

Anisotropic thermal expansion in silicates: A density functional study of β -eucryptite and related materials

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Linear response density functional calculations of the structures, phonon spectra, and thermal expansion have been performed for the hexagonal silicate β -eucryptite [β -LiAlSiO₄] and related materials, extending and refining earlier work using direct diagonalization of the dynamical matrix. The temperature (T) dependence of the lattice constants of β -eucryptite agrees well with measurements, including the minimum in $a(T)$ found at low T . Mg ions are predicted to occupy octahedral sites in Mg_{0.5}SiAlO₄, in agreement with neutron scattering data. We present calculations of the thermal expansion coefficients in β -quartz that are free of adjustable parameters, and we extend the earlier work to calculate the thermal expansion coefficients of the low- T form of β -eucryptite (84 atoms per unit cell).

I. INTRODUCTION

Glass ceramics in the LAS (Li₂O–Al₂O₃–SiO₂) system can achieve very low bulk thermal expansion.¹ Their thermal stability and resistance to thermal shock have led to many applications in domestic cookware, precision optical devices, turbine engine heat exchangers, and other areas.² The hexagonal β -eucryptite (LiAlSiO₄) (Ref. 3) is a prominent member of this family. Its thermal expansion coefficients are highly anisotropic⁴ ($\alpha_a \sim 7.26 \times 10^{-6}$ deg.⁻¹; $\alpha_c \sim -16.35 \times 10^{-6}$ deg.⁻¹),⁵ and the relationship $\alpha_c \approx -2\alpha_a$ suggests that the polycrystalline glass ceramics should have a low “average” volume thermal expansion. In fact, over a wide range of temperature (300 K < T < 1400 K) the contraction along the hexagonal c axis is approximately cancelled by expansion in the (001) plane, and β -eucryptite is the basis for most modern ceramic range tops.^{1,3} It also has a pronounced one-dimensional superionic conductivity and a reversible order-disorder structural phase transition at ~ 755 K.⁶ It is not surprising that it has been the subject of much study for many years.

The high-temperature structure of β -eucryptite (Fig. 1) is a lithium-stuffed derivative of β - or high-quartz,³ comprising parallel double helices of SiO₄ and AlO₄ tetrahedra. The alternation of layers containing Si and Al atoms leads to a doubling of the c axis of β -quartz. The one-dimensional channels parallel to this axis are occupied by Li⁺ ions, which compensate the charge imbalance of the Si⁴⁺ and Al³⁺ ions. Below the order-disorder transition the Li⁺ ions form a superstructure occupying sites in the Si and Al planes in the ratio 3:1.⁷ A recent electron diffraction and dark field transition electron microscopy study of β -eucryptite showed no indication of a structural collapse analogous to the β - α transition in quartz (846 K),⁸ and this was seen as evidence that the framework has true hexagonal symmetry. The structural phase transition at 755 K arises from positional order-disorder of the Li ions.

A survey of the mechanisms involved in the highly anisotropic and anomalous thermal expansion in β -eucryptite is given in Ref. 9. They include elastic effects associated with the interconnected helices,^{7,10} the progressive disorder of the Li ions with increasing T , which favors increased occupancy of the octahedrally coordinated positions,¹¹ and electrostatic repulsion between the channel ions (Li) and the Al and Si cations.³ Neutron and x-ray (synchrotron radiation) diffraction work in the range 20 K < T < 873 K has been performed on (a) ordered β -eucryptite and (b) a sample synthesized with complete Al/Si long-range disorder.⁵ The structure of the latter is almost identical to that of β -quartz,

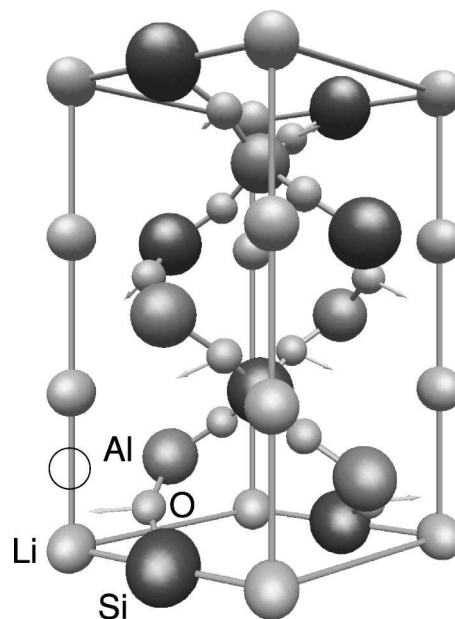


FIG. 1. “Average” structure of β -LiAlSiO₄ and the eigenvectors for a typical bending phonon mode. The circle shows the position of Li ions in a second local minimum in the energy surface.

and its thermal expansion is much more isotropic than in ordered β -eucryptite. Three interdependent processes could be identified: (1) Si/Al tetrahedral deformation, (2) Li positional disordering, and (3) tetrahedral tilting. It has been noted that specific mechanisms applied to β -eucryptite seem less applicable to the silica polymorphs.⁹

Recently we performed density functional (DF) calculations for different crystalline structures of β -eucryptite.¹² The structures are determined from minima in the energy surfaces, and phonon frequencies from total energy changes with changing atomic positions. The coefficients of thermal expansion can then be determined—within the framework of the quasiharmonic approximation—from the variation of these frequencies with unit cell parameters. The T dependence of the lattice constants a and c , calculated for the “average” or high- T structure, agreed well with new neutron diffraction measurements in the range $20 \text{ K} \leq T \leq 873 \text{ K}$. The anomalous behavior of the thermal expansion could be traced to the existence of phonons with negative Grüneisen parameters, and we speculated that the minimum in the $a(T)$ at low T could be related to the double-well nature of the energy surface along the Li chains.

In this paper we extend the calculations described in Ref. 12 in several ways. Using the methods of the previous paper, we calculate the phonon spectra and thermal expansion in the low- T structure of β -eucryptite (84 atoms per unit cell), and we calculate the same quantities for the average structure using the linear response (LR) method. This approach improves both the electronic structure and phonon calculations by incorporating additional points in the Brillouin zone (BZ), and it has provided a reliable description of phonon spectra in materials with relatively simple structures.¹³ We describe DF calculations for materials with related structures, $\text{Mg}_{0.5}\text{AlSiO}_4$ and β -quartz. The results for $\text{Mg}_{0.5}\text{AlSiO}_4$ are compared with new neutron diffraction data, and the comparison between β -quartz and β -eucryptite allows us to comment on other theoretical work in this area. In Sec. II we outline the methods of calculation we use, in Sec. III we present the results for the materials mentioned above, and our concluding remarks are given in Sec. IV.

II. METHODS OF CALCULATION

A. Structures

The DF calculations were performed with the local density (LD) approximation for the exchange-correlation energy, a plane wave basis with a kinetic energy cutoff of 70 Ry, and nonlocal pseudopotentials to represent the electron-ion interactions.^{14,15} Details of the structural optimization of both the high- T (“average,” 21 atoms per unit cell, Fig. 1) and low- T (twelve formula units—84 atoms—per unit cell) structures are given in Ref. 12. Optimization is performed with respect to V and c/a ratio by allowing *all* internal degrees of freedom to relax, and the lattice constants of the hexagonal structures found agree well with the measured values.¹⁶ We have noted above that the phase transition between the two structures corresponds to a progressive disordering of the Li distribution as T increases.³

B. Thermal expansion

The thermal expansion of an anisotropic crystal with elastic deformation u_i , temperature T and volume V can be determined from the free energy¹⁷

$$F(u_i, T) = E(0, 0) + \frac{1}{2} V \sum_{i,j} B_{ij} u_i u_j + F^*(u_i, T),$$

where $E(0, 0)$ is the ground state total energy, V is the volume, B_{ij} the elastic compliances, and F^* is temperature dependent. In the absence of stresses, the equilibrium values of u_i can be determined from $\partial F / \partial u_i = 0$, yielding the thermal expansion coefficients $\alpha_i = du_i / dT = \sum_j (B^{-1})_{ij} \partial S / \partial u_i$, where the entropy $S = -\partial F^* / \partial T$.

For uniaxial crystals we define independent volume and tetragonal deformations $du_1 = d \ln V$ and $du_2 = d \ln(c/a)$. If the vibrations are assumed to be harmonic but with deformation-dependent frequencies (the quasiharmonic approximation), the anisotropic thermal expansion can be written¹⁷

$$\alpha_a(T) = \frac{1}{3BB_{22}} [(B_{22} + B_{12}) \gamma_1 - (B_{11} + B_{12}) \gamma_2],$$

$$\alpha_c(T) = \frac{1}{3BB_{22}} [(B_{22} - 2B_{12}) \gamma_1 + (2B_{11} - B_{12}) \gamma_2]. \quad (1)$$

The bulk modulus B and the compliances B_{ij} can be calculated from the energy surface at $T=0$, and the results agree well with measured values for β -eucryptite.¹² The temperature-dependence arises from the Grüneisen parameters $\gamma_i (i=1, 2)$:

$$\gamma_i(T) = - \sum_{\mathbf{q}, \mathbf{n}} \frac{\partial \omega_n(\mathbf{q})}{\partial u_i} \frac{\partial n_B[\omega_n(\mathbf{q})]}{\partial T}. \quad (2)$$

Here $n_B(\omega) = [\exp(\hbar\omega/k_B T) - 1]^{-1}$ is the Bose-Einstein function, and $\omega_j(\mathbf{q})$ are the frequencies of the j th branch of the phonon spectrum with wave vector \mathbf{q} . The phonon contribution to thermal expansion can then be found by calculating all phonon frequencies and their derivatives with respect to V and c/a :

$$\frac{\partial \omega_n}{\partial u_i} = \frac{1}{2\omega_n} \sum_{\alpha\beta} C_{\alpha n}^* \frac{\partial D_{\alpha\beta}}{\partial u_i} C_{\beta n}. \quad (3)$$

C. Phonon spectra

Density functional calculations of phonon spectra are numerically demanding, and earlier calculations of thermal expansion have been limited to relatively simple systems with one or two atoms in the unit cell. The structures of β -eucryptite are complex (four elements, 21 or 84 atoms in the unit cell), and we require numerically accurate values of the phonon frequencies *and* their derivatives with respect to the (highly anisotropic) distortions.

We have used two methods to determine the phonon frequencies. The first (used in Ref. 12) determines them from the eigenvalues of the dynamical matrix $(\mathbf{D} - \omega^2 \mathbf{I})\mathbf{C} = 0$, where $D_{\alpha\beta} = (M_\alpha M_\beta)^{-1/2} (\partial^2 E / \partial R_\alpha \partial R_\beta)$ and \mathbf{I} is the unit matrix. The energy E is calculated using a single point (\mathbf{k}

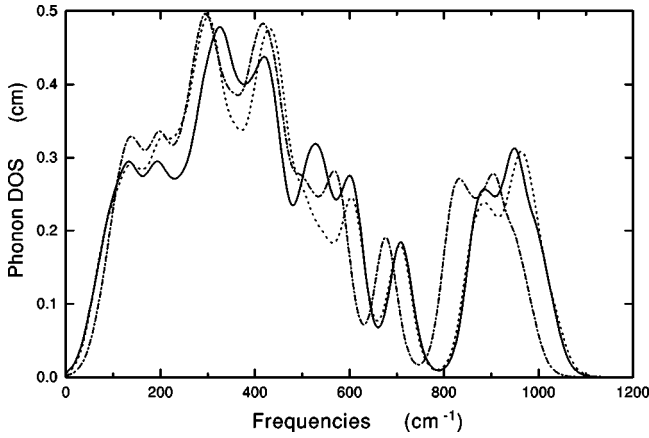


FIG. 2. Dependence of phonon spectrum of β -eucryptite on changes in volume V and c/a ratio. Full curve: equilibrium structure $[V_0, (c/a)_0]$, dashed curve: $V = 1.03 V_0$; dot-dashed curve: $c/a = 0.95(c/a)_0$. Each mode is broadened by 15 cm^{-1} .

$= 0$) in the BZ, and the partial derivatives of E with respect to variations in the ionic coordinates R_α are determined by finite differences. The dynamical matrix \mathbf{D} is diagonalized by a standard routine.

The harmonic lattice dynamics of a perfect crystal can also be derived within the framework of static linear response (LR) theory, since the lattice distortion corresponding to a given phonon can be considered as a static perturbation acting on the electrons in the crystal. For an external potential acting on the electrons one can use the Hellmann-Feynman theorem to derive expressions for the second derivatives of the ground state energy. This has been implemented within the DF framework¹³ and is used here. A similar scheme has been used by Gonze *et al.*^{18,19} to calculate the phonon spectra of α -quartz and stishovite, as well as related quantities such as the constant volume specific heat, the entropy, and the atomic temperature factors. The agreement with experiment was very satisfactory. The LR calculations for β -eucryptite and β -quartz are performed using four \mathbf{k} points in the respective Brillouin zones, and the phonons are calculated for the corresponding \mathbf{q} points.^{13,20}

III. RESULTS

A. β -Eucryptite

We have calculated the phonon spectra for the high- T and low- T structures of β -eucryptite, with 3 and 12 formula units, respectively. The spectra calculated for the high- T structure using the linear response formalism and four \mathbf{k} points are shown in Fig. 2 for changes in both c/a ratio and volume V . The phonon density of states shows pronounced features from 150–700 and 900–1000 cm^{-1} . The picture is the same as found in our earlier calculations. The c/a Grüneisen parameters (γ_2) for modes around 400 cm^{-1} (“bending” Si-O and Al-O modes, eigenvectors of a typical phonon in this frequency range are shown in Fig. 1) are large and negative, and this is also true for some modes around 700 cm^{-1} . On the other hand, the highest energy phonons (“stretching” Si-O and Al-O modes) have normal (positive) Grüneisen parameters, and the frequencies increase when the structure is compressed.

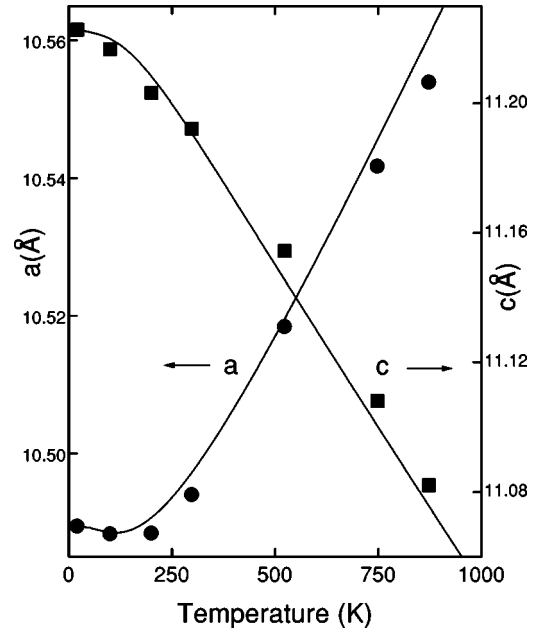


FIG. 3. Temperature dependence of lattice constants a (left scale, experiment: circles) and c (right scale, experiment: squares) in β -eucryptite (LR calculations). The theoretical lattice constants at $T=0$ are set equal to the experimental values.

The subtle cancellation of the contributions to thermal expansion of phonons up to 700 and around 900 cm^{-1} results in a small average volume expansion. Since $|B_{11}\gamma_2| > |B_{22}\gamma_1|$ and all combinations of elastic constants in the brackets of Eq. (1) are positive, α_a and α_c have opposite signs. The calculated temperature dependence of the lattice constants a and c agree well with experiment (Fig. 3). There is some scatter in the experimental estimates of α_a and α_c , so that the values calculated for the high- T structure ($12.0 \times 10^{-6} \text{ deg}^{-1}$, $-17.5 \times 10^{-6} \text{ deg}^{-1}$, respectively) are satisfactory.²¹

The differences between Fig. 3 and the results of our earlier calculation¹² reflect the differences in the phonon frequencies, and we compare spectra using both methods in Fig. 4. There are obvious similarities between the spectra for the high- T structure of β -eucryptite calculated by the two methods, but the LR calculations lead to lower frequencies, particularly in the regions 100–300 and 800–900 cm^{-1} . The lower frame of Fig. 3 shows distinct differences between the phonon spectra calculated with the CPMD method for the low- T and high- T structures of β -eucryptite. The low- T structure shows, in particular, a peak at $\sim 150 \text{ K}$ that is absent in the high- T structure.

The neutron diffraction data in Ref. 12 showed an unusual minimum in the lattice constant a as a function of T . Our earlier calculations¹² showed that the Li atoms formed a two-level system, with the second minimum in the plane of the Al atoms (see Fig. 1) $\sim 0.1 \text{ eV}$ per Li atom above the more stable form and lattice constants a and c are both approximately 1% shorter. Increasing T would favor population of the compacter structure, leading to the observed effect in $a(T)$.¹² This mechanism is similar to that proposed by Schulz in this material,¹¹ and it is reminiscent of the Fe-Ni alloy invar, where the two-level system comprises a com-

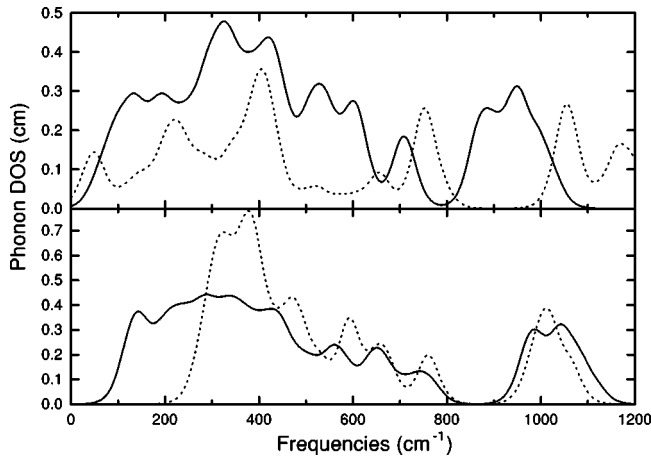


FIG. 4. Phonon spectra. Lower frame: CPMD results for the low- T (full curve) and high- T (dotted curve) structures; Upper frame: LR results for the high- T structures of β -eucryptite (full curve) and β -quartz (dotted curve).

pact, nonmagnetic state and the magnetic ground state. We noted previously¹² that the role of phonons with $\mathbf{q} \neq 0$ remained to be investigated.

In Fig. 5 we compare the measured changes of a with increasing T (circles) with the results of different calculations. The effect of assuming different structures can be seen by comparing the results for the CPMD method (direct diagonalization of the dynamical matrix) for the average (high- T) and low- T structures (dashed and dot-dashed curves, respectively). The latter shows a pronounced minimum in fair agreement with experiment. A weak minimum can be seen in the results of the linear response calculations for the average structure (full curve). It is evident that both an improved

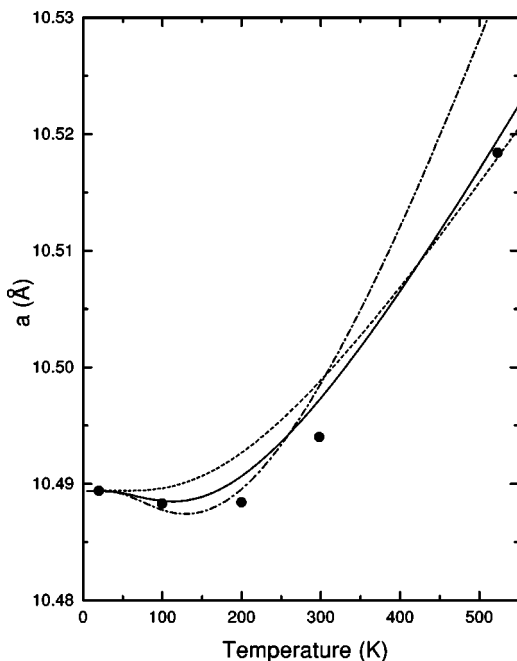


FIG. 5. Temperature dependence of lattice constant a in β -eucryptite (\AA). Circles: from neutron diffraction data (Ref. 12); Dashed curve: CPMD results for high- T structure (Ref. 12); Dot-dashed curve: CPMD calculations for low- T structure; Full curve: LR calculations for high- T structure.

description of the phonons and the assumption of the low- T structure tend to improve agreement between theory and experiment. An invarlike mechanism for the two-level system of the Li ions would enhance this minimum, but it is not necessary to explain its existence.

B. β -quartz

Silica comprises a network of neutral SiO_4 tetrahedra, and the negative thermal expansion coefficient originates in the low-frequency phonons that are responsible for the α - β phase transition. For β -quartz there are low-energy rigid unit modes (RUM's) (Ref. 22) for \mathbf{q} at high symmetry points in the BZ, in the (001) plane and along the [001] directions, and the soft mode of the displacive transition (at $\mathbf{q}=0$) has a low frequency ($\sim 30 \text{ cm}^{-1}$) even for $T \sim 1200 \text{ K}$.²³ The Grüneisen parameters γ_i [Eq. (2) and (3)] have approximately $1/\omega_n^2$ dependences at high T , and the presence of low-frequency phonons and their spread across the BZ mean that they dominate γ_i in β -quartz. The corresponding modes in β -eucryptite have higher frequencies ($> 100 \text{ cm}^{-1}$), and *all* contribute to thermal expansion. This is an essential difference between β -eucryptite and β -quartz. We return to this point below.

The negative thermal expansion in β -quartz has been described by Welche *et al.*²⁴ as a geometrical effect due to the rotation of the tetrahedra, which fold together as they rotate. These authors calculated the phonon frequencies using the pair-potential parameters of Tsuneyuki *et al.*²⁵ Theoretical studies of β -quartz are complicated by the instability of its structure below 846 K, and the energy surfaces leading to the phonon frequencies are calculated at $T=0$. Calculations of thermal expansion are complicated by the high anisotropy of the soft mode, particularly close to the transition temperature, but they can be performed by applying a negative pressure such that all phonon frequencies are real and the experimental frequency of the soft mode is reproduced.²⁴ We have adopted a similar strategy in β -quartz, where a negative pressure of 40 kbar (corresponding to a volume expansion of approximately 5%) has been applied.

Measurements of the changes of the lattice constants of quartz as T is increased through the α - β transition have been performed using x-ray^{26,27} and neutron diffraction.²⁸ The changes in the lattice constants a and c above the transition are very small, and the neutron diffraction data²⁸ indicate that α_c is negative ($\sim -2 \times 10^{-6} \text{ deg}^{-1}$), with α_a being almost vanishingly small. The present results are shown in Fig. 6, where we also show those for β -eucryptite. For temperatures above the α - β -transition, the thermal expansion coefficients ($\alpha_a = -6.1 \times 10^{-6} \text{ deg}^{-1}$, $\alpha_c = -7.5 \times 10^{-6} \text{ deg}^{-1}$) are negative and approximately half of the estimates of Welche *et al.*²⁴ using a classical force field. Additional measurements of the T dependence of the lattice parameters in β -quartz, such as by powder neutron diffraction, would be very interesting.

C. Energy surface of $\text{Mg}_{0.5}\text{AlSiO}_4$

The structures of β -quartz and β -eucryptite are closely related, but the presence of channel ions (Li) and alternating layers with different charges in β -eucryptite lead to distinc-

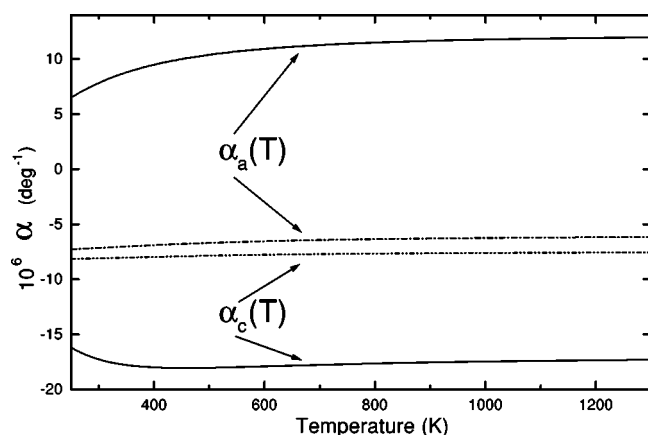


FIG. 6. Temperature dependence of the thermal expansion coefficients α_a , α_c of β -eucryptite (full curves) and β -quartz (dot-dashed curves). The α - β transition temperature is 846 K.

tive differences in the phonon spectra and thermal expansion properties. The role of channel ions can be investigated by studying systems where the monovalent Li ions are replaced by other elements, e.g., half the number of the divalent elements Mg or Zn. Channel sites with octahedral oxygen coordination are not occupied by Li ions at room T , but they are occupied by Mg ions in Mg-alumino silicates with high-quartz structures.²⁹ Thermal expansion has been measured in two analogs of β -eucryptite containing group 12 ions, $\text{Mg}_{0.5}\text{AlSiO}_4$ and $\text{Zn}_{0.5}\text{AlSiO}_4$,³⁰ and powder neutron diffraction data have been analyzed for the former.³¹ The latter show that both lattice constants a and c increase with increasing T , so that the volume thermal expansion coefficient is positive in $\text{Mg}_{0.5}\text{AlSiO}_4$. Difference electron density maps show also that Mg cations occupy octahedral channel sites, so that there are substantial differences between this material and β -eucryptite.

We know of no published calculations or x-ray diffraction studies of these materials, and we have performed DF calculations for the structures of $\text{Mg}_{0.5}\text{AlSiO}_4$. The variation of the energy with the displacement of three Mg atoms per unit cell are compared in Fig. 7 with the corresponding results for Li in β -eucryptite.¹² Mg ions occupy only octahedral sites in the stuffed aluminosilicate $\text{MgAl}_2\text{Si}_3\text{O}_{10}$, and the absence of tetrahedral occupancy has been related to the fact that the ionic radius is larger in Mg than in Li.²⁹ This also appears to be the case in $\text{Mg}_{0.5}\text{AlSiO}_4$, as the present calculations do not show the second minimum in the energy surface found for the diffusion of the channel ions (Li) in β -eucryptite (Fig. 7). Calculations of the phonon spectra using LR theory and several \mathbf{k} points in the BZ presently place excessive demands on computing resources in a system of this size (42 atoms per unit cell).

IV. DISCUSSION AND CONCLUDING REMARKS

The quartz polymorphs of silica are technologically important, and their stuffed aluminosilicate derivatives are amongst the most important glass ceramics. These materials can have positive or negative thermal expansion coefficients, and β -eucryptite (LiAlSiO_4) is remarkable in having a very small volume expansion coefficient over a large temperature

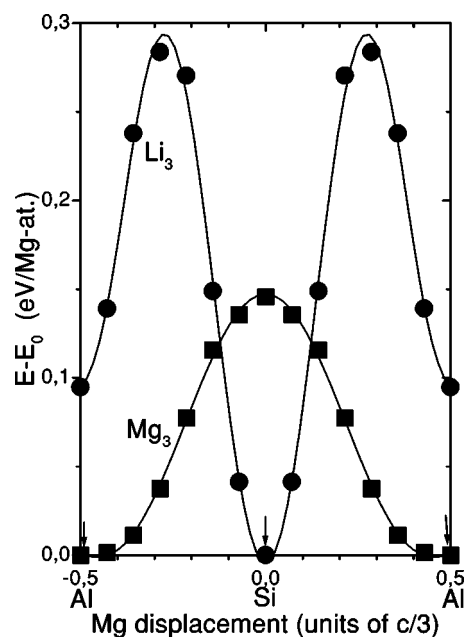


FIG. 7. Energy barrier for diffusion of Li chains in β -eucryptite (full circles) and Mg in $\text{Mg}_{0.5}\text{AlSiO}_4$ (squares). A displacement of 0.5 (in units of $c/3$) corresponds to half the distance between two Si layers.

range. We have performed density functional calculations on this and related materials (β -quartz and $\text{Mg}_{0.5}\text{AlSiO}_4$) to help clarify the mechanisms involved. The thermal expansion coefficients have been determined from the changes in the phonon frequencies on varying the lattice constants, and the use of DF calculations avoids the parametrization of the forces that is often necessary.

There are several encouraging results of wider interest. The first is that phonon frequencies *can* be calculated for very complicated structures (with four elements and up to 84 atoms in the unit cell) using a method that is free of adjustable parameters. The numerical demands of the calculations are very high, but both the evaluation and diagonalization of the dynamical matrix (Ref. 15) and the use of LR theory (Ref. 13) lead to phonon frequencies and their derivatives with respect to unit cell changes that provide a consistent picture of thermal expansion in β -eucryptite. Second, the use of linear response theory has advantages over direct diagonalization of the dynamical matrix in terms of both numerical stability and reliability. At the present time the numerical demands of the former have restricted its use to systems with up to 21 atoms in the unit cell, and our results for more complicated structures ($\text{Mg}_{0.5}\text{AlSiO}_4$, low- T form of β -eucryptite) are restricted to the latter.

Both methods of calculation we use provide a very good overall description of the measured changes in the lattice constants of β -eucryptite, with a negative value of α_c that is approximately twice as large as the positive α_a . The thermal expansions calculated for the low- T and high- T structures are generally very similar, although the details differ at low temperatures. LR theory leads to a weak minimum in $a(T)$ at low T if the average structure is assumed, and CPMD calculations for the much more complex low- T structure lead to a similar effect. Although this minimum could be understood in terms of a two-level system where the Li ions have tetra-

hedral or octahedral coordination,¹² it does not need to be invoked in the light of the present results. Recent experiments on β -eucryptite⁵ found no evidence for Li occupancy of octahedral sites, but the present calculations predict that the channel ions in $\text{Mg}_{0.5}\text{AlSiO}_4$ occupy *only* the octahedral sites. This is consistent with very recent powder neutron diffraction measurements,³¹ and a two-level description would be inappropriate in this case.

A variety of mechanisms has been invoked to explain the small thermal expansion coefficients in β -eucryptite and related LAS glass ceramics, and the recent experimental work on ordered and disordered β -eucryptite⁵ has emphasized the interrelationship of the possible mechanisms and the difficulty of identifying a single cause. The present calculations, which show that the effect arises from the subtle cancellation of positive and negative contributions, support this assessment. A recent theory of the negative contribution to thermal expansion in framework structures²⁴ showed that it could be viewed as a geometrical effect due to the rotation of the rigid structural units, which fold together as they vibrate. The most important finding was that this contribution extends throughout the phonon spectrum.

This theory has an appealing simplicity and provides a satisfactory description of thermal expansion in β -quartz. Our calculations show, however, that β -eucryptite and β -quartz are quite different. The negative Grüneisen parameters in the c -direction of the former arise from Si-O and Al-O bending modes (see Fig. 1) with energies well above 100 cm^{-1} , much higher in energy than the soft modes responsible for the negative coefficient of thermal expansion (and the structural phase transition) in β -quartz. The higher

frequencies in β -eucryptite reflect the electrostatic repulsion between ions in the system and the presence of Al/Si and Li positional ordering.

Additional experimental information in two areas would be very interesting: First, we know of no measurements of phonon frequencies in β -eucryptite, and such data would provide a valuable test of the present calculations. Second, precision measurements of the (very small) thermal expansion in quartz above the transition temperature would also be very useful. Finally, the calculated energy surfaces should provide a useful and consistent data base for generating or refining the parameters of a classical force field that could be applied to more complex silicate systems. Our first attempts in this direction have been complicated by the structural complexity and the small energy differences involved in processes such as channel ion diffusion, but further work is planned.

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²¹The thermal expansion coefficients calculated for the low- T structure using the CPMD method are $\alpha_a \sim 9.9 \times 10^{-6}\text{ deg}^{-1}$; and $\alpha_c \sim -12.5 \times 10^{-6}\text{ deg}^{-1}$.

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