel (1951) measured the volume expansion of an aggregate of β-eucryptite crystals. He noted the presence of negative thermal expansion for the aggregate up to 1000°C. Gillery and Bush (1959) correlated lattice parameter changes obtained by X-ray methods with bulk expansion recorded on a dilatometer. These results showed that the volume expansion of the unit cell is slightly negative. Gillery and Bush further postulated a mechanical model, based on an analogy of the spirals of tetrahedra with the uncoiling of a spring, to account for the highly anisotropic expansion. Tscherry, Schulz, and Czank (1972) measured the temperature dependence of

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the *a*- and *c*-axes by single crystal methods. They obtained slightly lower values of thermal expansion for both axes than did Gillery and Bush.

Tscherry and Laves (1970) noted the reversible disappearance of certain superstructure reflections "at about 400°C," which they tentatively attributed to "displacive order-disorder phenomena of the $SiAlO_4$ framework." Schulz and Tscherry (1972b) interpret this to be due to a first order transition, attributing it to displacements in the positions of the framework atoms and to a change to a random distribution of Li atoms over all available framework channel sites.

The purpose of this study is to determine (1) which, if either, of the two refined structures on record is correct and (2) the nature of the transition near 400°C. This study has been carried out in two phases. First, to define or confirm the general nature of changes in parameters such as reflection intensity as a function of temperature, with special reference to the transformation, several selected reflections have been studied as a function of time and temperature. Second, using the latter data in part as a guide, three-dimensional intensities have been determined for several temperatures, and the crystal structure has been refined for each set of data.

Experimental

The specimens used in this study were provided by Emery J. Hornyak of the Owens Illinois Technical Center, Toledo, Ohio. The method of synthesis is described in his report of the crystal structure (Hornyak, 1969). Lattice parameters ($a = 10.497 \pm .003$, $c = 11.200 \pm .005$ Å) were determined through the least-squares refinement of powder diffractometer data, obtained using an internal standard. The space group was confirmed to be $P6_422$ (or $P6_222$) through the observation of precession and Weissenberg patterns. Single crystals measuring approximately 0.2 × 0.2 × 0.5 mm were mounted in silica glass capillaries for rotation about a^* on a Weissenberg-geometry diffractometer fitted with the furnace described by Foit and Peacor (1967). A scintillation counter was used for measuring intensities, in conjunction with $MoK\alpha$ radiation monochromated with a flat graphite crystal. Temperatures were determined using a chromel-alumel thermocouple placed within 2 mm of the crystal.

For the initial part of this study when selected reflections were studied as a function of temperature, reflections were recorded on a strip chart recorder, and their intensities determined using a planimeter. Two-theta values were determined for 0-level reflections by averaging the upsilon values of the high and low upsilon sides of a peak, assuming that peaks were approximately symmetrical as a function of upsilon. Measurements of integrated intensity and two-theta were made at a given temperature only after it was determined that intensities had reached a steady-state value. For this purpose, the temperature was held constant for up to sixteen hours following a change in temperature. All intensity changes were thus observed to occur immediately after temperature change and to be independent of time.

Three-dimensional intensity data were measured at six temperatures (23, 200, 335, 440, 484, and 647°C) using the Supper-Pace automated system. All data were corrected for Lorentz and polarization factors (including a monochromator polarization factor) but not for absorption ($\mu_l = 7.6$ cm^{-1}). Minimum observed values were assigned on the basis of standard counting statistics. Each data set included two asymmetric units. Symmetry equivalent intensities $[I(hkl) = I(khl)]$ were averaged, resulting in 560 to 565 reflections for each of the first four temperatures. Above approximately 460°C, reflections with h or $k = 2n + 1$ were no longer observable. Therefore, for the highest two temperatures at which intensities were determined, there were only 161 to 163 symmetry independent reflections.

The least-squares structure refinements were initially carried out by applying the weighting scheme of Cruickshank (1965), and including only those reflections with amplitudes greater than F_{min}. Starting parameters were those of Tscherry *et al* (1972b). Form factors were formulated assuming half-ionization of all atoms. Under these conditions, refinement did not proceed satisfactorily. The use of unit weighting resulted in significant improvement, but with unacceptable agreement between observed and calculated structure amplitudes. This was particularly true for the higher temperature data sets. In these cases, only a small number of superstructure reflections had observed intensities greater than F_{min}, due to the general decrease in the intensities of these reflections as a function of temperature. With the inclusion of all reflections in the refinement for the high temperature sets of data, discrepancies between observed and calculated structure amplitudes decreased significantly and the refinements rapidly converged. The final cycles of refinement were carried out using unit weighting and all data, even for the low temperature sets of data, in order to maintain uniformity of refinement conditions. The final *R*-values are 11.5 (23°C), 13.2 (200°C), 14.8 (335°C), 15.7 (440°C), 9.2 (484°C) and 10.0 percent (647°C). The values are high due to the presence of a large proportion of superstructure reflections with amplitudes below $F_{\min}$. (For the four lower temperature sets of data, 88 percent of the reflections are superstructure reflections of weak intensity.) Tables 1a and 1b[2] are listings of structure factors for the 23°C and the 647°C sets of data, respectively.

Selected Intensities as a Function of Temperature

The diffraction pattern of β-eucryptite is dominated by a β-quartz-like subcell, with superstructure reflections occurring due to doubling of both *a* and *c*, relative to the β-quartz unit cell. Reflections with h, k, and $l = 2n$ are substructure reflections. The superstructure reflections are classified into two groups by the scheme of Tscherry and Schulz (1970): (1) *c*-reflections; $h, k = 2n, l = 2n + 1$. (2) *a*-reflections; $h, k = 2n + 1$ or $h + k = 2n + 1, l = 2n + 1$.

The structures determined by both Hornyak (1969) and Tscherry *et al* (1972a,b), although different in detail, are consistent in their kinds of contributions to the superstructure reflections. There are eight subcells, each similar to the quartz structure. Doubling of the *c*-axis is caused in part by ordering of Al and Si, such that *c*/2 related cells, although dimensionally similar, have reversed Al, Si occupancy of tetrahedra. Doubling of the *a*-axis is caused largely through positional differences between *a*/2 related subcells. The *a*/2 translation relates tetrahedra which are chemically equivalent (Fig. 1). In addition, the Li atoms are non-periodic with respect to both the *a*/2 and *c*/2 subtranslations and thus contribute to all superstructure reflections.

Determination of intensity as a function of temperature has been shown in several cases to provide evidence for the nature of change in structure as a function of temperature. Since the several classes of reflections in β-eucryptite have their origin in differing structure parameters, we first attempted to determine the temperature dependence of intensity for each type of reflection. For this purpose, the intensities of both *a* and *c* superstructure reflections, as well as those of selected substructure reflections, were monitored as a function of temperature. No reflections with $h, k = 2n + 1$ or $h + k = 2n + 1$, $l = 2n$ were monitored since their intensities are all so small as to soon merge into the background after an increase of only a few degrees above room temperature.

Two crystals were chosen for this preliminary study, each of which was used for the observation of seven reflections. The first crystal was used to study three substructure reflections, two *c*-reflections, and two *a*-reflections. (Two of these reflections, 006 and 040, were also used for the measurement of lattice parameters.) The intensities of two substructure reflections (020 and 040) decreased slightly while that of the third substructure reflection (006) increased gradually with temperature. Of the *c*-reflections, one decreased considerably in intensity, while the other remained constant (Fig. 2). Both of the *a*-reflections decreased steadily in intensity until they merged with the background between 410°C and 508°C. All seven reflections were also monitored with decreasing temperature. The *a*-reflection became observable again at about 457°C. At this

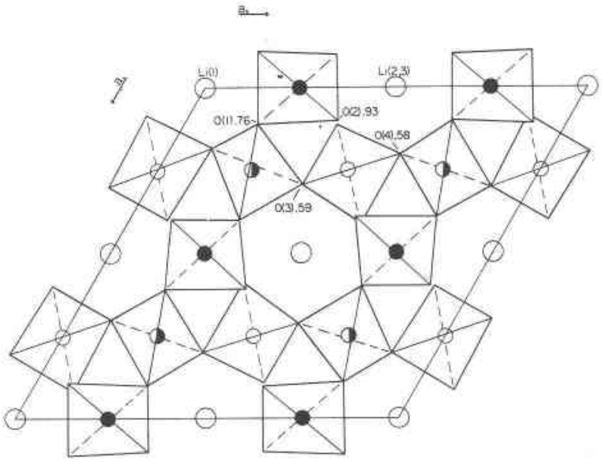

FIG. 1. Projection along *c* of the beta-eucryptite structure, including atoms from $z = 0$ to $z = ½$. Si-tetrahedra are stippled and Al-tetrahedra unstippled. The smaller circles correspond to the projected positions of both an Al and Si atom, with the following code: open circles, $z = 0, ½$; darkened circles, $z = 2/6, 5/6$; half-darkened circles, $z = 1/6, 4/6$.

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[2] Tables 1a and 1b may be ordered as NAPS Document No. 02124 from the National Auxiliary Publication Service, by remitting $1.50 for microfiche or $5.00 for photocopies, payable to Microfiche Publications, 305 East 46th Street, New York, N.Y. 10017. Please check the most recent issue of this journal for the current address and prices.

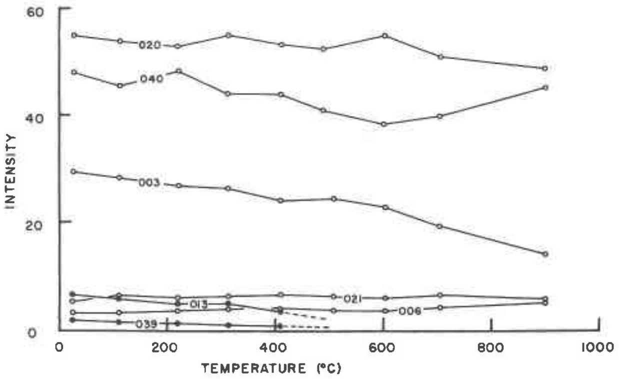

FIG. 2. Integrated intensity *vs* temperature for three substructure reflections (020, 004 and 006), two *c*-reflections (003 and 021), and two *a*-reflections (013 and 039).

temperature they were barely resolvable from the background. Their intensities increased steadily as the temperature was decreased further. However, neither the *a*-reflections nor *c*-reflections, nor those due to the substructure, completely regained their original intensities. The peak widths of all reflections were also monitored as a function of temperature. No significant change in the width of any of the peaks was observed.

To confirm the above results, a second crystal was studied. Two *c*-reflections and five *a*-reflections, which were among the most intense at room temperature, were monitored. Again, one *c*-reflection steadily decreased in intensity with increasing temperature while the other remained constant. The two weakest *a*-reflections could no longer be observed at 442°C. The other three merged into the background at approximately 454°C. The most intense of these five *a*-reflections, 057, was carefully monitored with decreasing temperature and reappeared at 446°C. Extrapolation of all the intensity plots *vs* temperature for the *a*-reflections led us to conclude that they all become unobservable at approximately 460°C.

That all reflections requiring a doubling of the *a*-axis become unobservable at approximately the same temperature implies that a transition is taking place. Tscherry and Laves (1970) observed that *a*-reflections disappear "at about 400°C." They suggested that the effect may be due to displacive order/disorder phenomena of the $SiAlO_4$ framework. Schulz and Tscherry (1972b) thus interpret this to be a first order transition.

The temperature-time-intensity relationships reported here provide some evidence of the nature of the transition. First, they show that the transition is not first order since that would require intensities to change discontinuously as a function of temperature. Even in the case of the α-β quartz displacive transformation, Young (1962) observed discontinuities in intensity as a function of temperature. In addition, Gillery and Bush (1959), Tien and Hummel (1964) and Tscherry, Schulz, and Czank (1972) all showed that there is no discontinuity in lattice parameters at the transition temperature as would be required by the volume change for a first order transition. Our own determination (Fig. 3) of the linear thermal expansion coefficients ($\alpha_a = 8.6 \times 10^{-6}/°C$, $\alpha_c = -18.4 \times 10^{-6}/°C$) is in good agreement with their observations.

The form of the intensity versus temperature functions implies that the transformation is of second order and is thus of the order-disorder type. There are only two reasonable possibilities for change in structure: (1) order-disorder of the Li atoms in the framework channels, or (2) order-disorder involving Al and Si. That the latter is not the case is shown by the fact that the intensity changes are not sluggish, are in large part reversible, and occur at relatively low temperatures. The Li atoms, however, occupy only one half of the available sites in the channels, and the barriers to intersite diffusion are low; thus, Li order-disorder is a probable primary factor in the transition. However, since the *a*/2 subtranslation relates chemically similar but topologically different tetrahedra, it appears that the transition would also require positional adjustments in atom coordinates which would culminate in the atoms becoming pre-

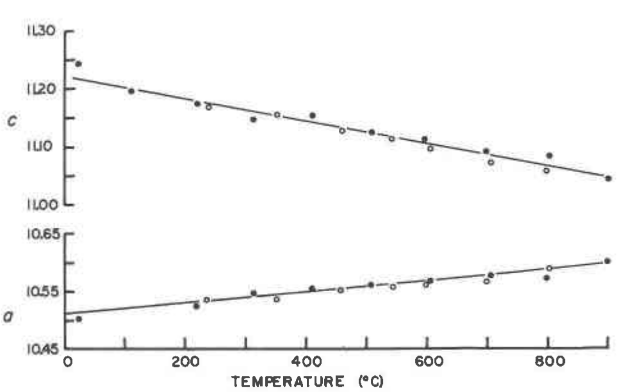

FIG. 3. Magnitudes of *a* and *c* as a function of temperature. The filled and open circles correspond to measurements obtained with increasing and decreasing temperature, respectively. These values of *a* and *c* are corrected for experimental error.

cisely $a/2$ translation-related. The relative significance of Li order-disorder and framework positional adjustments can only be determined through crystal structure refinements. These results are described in the following sections.

Confirmation of the Crystal Structure

In order to compare models of the crystal structure, Tscherry *et al* (1972b) refined the parameters of Hornyak's model using their observed data. The temperature factors of the Al, Si, and Li atoms refined to unreasonably high values, and it was concluded that Hornyak's model was not consistent with their observed structure amplitudes. The two structure models differ in two ways. First, the displacements of framework atoms from substructure positions, while of similar magnitude, are arranged in different ways. Secondly, the distribution of Li atoms in the channels differs. In the Hornyak model, the Li atoms in three of the four channels are disordered while those in the fourth channel are ordered and coplanar with the Si atoms. All four channels of the model of Tscherry *et al* have fixed Li positions. The Li atoms in three of these channels are coplanar with the Si atoms while those in the fourth are coplanar with Al atoms. Since the Li distribution might be expected to be variable as a function of the method of crystal synthesis, we first attempted to test the validity of the two models.

Refinement was first carried out using Hornyak's observed structure amplitudes with the model of Tscherry *et al.* After seven cycles, the temperature factors for the Al and Si atoms had refined to unreasonably high values. We next attempted to refine both models using our observed data. After five least-squares cycles using the Hornyak model, the temperature factors of all Li, Al, and Si atoms had refined to very high values. The refinement with the model of Tscherry *et al* resulted in isotropic temperature factors which were consistent with those of other, well-refined silicate structures. Accordingly, we concluded that the model of Tscherry *et al* was correct. All of our subsequent refinements were therefore based upon this structure.

Refinements

The crystal structure was first refined for each of the four sets of data obtained below the transition temperature. Refinement of all variables proceeded normally, except for the Li isotropic temperature factors. Some of these refined to anomalously high values for the higher temperature data, while others were unreasonably low.

Li occupies sites in the channels which are fourfold coordinated by oxygen. The ordered structure of Tscherry *et al* requires that only one half of the available sites be occupied. Occupied and vacant sites alternate along each framework channel parallel to the *c*-axis. The possibility exists, therefore, that disorder occurs with increasing temperature, with the Li atoms in some channels diffusing to the alternate sites. Electron density syntheses, based on structure factors calculated with the Li atoms omitted, were calculated for both the 440°C and the room temperature data. Small peaks (20 to 40 percent of the peak height of the occupied Li sites) occurred at the supposedly vacant Li sites for the room temperature data. Refinement with disordered Li atoms confirmed that the site occupancy for the previously assumed vacant sites was so small as to be negligible. For the 440°C data, the magnitudes of the peaks in the sites assumed to be vacant were greatly increased (60 to 80 percent of the peak height of the sites assumed to be occupied by Li) over the values for the room temperature data. This indicates that the Li atoms are interchanging with the initially vacant sites as temperature increases. Because there was only a limited number of observed *a*-reflections for the high temperature sets of data, refinement for all data sets was completed using only the three occupied Li sites. Occupancy by Li of six sites increases the number of variables per reflection to the point where the accuracy of refined variables is questionable, particularly since it requires fractional occupancy by ions with only two electrons. Table 2 is a compilation of final atomic parameters for the data sets measured at 23, 200, 335, and 440°C.

For the crystal structure above the transition, the *a*-axis has an apparent magnitude one half that of the structure below the transition, as evidenced by the absence of *a*-reflections. The space group is still $P6_422$, however. This has the consequence that atoms of the same element must all occupy the same equipoint. Whereas in the low-temperature structure there are three symmetrically non-equivalent Li atoms, two Al, two Si, and four O atoms, the Li, Al, Si and O each occupy a single equipoint above the transition. The Li, Al, and Si atoms each occupy special equipoints of rank 3, while the O atoms occupy the general equipoint (rank 12).

Above the transition, the four low-temperature subcells related by the $a/2$ translation become

TABLE 2. Atomic Coordinates and Isotropic Temperature Factors for the Structure below the Transition

		23°C	200°C	335°C	440°C
Li(1)	x	0	0	0	0
	y	0	0	0	0
	z	1/2	1/2	1/2	1/2
	B	3.0(7) Å^2	1.7(5)	3.2(11)	6.6(17)
Li(2)	x	1/2	1/2	1/2	1/2
	y	0	0	0	0
	z	0	0	0	0
	B	3.6(9)	6.1(17)	2.7(8)	2.9(9)
Li(3)	x	1/2	1/2	1/2	1/2
	y	0	0	0	0
	z*	.324(3)	.324(3)	.324(3)	.324(3)
	B	.8(3)	1.8(4)	2.3(5)	3.6(7)
Al(1)	x	.2520(3)	.2532(3)	.2530(4)	.2523(4)
	y	0	0	0	0
	z	1/2	1/2	1/2	1/2
	B	.21(4)	.49(5)	.60(6)	.87(6)
Al(2)	x	.2506(2)	.2499(2)	.2503(2)	.2500(3)
	y	.5012(4)	.4998(4)	.5006(4)	.5000(6)
	z	1/2	1/2	1/2	1/2
	B	.24(4)	.64(5)	.78(6)	.81(6)
Si(1)	x	.2486(3)	.2499(3)	.2502(4)	.2497(4)
	y	0	0	0	0
	z	0	0	0	0
	B	.24(4)	.37(4)	.54(5)	.66(5)
Si(2)	x	.2477(2)	.2476(2)	.2474(2)	.2483(2)
	y	.4954(4)	.4952(4)	.4948(4)	.4966(4)
	z	0	0	0	0
	B	.34(4)	.55(4)	.73(5)	.73(5)
O(1)	x	.0853(6)	.0860(7)	.0870(9)	.0877(8)
	y	.1942(6)	.1947(7)	.1945(8)	.1942(8)
	z	.2428(5)	.2435(5)	.2454(6)	.2451(6)
	B	.44(8)	.99(9)	1.24(11)	1.01(10)
O(2)	x	.6023(7)	.6038(7)	.6035(9)	.6033(9)
	y	.7008(7)	.7006(8)	.7019(9)	.7020(9)
	z	.2651(5)	.2655(5)	.2653(6)	.2666(6)
	B	.53(9)	.81(10)	1.04(11)	.96(11)
O(3)	x	.1101(7)	.1067(9)	.1061(11)	.1054(12)
	y	.7099(8)	.7106(10)	.7109(13)	.7089(13)
	z	.2597(5)	.2572(6)	.2585(8)	.2560(9)
	B	1.06(10)	1.84(13)	2.58(17)	2.82(19)
O(4)	x	.5902(7)	.5906(8)	.5924(10)	.5927(11)
	y	.2011(6)	.2017(7)	.2035(9)	.2067(10)
	z	.2494(5)	.2499(6)	.2497(7)	.2497(8)
	B	.66(9)	1.10(10)	1.36(12)	1.84(14)

*This value is taken from the paper of Tscherry, Schulz, and Laves, and was not varied during the refinement.

translation-equivalent. Thus each O, Al, or Si position above the transition corresponds to four positions below it. The possibility arises that the four atom positions below the transition do not become symmetrically equivalent. Thus the position above the transition may be an average for the four below the transition. This is the so-called "split-atom" condition. This situation would arise if the *a*-reflections are not extinct, but are simply too weak to be observed.

For the refinements above the transition, the Si and O temperature factors became abnormally high. This is consistent with the occurrence of split atoms, since the temperature factors may have both a normal thermal and a positional disorder component. In such situations, the geometry of thermal ellipsoids is a measure of the splitting. The four O atoms could be split, but arranged symmetrically in pairs about a center of gravity so as to result in a thermal ellipsoid which is anomalously elongated parallel to the vector between atom pairs. Accordingly, anisotropic temperature factors were refined, and the geometries of the thermal ellipsoids calculated. The magnitudes of the principal axes for Si were large, but approximately equal. However, this is not inconsistent with a split atom situation. Schulz and Tscherry (1972a) showed that even for refinements using only substructure reflections, the Si temperature factors were not anomalous because of the small value of the split vectors. However, the thermal ellipsoid for the O atom was greatly elongated parallel to *c*. Refinement was therefore continued using doubly split O atoms. The thermal ellipsoids of these two individual atoms were still elongated along *c*. The magnitude of the split vector was 0.38 Å, and the individual oxygen isotropic temperature factors were 1.2 and 1.8 Å^2.

The successful refinement of the doubly split atom model is confirmation that O atoms do not become *a*/2 translation equivalent. If no displacement of oxygen atoms occurs at the transition, then the average oxygen position for the 484°C data should be the average of the four oxygen positions in the *a*/2-related subcells at 440°C. These atoms, when plotted in a single subcell, do not plot in two pairs such that the split vector for each pair is small relative to the split vector between pairs. The double atom model is therefore not a realistic approximation to the existing four-fold splitting of the oxygen atom. Resolution of four split atoms would be unlikely. The coordinates of a single oxygen atom were therefore computed as the average of the four pseudo-*a*/2 translation-related oxygen atoms of the structure at 440°C. This initial average position (0.212, 0.405, 0.745) is very nearly that of the final position obtained by refinement of the 484 and 647°C data.

Since refinement of the lower temperature data sets had indicated that Li could be distributed over all of the available channel sites, refinement was attempted with Li on the sites at both $z = 0$ and $z = 1/6$. With the Li atom at $z = 1/6$, temperature factors as high as 20 Å^2 indicated little or no occupancy of this position. Refinement with threefourths occupancy of the site at $z = 0$, and 1/4 for the site with $z = 1/6$, yielded a reasonable Li temperature factor for the former site, but a value which was still unreasonably high for the latter. A difference Fourier synthesis, computed omitting the Li contribution to the calculated structure factors, confirmed that most of the Li atoms occupy the site with $z = 0$. Refinement was therefore completed with Li assumed to be present only on the site having $z = 0$. Table 3 is a listing of the refined atomic parameters for the crystal structure at 484 and 647°C.

Crystal Structure as a Function of Temperature

Interatomic distances and angles for the refinements with intensity data obtained below and above the temperature corresponding to disappearance of the *a*-reflections are listed in Tables 4–6 and 7, respectively. Standard errors were computed utilizing lattice-parameter standard errors and the least-squares variance-covariance matrix. For the structure at room temperature, the distances and angles are generally similar to those obtained by Tscherry *et al* (1972b). Since the values reported by Tscherry *et al* appear to be more precise than those reported here, and since those authors have given a complete discussion of their meaning, we will not further describe their significance here.

The *T*–O distances for the structure at 23°C are consistent with ordering of Al and Si. In particular, the average distances for Al(1) (1.75 Å) and Si(2) (1.59 Å) are indicative of occupancy only by Al and Si, respectively. The Al(2)–O and Si(1)–O distances (1.71 and 1.64 Å, respectively) indicate the presence of limited Al–Si disorder between these two sites. The average O–O distances for the four kinds of tetrahedra (Table 5) confirm this relation. The distances reported by Tscherry *et al* are consistent with complete Al and Si order over all four sites. The differences in these results are probably a measure of the differences in synthesis conditions for the crystals which were investigated.

TABLE 3. Atomic Coordinates and Isotropic Temperature Factors for the Crystal Structure at 484 and 647°C

		484°C	647°C
Li	x	0	0
	y	0	0
	z	0	0
	B	7.1(12) Å^2	7.6(14)
Al	x	1/2	1/2
	y	0	0
	z	1/2	1/2
	B	.94(8)	1.12(8)
Si	x	1/2	1/2
	y	0	0
	z	0	0
	B	.99(7)	1.11(7)
O	x	.2105(15)	.2111(16)
	y	.4046(13)	.4045(13)
	z	.7456(4)	.7458(4)
	B	2.4(1)	2.8(1)

TABLE 4. Cation-Oxygen Distances for the Structure below the Transition (standard errors in parentheses)

	23°C	200°C	335°C	440°C
Li(1)-4 O(1)	1.964(5) Å	1.973(6)Å	1.980(7)Å	1.977(7)Å
Li(2)-4 O(3)	2.080(7)	2.097(9)	2.095(11)	2.091(12)
Li(3)-2 O(2)	2.017(6)	2.015(7)	2.028(8)	2.024(8)
2 O(4)	2.017(6)	2.022(7)	2.037(8)	2.066(9)
ave.	2.017	2.018	2.033	2.045
Al(1)-2 O(1)	1.759(6)	1.767(7)	1.767(8)	1.755(8)
2 O(2)	1.744(6)	1.727(7)	1.731(8)	1.746(8)
ave.	1.752	1.747	1.749	1.751
Al(2)-2 O(3)	1.679(7)	1.684(8)	1.701(10)	1.683(11)
2 O(4)	1.747(7)	1.755(7)	1.739(9)	1.746(10)
ave.	1.713	1.720	1.720	1.715
Si(1)-2 O(1)	1.633(6)	1.638(7)	1.637(8)	1.643(8)
2 O(3)	1.646(7)	1.618(8)	1.602(11)	1.626(11)
ave.	1.640	1.628	1.620	1.635
Si(2)-2 O(2)	1.575(6)	1.588(6)	1.574(7)	1.575(8)
2 O(4)	1.613(6)	1.609(7)	1.616(9)	1.589(10)
ave.	1.594	1.599	1.595	1.582

Average cation–O and O–O distances remain essentially constant for the structure at the four lower temperatures. With limited exception, the distances show no regular changes as a function of temperature, but simply fluctuate around the values for 23°C, within standard error. This is largely due to the relatively high values of standard errors. In all other cases where we have refined structure parameters over several temperatures, interatomic distances have shown regular change. Only the Li(3)–O and corresponding O–O distances exhibit regular change with increasing temperature, the average Li(3)–O distance increasing from 3.24 Å at 23°C to 3.29 Å at 440°C. In general, however, these results substantiate the lack of significant change in structure as temperature increases and the transformation is approached.

The isotropic temperature factors for the lower four temperatures (Table 2) in general exhibit regular increase with increasing temperature. Exceptions to this include the temperature factors for O(1) and O(2) which increase regularly from 23 to 335°C, but decrease slightly from 335°C to 440°C. This deviation of change in *B* as a function

TABLE 5. Oxygen-Oxygen Distances for the Structure below the Transition (standard errors in parentheses)

	23°C	200°C	335°C	440°C
Li(1) tetrahedron				
2 O(1)-O(1)'	3.54(1) Å	3.55(1) Å	3.55(1) Å	3.55(1) Å
2 O(1)-O(1)''	2.61(1)	2.62(1)	2.63(2)	2.61(2)
2 O(1)-O(1)'''	3.39(1)	3.41(1)	3.44(1)	3.44(1)
ave.	3.18	3.19	3.21	3.20
Li(2) tetrahedron				
2 O(3)-O(3)'	3.82(1)	3.83(2)	3.85(2)	3.81(2)
2 O(3)-O(3)''	2.59(1)	2.58(2)	2.55(2)	2.58(2)
2 O(3)-O(3)'''	3.65(1)	3.72(2)	3.72(2)	3.71(2)
ave.	3.35	3.38	3.37	3.37
Li(3) tetrahedron				
O(2)-O(2)'	3.65(1)	3.65(1)	3.68(2)	3.69(2)
2 O(2)-O(4)	2.44(1)	2.45(1)	2.46(1)	2.45(1)
2 O(2)-O(4)'	3.63(1)	3.63(1)	3.65(1)	3.68(1)
O(4)-O(4)'	3.66(1)	3.68(1)	3.71(2)	3.78(2)
ave.	3.24	3.25	3.27	3.29
Al(1) tetrahedron				
O(2)-O(2)'	2.84(1)	2.82(1)	2.84(1)	2.86(1)
2 O(2)-O(1)	2.90(1)	2.88(1)	2.88(1)	2.88(1)
2 O(2)-O(1)'	2.94(1)	2.94(1)	2.94(1)	2.94(1)
O(1)-O(1)'	2.61(1)	2.62(1)	2.63(2)	2.61(2)
ave.	2.86	2.85	2.85	2.85
Al(2) tetrahedron				
O(3)-O(3)'	2.81(1)	2.79(2)	2.81(2)	2.79(2)
2 O(3)-O(4)	2.80(1)	2.84(1)	2.83(1)	2.84(1)
2 O(3)-O(4)'	2.75(1)	2.76(1)	2.77(1)	2.76(1)
O(4)-O(4)'	2.87(1)	2.87(1)	2.84(2)	2.81(2)
ave.	2.80	2.81	2.81	2.80
Si(1) tetrahedron				
O(1)-O(1)'	2.55(1)	2.54(1)	2.52(1)	2.53(1)
2 O(1)-O(3)	2.71(1)	2.67(1)	2.68(1)	2.70(1)
2 O(1)-O(3)'	2.75(1)	2.74(1)	2.71(1)	2.75(1)
O(3)-O(3)'	2.59(1)	2.58(2)	2.55(2)	2.58(2)
ave.	2.68	2.66	2.64	2.67
Si(2) tetrahedron				
O(2)-O(2)'	2.60(1)	2.61(1)	2.59(1)	2.57(2)
2 O(2)-O(4)	2.69(1)	2.71(1)	2.71(1)	2.68(1)
2 O(2)-O(4)'	2.44(1)	2.45(1)	2.46(1)	2.45(1)
O(4)-O(4)'	2.73(1)	2.71(1)	2.70(2)	2.65(2)
ave.	2.60	2.61	2.61	2.58

of temperature from the value expected is not large, however. Only the temperature factors for Li(1) and Li(2) exhibit significant non-linear or irregular changes with changing temperature. This is apparently caused by several factors, including the low electron density of Li and the limited number of superstructure reflections having observed intensities above the minimum observable values. The Li temperature factors are also affected by the apparent shift of some Li atoms to sites unoccupied at room temperature, for which no accurate correction could be made in the refinement procedure. The temperature factor for Li(3) does exhibit a regular increase with increasing temperature, however, from 0.7 Å^2 at 23°C to 3.6 Å^2 at 440°C.

TABLE 6. Cation-Oxygen-Cation Angles for the Structure below the Transition (standard errors in parentheses)

	23°C	200°C	335°C	440°C
Al(1)-O(1)-Si(1)	143.6(3)°	143.4(4)°	143.6(5)°	143.7(5)°
Al(1)-O(2)-Si(2)	146.9(4)	146.7(4)	147.5(5)	147.4(5)
Al(2)-O(3)-Si(1)	153.1(5)	154.3(6)	154.6(8)	153.3(8)
Al(2)-O(4)-Si(2)	149.6(4)	150.2(4)	151.3(5)	152.8(6)
Si(1)-O(3)-Li(2)	89.4(3)	89.1(4)	89.6(5)	89.4(5)
Al(1)-O(1)-Li(1)	90.4(3)	90.6(3)	90.4(3)	90.7(3)
Si(2)-O(4)-Li(3)	92.0(3)	92.1(3)	91.5(4)	91.3(4)
Si(2)-O(2)-Li(3)	93.1(3)	93.0(3)	93.1(4)	93.3(4)
Al(2)-O(4)-Li(3)	114.4(3)	113.8(4)	113.7(4)	112.1(5)
Al(2)-O(3)-Li(2)	117.5(4)	116.3(5)	115.6(6)	116.7(6)
Al(1)-O(2)-Li(3)	119.9(3)	120.3(3)	119.4(4)	119.2(4)
Si(1)-O(1)-Li(1)	125.9(3)	125.9(4)	125.6(4)	125.2(4)

For the crystal structure above the transition, interatomic distances involving the O atoms (Table 7) cannot be interpreted in detail since the oxygen position is an average for four separate oxygen atoms, each with slightly different positions. All cation–O and O–O distances are similar to those for the structure at low temperature, however. This further confirms that there is no significant change in the geometry of the framework at the transition. The isotropic temperature factors for all atoms (Table 3) show a significant increase over the values for equivalent atoms for the structure at 440°C. This is due to the fact that the isotropic temperature factors for the structure at 484 and 647°C are

TABLE 7. Interatomic Distances and Angles for the Structure at 484 and 647°C

	484°C	647°C
Li tetrahedron		
Li-O	2.04 Å	2.05 Å
O-O'	3.69	3.70
O-O''	2.49	2.49
O-O'''	3.68	3.69
Al tetrahedron		
Al-O	1.73	1.73
O-O'	2.86	2.87
O-O''	2.74	2.73
O-O'''	2.88	2.87
Si tetrahedron		
Si-O	1.61	1.61
O-O'	2.49	2.49
O-O''	2.68	2.68
O-O'''	2.69	2.69
Si-O-Al	149.7°	149.6°
Si-O-Li	91.6	91.7
Al-O-Li	116.9	116.7

in part a function of positional disorder due to the presence of split atoms.

Tscherry and Laves (1970) suggested that the transition which occurs with the apparent halving of the *a*-axes may in part be displacive in nature. Schulz and Tscherry (1972b) also interpret the transition as first order, from the viewpoint of the framework. They note that the structures below and above the transition are analogous to low- and high-quartz, respectively. They postulate the occurrence of displacements at the transition in β-eucryptite which are similar to those between low- and high-quartz. They also note that the Li distribution at high temperatures is required by symmetry to be different than that at room temperatures, and postulate that at high temperatures there is probably a random distribution of Li over all framework channel sites.

The results of the crystal structure refinements reported here, in combination with the results of the survey of intensity as a function of temperature, serve to define the nature of the transformation. First, as noted above, the form of the changes in both intensities and lattice parameters with temperature are inconsistent with the occurrence of a first order transition. Although the coordinates of the framework atoms do not displacively change at the transition, it is still possible that they shift continuously from their values at room temperature to the higher symmetry values above the transition temperature. However, as can be seen in Table 2, the coordinates of the Al, Si and O atoms show little change over the temperature range 23 to 440°C. Coordinates of pseudo-$a/2$ related atoms do not shift toward the average values required by the absence of reflections with h or $k = 2n + 1$.

The distribution of Li atoms does change as a function of temperature, however. At room temperature Li atoms are ordered in 1/2 of the four-fold coordinated sites in the four channels parallel to the *c*-axis. Li(1) occupies sites with $z = 1/6, 1/2, 5/6$ (coplanar with Al atoms) in the origin channel ($x = y = 0$). Li(2) and Li(3) occupy the other three channels on sites with $z = 0, 1/3, 2/3$ (coplanar with Si atoms). Difference Fourier syntheses and refinement of Li temperature factors were previously shown to indicate that Li occupies sites having $z = 0, 1/3, 2/3$ at temperatures above the transition. Furthermore, peaks in Fourier syntheses at 440°C, below the transformation, showed the presence of some disorder in Li positions, relative to the well-ordered distribution at room temperature. These relations are all consistent with the existence of a diffusive type of transformation involving Li. Li atoms in the origin channel having $z = 1/6, 1/2, 5/6$ shift to the alternative sites having $z = 0, 1/3, 2/3$ within the same channel.

The continuous decrease in the intensities of *a*-reflections with increasing temperature is due to two separate factors. First, the redistribution of Li atoms causes Li atoms to be translationally periodic with respect to the $a/2$ translation. Second, intensities decrease due to the normal increase in thermal motion of the framework atoms. Superstructure reflections of the *c*-type do not decrease in intensity as rapidly as the *a*-reflections, because they arise in part from the ordering of Al and Si. The evidence presented here indicates that the framework atoms retain the double-*a* periodicity to very high temperatures. Above 460°C, *a*-reflections are not extinct, but have intensities too weak to be observed. This is verified in part by the existence of split oxygen atoms in the high temperature structure and the fact that the refined position of a single oxygen atom at high temperatures is close to the position of the oxygen atom obtained by taking an average of the pseudo-$a/2$ translation-related oxygen positions for the low temperature structure.

In order to obtain independent data regarding the nature of change in structure as a function of temperature, DTA results were obtained. Figure 4 is a plot of these results. The material used for this analysis was obtained from the same batch from

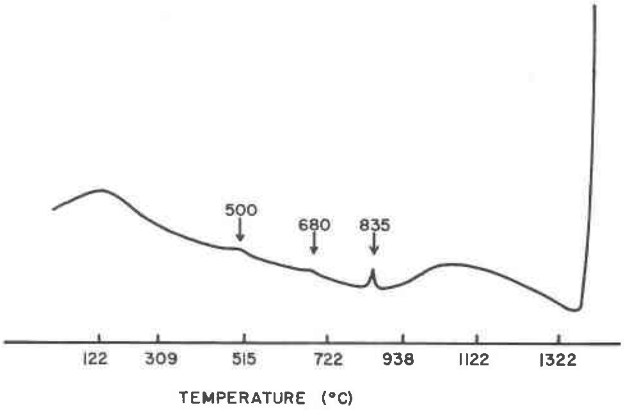

FIG. 4. DTA curve for β-eucryptite. The endotherm at 835°C probably corresponds to the melting of some impurity LiF. This peak has approximately one-fourth the area of that peak corresponding to the inversion in quartz, as observed in a separate curve.

which crystals had been selected for X-ray investigations. Although the crystals were carefully hand-sorted with the aid of a binocular microscope, small quantities of impurities were present, consisting principally of the flux used in the crystal synthesis. The DTA curve exhibits no significant endothermic peak at or near 460°C. Small, broad endothermic peaks are present at about 500 and 680°C, but these are orders of magnitude lower in area than the endotherm corresponding to the α-β quartz inversion. The small endotherm at about 835°C corresponds to the melting point of LiF, which was identified as an impurity phase by X-ray diffraction. These results thus provide separate confirmation of the lack of a first-order, displacive transformation in β-eucryptite, at or near 460°C.

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