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Anatomy of a structural phase transition: theoretical analysis of the displacive phase transition in quartz and other silicates

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Abstract A theoretical analysis and computer modelling of quartz gives a picture of the α–β phase transition in terms that would appear to be widely applicable to other silicate framework structures. The picture is based upon the fact that the structure of the β-phase can distort to the α form through the rotations of the SiO_4 tetrahedra without necessitating any distortions of the individual tetrahedra. A simple model based upon this premise and augmented by lattice energy calculations of the ordering potential gives a value for the phase transition temperature that is in semi-quantitative agreement with experiment. The reasons for the success of this model are then explored using a full anharmonic lattice dynamics calculation of the phase transition using renormalised phonon theory, highlighting the particular significance of the soft phonon branch compared to all the other phonon branches. The basic picture also explains the variation of the transition temperature with cation concentration in other aluminosilicates, and gives further insight into the validity of the mean-field description in these phase transitions.

Key words: Quartz · Phase transition · Rigid unit modes

Introduction

The study of structural phase transitions extends back more than a century to the first studies of the displacive phase transition in quartz (see Dolino 1990). Since that time, refined experimental studies and theoretical initiatives have shown that there is a rich diversity of unexpected behaviour associated with structural phase transitions. For example, over the past decade it has been appreciated that the classical α–β phase transition in quartz is really two separate phase transitions, with a stable intermediate incommensurate phase that exists over a temperature range of 1.5 K (Dolino 1990). The soft mode model developed in the 1960s has provided a general mechanism for displacive phase transitions. Much of the later experimental and theoretical work on structural phase transitions, as summarized in the reviews of Bruce and Cowley (1981) and Dove (1997a, b), has been concerned with what happens at temperatures close to the transition, the so-called "critical-point phenomena".

Despite these decades of work we can come back to quartz and still ask some fundamental questions about the α–β phase transition that have some bearing on many phase transitions we encounter in framework aluminosilicates. For example, why does the phase transition occur at all? If we start in the high temperature β-phase, why on cooling will we get to a point where the structure will want to start buckling? There is a viewpoint that the β phase is no more than a disordered array of small domains of the α form. This view has been countered by recent experiments (Salje et al. 1992), but even so, there has been no attempt to provide a quantitative theory for the domain viewpoint. Then we can ask what determines the size of the transition temperature T_c? In general we might simply argue that the interatomic potentials work that way, and indeed a big calculation would doubtless get the right answer. However, many components of such a calculation will be irrelevant, so our aim is to determine the *fundamental* factors that determine the value of T_c. Furthermore, in systems that have simple solid solutions, such as the alkali feldspars, $K_xNa_{1-x}AlSi_3O_8$, and the leucite series, (K,Rb,Cs)$AlSi_2O_6$ (Palmer et al. 1997), the transition temperature is a function of cation concentration. It is found in these examples that the larger the average size of the cation site the lower is the size of T_c. One might have argued that the opposite could be expected, because the larger cations cations stiffen the structure and consequently may require greater thermal motion to distort it. Finally, we also need to consider how close to the soft mode limit these phase transitions are, and in conse-

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quence explain why Landau theory appears to provide such a good description of the phase transitions in these materials.

In order to tackle these issues we are going to focus mainly on quartz, and make use of a simple model appropriate for any framework silicate (or aluminosilicate) crystal that was first proposed by Grimm and Dorner (1975). The fundamental idea is that the displacive phase transition occurs as the framework of connected SiO_4 tetrahedra buckles by rotations and translations of the tetrahedra, which do not themselves distort significantly. This model was taken a significant step forward by the work of Vallade and coworkers (Vallade et al. 1992; Dolino et al. 1992; Berge et al. 1986), who showed that this simple model can also account naturally for the incommensurate phase in quartz. These workers showed that the soft mode that drives the phase transitions in quartz can propagate as a phonon that moves the SiO_4 tetrahedra as rigid units. They also showed that these phonons, the so-called Rigid Unit Modes (RUMs) (Dove et al. 1991, 1992, 1997b; Giddy et al. 1993; Hammonds et al. 1996), occur for a number of wave vectors in the Brillouin zone, and not only at the wave vector of the soft mode. We have shown that the existence of rigid unit modes in any framework silicate can have a number of other important implications (Dove et al. 1991, 1992; Hammonds et al. 1996), which we develop quantitatively in this paper.

The first stage is to examine the essential physical effects involved in RUM rotations of stiff tetrahedra and reduce these to a few variables and parameters. An expression for the crystal energy in terms of these parameters is shown to enable a mapping of a Rigid Unit structure onto a simple model for displacive phase transitions. It is seen that the phase transition temperature calculated using the simple model is remarkably close to the true value and the reasons for this are examined in subsequent sections. The importance of the maximum rotation angle of the SiO_4 and AlO_4 tetrahedral units of aluminosilicates emerges from this analysis, and the theory is further corroborated through results from alkali feldspars. Finally, as seen above, the crucial role played by the stiffness of the tetrahedral units is shown to cause several framework aluminosilicates to fall within the displacive (soft mode) limit of phase transitions and subsequently to follow the simplest form of Landau theory very closely.

A model Rigid Unit system

Before examining α–β phase transition in quartz we formulate a simple model of a displacive phase transition based upon physical principles alone and involving stiff molecular units at each site. This model provides great insights into the important factors dictating the nature of these transitions and opens the way for the further investigations of the rest of the paper. We begin by considering a pair of SiO_4 units joined by a common oxygen atom within a framework crystal structure of such units. Rotations of both units in the same direction will result in distortions of the tetrahedra since they must maintain their linkage. RUM type rotations, however, preserve the tetrahedra and their energy cost is zero to first order. We label the rotations of a pair of adjacent tetrahedra about a common axis θ_i and θ_j, using the convention that equivalent rotations of neighbouring units are assigned opposite signs (this may appear to be an odd convention, but it has the merit that it gives us a final result that has an identical appearence to another popular simple model of a phase transition). With this convention, a Rigid Unit Mode type rotation is such that $\theta_i=\theta_j$. The potential energy expression associated with a general motion is given by

$$\frac{1}{2}L(\theta_i-\theta_j)^2, \tag{1}$$

where L is a large restoring force constant against deformation of the tetrahedra. In any structure which undergoes a displacive phase transition there must also be a force which encourages rotations of the stiff tetrahedral units to occur. An associated energy expression would be

$$-\frac{1}{2}S(\theta_i+\theta_j)^2, \tag{2}$$

where S is a small force constant driving the rotations. The origin of this force can be thought of as inter-tetrahedral and it is known that *intra*-tetrahedral force constants, such as L, are considerably larger (Dove et al. 1991; Heine et al. 1992). Hence S is small compared with L and the picture becomes one in which the tetrahedra are encouraged to rotate but, due to the large energy penalty incurred in deforming, they do so cooperatively so that $\theta_i=\theta_j$. The total contribution to the energy of the crystal from these terms (E) is equal to the sum over all individual sites

$$E=\sum_{i,j}^{nn}\frac{1}{2}L(\theta_i-\theta_j)^2-\frac{1}{2}S(\theta_i+\theta_j)^2 \tag{3}$$

$$=\sum_{i,j}^{nn}\frac{1}{2}(L-S)\left(\theta_i^2+\theta_j^2\right)-\sum_{i,j}^{nn}(L+S)\theta_i\theta_j \tag{4}$$

$$=\sum_{i}\frac{Z}{2}(L-S)\theta_i^2-\sum_{i,j}^{nn}(L+S)\theta_i\theta_j \tag{5}$$

where Z is the number of nearest neighbours of each tetrahedron (=4 for framework silicates). In addition to the two energy terms above, it is necessary to add a term representing the repulsion experienced when the tetrahedra rotate through large angles. Considering the rotation at site i only, this repulsive energy takes the form $\beta\theta_i^4$ where β is a constant which subsumes both the contribution of the fourth order anharmonic energy associated with tetrahedral distortions and also the steric repulsions. In the latter case, a quartic term has been chosen since (1) repulsive energies build up rapidly when atoms are close to one another so the exponent should be large, (2) the exponent must also be an even number given the rotational symmetry of the energy and (3) a quartic term is easily incorporated into the calculations that follow. The total energy for the crystal becomes

$$E_{tot}=\sum_{i}\left(\frac{Z}{2}(L-S)\theta_i^2+\beta\theta_i^4\right)-\sum_{i,j}^{nn}(L+S)\theta_i\theta_j. \tag{6}$$

Rearranging in terms of this expression gives

$$E_{tot}=\sum_{i}\left(-ZS\theta_i^2+\beta\theta_i^4\right)+\sum_{i,j}^{nn}\frac{(L+S)}{2}\left(\theta_i-\theta_j\right)^2, \tag{7}$$

This has the physically intuitive form of a much-studied model of a structural phase transition alluded to above, which is sometimes referred to as the 'ϕ^4 model' (see, for example, the review by Bruce and Cowley 1981). The energy consists of a double-well single-particle potential and a purely harmonic component bonding each of the sites with spring constant (L+S). Following Bruce and Cowley (1981), a useful measure of the extent to which the system is order-disorder or displacive in character is given by the ratio

$$s=\frac{E_1}{E_2}, \tag{8}$$

where E_1 is the energy change in taking the variable θ_i from a minimum of the single particle double well to the maximum at θ_i=0 and E_2 is the subsequent change in the harmonic energy of the bonds joining the sites under the assumption of a completely homogeneous ordered state i.e., all of the surrounding variables θ_j occupy the minimum of the double-well as does θ_i initially. In the model of Eq. 7 the two energies E_1 and E_2 are given by the following expressions

$$E_1=\frac{(ZS)^2}{4\beta},\quad E_2=\frac{Z^2S(L+S)}{4\beta}. \tag{9}$$

The displaciveness measure follows:

$$s=\frac{S}{(L+S)}. \tag{10}$$

In the limit $s\gg 1$, the model shows behaviour similar to a typical order-disorder phase transition. In this case the depth of the single-particle double-well potential is much larger than the bond energy increment associated with energy E_2. In the other limit, $s\ll 1$ (the so-called *displacive limit*), where the depth of the single-particle double-well potential is much smaller than the energy E_2, the model has many features found in typical displacive phase transitions, such as underdamped soft modes. As mentioned, L is the large spring constant associated with high energy tetrahedral deformations and is considerably larger than S, which is loosely viewed as inter-tetrahedral. Therefore, $s\ll 1$ and the system is firmly at the displacive end of the spectrum. Since Rigid Unit systems map onto the ϕ^4 model we examine this model further in the next section.

A simple theory of structural phase transitions

Outline of the theory

The generalised model of that obtained in Eq. 7 states that each unit cell has one *relevant* structural variable, ϕ_i, which is most simply thought of as an atomic displacement, but which can be any other structural quantity, such as a rotation of a rigid body or a group of molecules. These variables represent the motions in each unit cell that *freeze in* as the temperature is reduced and the phase transition occurs. Therefore, when discussing real phase transitions in the context of this theoretical model, each on-site variable ϕ_i will have components corresponding to the eigenvector of the soft mode of the transition. The Hamiltonian $\mathcal{H}$ consists of three parts, a kinetic energy term, a single-particle double-well potential, and a harmonic nearest-neighbour interaction. A general form appears as follows:

$$\mathcal{H}=\frac{1}{2}m\sum_{i}\dot{\phi}_i^2+\sum_{i}\left(-\frac{\kappa_2}{2}\phi_i^2+\frac{\kappa_4}{4}\phi_i^4\right)+\frac{J}{2}\sum_{i,j}^{nn}\left(\phi_i-\phi_j\right)^2 \tag{11}$$

$$=\frac{1}{2}m\sum_{i}\dot{\phi}_i^2+\sum_{i}\left(-\frac{\kappa_2-ZJ}{2}\phi_i^2+\frac{\kappa_4}{4}\phi_i^4\right)-J\sum_{i,j}^{nn}\phi_i\phi_j \tag{12}$$

where κ_2 and κ_4 are the constants that define the single-particle potential, J is the constant for interactions between neighbours and Z is again the number of nearest neighbours. Comparing Eq. 7 and 11 it is seen that the mapping of the RUM model onto this simple theory can be effected if:

$$\begin{aligned}2ZS&\leftrightarrow\kappa_2,\\ 4\beta&\leftrightarrow\kappa_4,\\ (L+S)&\leftrightarrow J,\end{aligned} \tag{13}$$

and Z=4 for tetrahedral framework structures. The quantity s of Eq. 8 is given in the above case, by

$$s=\frac{\kappa_2}{2ZJ}. \tag{14}$$

If we define the normal mode coordinates $\phi_{\mathbf{k}}$:

$$\phi_{\mathbf{k}}=\sqrt{\frac{m}{N}}\sum_{j}\phi_j\exp\left(i\mathbf{k}\cdot\mathbf{R}_j\right), \tag{15}$$

we can write Eqs. 11 and 12 in the form:

$$\begin{aligned}\mathcal{H}=&\ \frac{1}{2}\sum_{\mathbf{k}}\dot{\phi}_{\mathbf{k}}\dot{\phi}_{-\mathbf{k}}+\frac{1}{2m}\sum_{\mathbf{k}}(J_{\mathbf{k}}-\kappa_2)\phi_{\mathbf{k}}\phi_{-\mathbf{k}}\\ &+\frac{\kappa_4}{4m^2N}\sum_{\mathbf{k}\cdots\mathbf{k}'''}\phi_{\mathbf{k}}\phi_{\mathbf{k}'}\phi_{\mathbf{k}''}\phi_{\mathbf{k}'''}\Delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}''+\mathbf{k}''')\end{aligned} \tag{16}$$

where

$$J_{\mathbf{k}}=\frac{1}{N}\sum_{i,j}^{nn}J\left(1-\exp\left(i\mathbf{k}\cdot\left(\mathbf{R}_j-\mathbf{R}_i\right)\right)\right) \tag{17}$$

and

$$\Delta(\mathbf{k}+\mathbf{k}'+\mathbf{k}''+\mathbf{k}''') = \begin{cases} 1 & \text{if } \mathbf{k}+\mathbf{k}'+\mathbf{k}''+\mathbf{k}''' = \text{a reciprocal lattice vector} \\ 0 & \text{otherwise.} \end{cases} \quad (18)$$

From renormalised phonon theory (e.g. Dove 1997a) we find

$$T_c = \frac{\kappa_2}{3k_B\kappa_4}\left(\frac{1}{N}\sum_{\mathbf{k}} J_{\mathbf{k}}^{-1}\right)^{-1} = \frac{\kappa_2 \tilde{J}}{3k_B\kappa_4}, \quad (19)$$

where $\tilde{J}$ is defined as an average squared frequency (multiplied my the constant m) over the phonon branch and is calculated by averaging the funciton $1/J_{\mathbf{k}}$ over the dispersion surface. For many framework silicates the existence of points, lines and planes of RUMs causes the phonon dispersion surface frequently to exhibit extremely low lying regions which correspond to the very low frequencies of these modes. It is essential to take the specific system geometry, and hence the RUMs, into account when averaging $J_{\mathbf{k}}$ over the dispersion surface and the section on calculation of T_c for quartz outlines how this is done for the case of quartz.

The canonical model of a phase transition gives us an important physical interpretation of the transition temperature as given by Eq. 19. We note that the ratio κ_2/κ_4 is equal to the squared maximum distortion at zero temperature, which we write as Φ_0^2. Thus we have

$$3k_B T_c = \tilde{J}\Phi_0^2. \quad (20)$$

There are just three factors involved in the value of T_c. The first is the stiffness of the tetrahedra given by the constant J (which is equal to the sum of the two stiffness (L+S) in Eq. 13 but we have established that $L \gg S$). The second is the geometric factor specific for any system and inherent in the calculation of $\tilde{J}$. The third is the value of Φ_0, which is determined by factors such as steric hindrance. In pure silicates such as quartz and cristobalite this is determined by the closest approach of nearest oxygen atoms. In aluminosilicates it is determined by the extent to which the framework can collapse around a cation in a cavity, and is thus determined by the size of the cation.

Test of the simple theory: application to the alkali feldspars

An illustration of the result obtained above is found in the displacive phase transitions of solid solutions. An example is the $C2/m - C\bar{1}$ phase transition in the alkali feldspar solid-solution series, $K_xNa_{1-x}AlSi_3O_8$. As the K content increases, the size of the maximum distortion is expected to decrease in proportion, as observed experimentally (Carpenter 1988). From Eq. 20 we expect the transition temperature to scale as the maximum distortion. In this specific phase transition, the order parameter varies as $\cos\alpha^*$, where α^* is the reciprocal unit-cell angle of the triclinic low-temperature phase. If $\cos^2\alpha_0^* \propto \Phi_0$ is the value at zero temperature, we expect that $T_c \propto \cos^2\alpha_0^*$. Data for both T_c and $\cos\alpha^*$ at T=300 K have been collected for a small number of samples and were obtained from the review by Carpenter (1988). The corresponding values of $\cos^2\alpha_0^*$ can be obtained by extrapolation from the experimental relationship that $\cos^2\alpha^* = \cos^2\alpha_0^*(T_c - T)/T_c$. In Fig. 1 we plot both T_c and $\cos^2\alpha_0^*$ as functions of K content, x. It can be seen that both lie on the same straight line, which confirms the theory and the remarkable fact that T_c essentially depends only upon the three factors listed above.

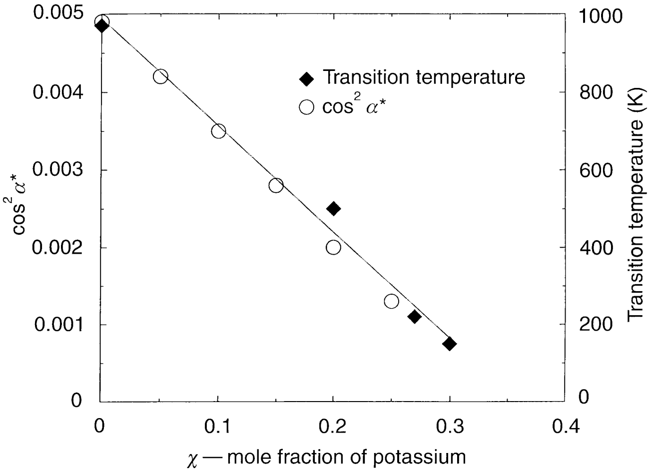

Fig. 1 Plots of the transition temperature and order parameter ($\cos^2\alpha^* \propto Q_0^2$) of the alkali feldspars as a function of K content (x)

The same explanation can also be applied to the substitution of alkali cations (K, Rb, Cs) in leucite. The larger ions reduce both the transition temperature for the cubic-tetragonal displacive phase transition, and the size of the tetragonal distortion consistent with this discussion (Hammonds et al. 1996).

Application of the simple theory to quartz

In this section we take the simple model further by attempting to use it to calculate specific quantities pertaining to the α–β phase transition in quartz. It should be stressed that the model, as outlined in the previous section, involves only one phonon branch whereas in true quartz there are 27 branches, so the theory represents a very significant simplification.

In order to perform calculations using Eq. 20 it is first necessary to obtain the coefficients κ_2 and κ_4 of the single-particle double-well potential. The known experimental value for T_c of 858 K then allows us to find a value for $\tilde{J}$ which can be compared with experimentally determined phonon frequencies in quartz.

Calculations of the ordering potential $V(Q)$

We have used the model silica potential of Tsuneyuki et al. (1988), which was obtained by parameterising the energy surfaces obtained from *ab initio* calculations of small clusters containing Si and O. These have been shown to give reasonable (albeit not perfect) structures and properties such as phonon dispersion curves and elastic properties, and Molecular Dynamics Simulations have shown that the potentials lead to the existence of the α–β phase transition at around the correct temperature (Tsuneyuki et al. 1990). We have found, moreover, that this model potential contains all the ingredients essential to predict the incommensurate phase transition (Tautz et al. 1990).

Here we present calculations of the ordering potential $V(Q)$, where Q is the order parameter of the α–β phase transition in quartz. A technical disucssion of the definition of the order parameter appropriate for this work is given in Appendix A. For each value of Q we have performed energy minimisation calculations to give the fully relaxed structure, which includes allowing the cell parameters to vary and allowing the SiO_4 tetrahedra to distort in response to the anisotropic local fields. The results of the calculations are given in Fig. 2. The curve represents the empirical function

$$V(Q) = 4V_0\left[-\frac{1}{2}\left(\frac{Q}{Q_0}\right)^2 + \frac{1}{4}\left(\frac{Q}{Q_0}\right)^4\right], \tag{21}$$

where V_0 is the energy difference between the minima and central maximum of the double well (1.542 $\mathrm{kJmol^{-1}}$) and Q_0 is equal to the order parameter value at the minima. If the energy is written as

$$V(Q) = -\frac{1}{2}\kappa_2 Q^2 + \frac{1}{4}\kappa_4 Q^4, \tag{22}$$

then $\pm Q_0 = \pm\sqrt{\kappa_2/\kappa_4}$. In principle $V(Q)$ can be extended to higher order in Q, but the agreement between the calculated and empirical data is sufficiently good in the region $|Q| \leq Q_0$ to not warrant additional terms.

There are three contributions to the function $V(Q)$: the long-range Coulomb interactions; the long-range $-r^{-6}$ interactions, which are principaly between the oxygen atoms; and the short-range repulsive interactions, of which the most important will be the steric repulsions that come into play as atoms get to close together when the structure distorts. We have decomposed $V(Q)$ into the separate components, which are drawn in Fig. 3. The important point about this figure is that it shows that the dominant contribution to the ordering potential is the long-range term, whereas the Coulomb interactions, which are presumably dominated by the nearest-neighbour oxygen-oxygen interaction, oppose ordering.

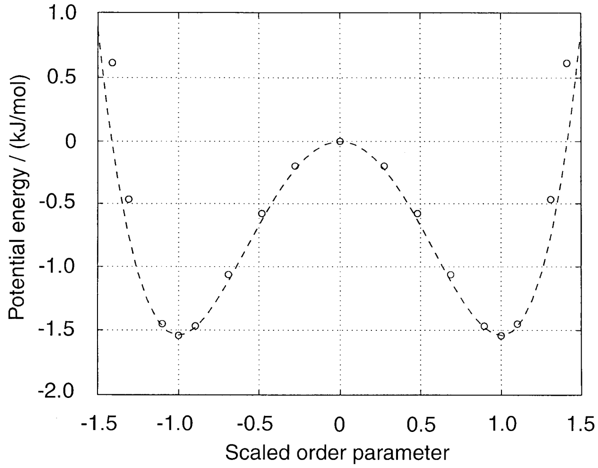

Fig. 2 The on site double-well potential calculated by relaxing the quartz structure for given values of the order parameter Q. The value of Q is set to ±1.0 at the minima of the double well. The units of energy are kJ/(mol of *atoms*)

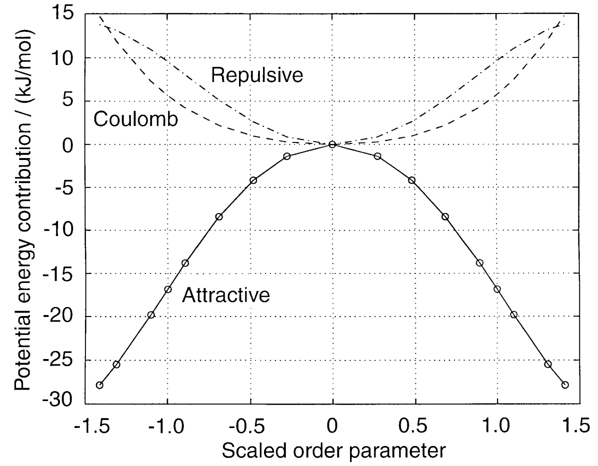

Fig. 3 Contributions to the double-well potential of Fig. 2 from Coulomb, attractive $-r^{-6}$ and short range repulsive energies

Calculation of T_c for quartz

It is straightforward to apply Eq. 19 to the case of quartz, but we need to make one important modification. The phonon dispersion surface given by Eq. 17 has a minimum at $\mathbf{k}=(0, 0, 0)$ with no valleys for particular directions in reciprocal space. However, we know from experimental results (Vallade et al. 1992) and from the RUM determination program CRUSH (Giddy et al. 1993; Hammonds et al. 1996) that for quartz the phonon dispersion surface that contains the soft mode has valleys along $\langle 1, 0, 0\rangle$ and $\langle 0, 0, 1\rangle$. We can model these assuming a phonon dispersion surface for quartz of the form:

$$J(\mathbf{k}) = J\left(\sin^2\left(\frac{\mathbf{k}\cdot\mathbf{a}}{2}\right) + \sin^2\left(\frac{\mathbf{k}\cdot\mathbf{b}}{2}\right) + \sin^2\left(\frac{\mathbf{k}\cdot(\mathbf{a}+\mathbf{b})}{2}\right) + \sin^2\left(\frac{\mathbf{k}\cdot\mathbf{c}}{2}\right)\right) \times (1-(1-d)f) \tag{23}$$

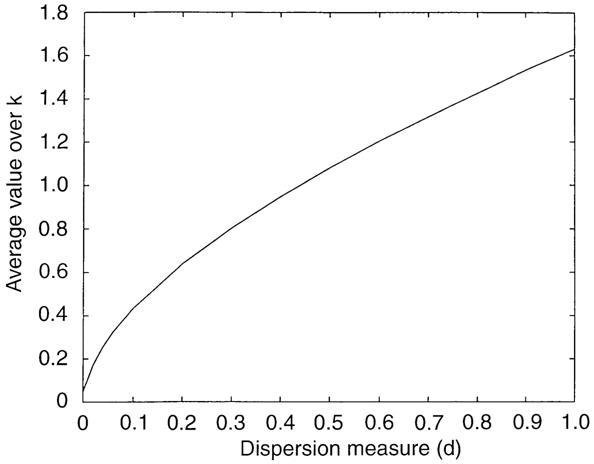

Fig. 4 The average value of the function $(J/J(\mathbf{k}))^{-1}$ over the Brillouin zone for various values of the dispersion measure d as outlined by Eq. 23. The parameter $\tilde{J}$ is obtained by multiplying this function by J for the correct value of d

where **a**, **b** and **c** are lattice vectors, and f and $0 \leq d \leq 1$ define the anisotropy of the phonon dispersion surface, with

$$f = \cos^2(3\Phi_{\mathbf{k}})\sin^2(\theta_{\mathbf{k}}) + \cos^2(\theta_{\mathbf{k}}). \tag{24}$$

Here $(\theta_{\mathbf{k}}, \Phi_{\mathbf{k}})$ are the polar coordinates of **k**, such that for the $\langle 1, 0, 0\rangle$ directions, $\theta_{\mathbf{k}}=\pi/2$ and $\Phi_{\mathbf{k}}=n\,\pi/3$ (this is correct for the region $0 \leq \Phi_{\mathbf{k}} \leq \pi/3$ which is the region sampled in the calculations which follow), and for $\langle 0, 0, 1\rangle$, $\theta_{\mathbf{k}}=0$. If the 'dispersion measure' d=1 there are no valleys corresponding to the positions of RUMs on the phonon dispersion surface, and in the other extreme when d=0 the phonon frequencies are zero for all wave vectors along the bottoms of the valleys. From experiment (see Appendix B) we find that $d \sim 0.1$.

The value for $\tilde{J}$ can be obtained from this new dispersion surface by summation over all **k** of the function $J/J(\mathbf{k})$ as shown in Eq. 19. We estimated this value by numerically integrating and finding the average value of $J/J(\mathbf{k})$ for different dispersion measures d. The results of these integrations are shown in Fig. 4 and $\tilde{J}$ itself may be obtained by multiplying the displaced values by J (the maximum angular frequency squared of the relevant phonon branch). We now have four parameters to use in our calculation of T_c. If we use our calculated values for κ_2 and κ_4, and assume that s=0.1, the experimental value of T_c=858 K implies a value for $\tilde{J}^{\frac{1}{2}}/(2\pi\sqrt{m})$ of 1.3 THz (where m is the correct mass for the mode ϕ_i as in Eq. 11). This corresponds to a typical frequency of a phonon lying on the soft mode's branch for quartz, so is a reasonable estimate. However, according to lattice dynamics data (see Appendix B) a better estimate for $\tilde{J}^{\frac{1}{2}}/(2\pi\sqrt{m})$ is 2.2 THz. It was not expected that the theory would give exactly correct results given the approximations inherent to it but it is important to note that a value for T_c is obtained that is in semi-quantitative agreement with the true value despite its simplicity. This is a very surprising result given that such a large number of vibrational modes have been left out the calculation. How is it possible that so simple a model can give us sensible results? We seek to answer this question by looking into a much more complete calculation of the transition temperature.

Model calculations of the $\alpha\beta$ phase transition in quartz

Our goal in this section is to understand the reasons why the simple ϕ^4 model works so well for the complicated quartz structure. To this end, the transition temperature of the α–β phase transition is calculated using a lattice dynamics program by including every phonon branch in a mean field approximation of T_c (see e.g. Dove 1997a). We will use the simplest form of anharmonic phonon theory within the mean-field approximation, and with the known problems of this approach we have effectively limited the expected accuracy of the calculation. The analysis of the relevant parameters contributing to T_c reveals why the reduced model of the previous section proves to be so useful.

Calculation of the transition temperature T_c

The simplest approach to calculating the transition temperature T_c is to use renormalised (quasiharmonic) phonon theory, in which we apply a mean field approximation to anharmonic phonon theory taken to fourth order. The basic ideas have been described elsewhere (Dove 1993, 1997a), and we simply cite the results. We first need to define terms. Any phonon frequency ω_k, where k labels both the wave vector and phonon branch, will be modified by anharmonic coupling to the order parameter:

$$\bar{\omega}_k^2 = \omega_k^2 + \frac{1}{2}\alpha_k Q^2 \tag{25}$$

where ω_k is the phonon frequency in the absence of any ordering (but incorporating all irrelevant anharmonic interactions), and $\bar{\omega}_k$ is the frequency modified (renormalized) by coupling to the ordering. α_k is a fourth-order anharmonic coupling coefficient. We define an average coupling coefficient $\tilde{\alpha}$:

$$\tilde{\alpha} = \frac{1}{3N}\sum_k \alpha_k \tag{26}$$

where N is the number of atoms in the crystal. Finally we define an 'average' frequency $\tilde{\omega}$:

$$\tilde{\omega}^{-2} = \frac{1}{3N\tilde{\alpha}}\sum_k \frac{\alpha_k}{\omega_k^2}. \tag{27}$$

We note that if the anharmonic coefficient α_k is only weakly correlated with the frequency ω_k, then we can rewrite Eq. 27 as:

$$\tilde{\omega}^{-2} \approx \frac{1}{3N} \sum_k \omega_k^{-2} \tag{28}$$

The transition temperature T_c is given by renormalised phonon theory (Dove 1997a) as

$$T_c = \frac{2\kappa_2 \tilde{\omega}^2}{3R\tilde{\alpha}} \tag{29}$$

where κ_2 is the coefficient in the expression for $V(Q)$ (Eq. 22), and R is the gas constant. Implicit in the derivation of T_c is the use of the classical limit ($\hbar\omega_k < k_B T$). The same result can be obtained from more rigorous reasoning within the mean-field approximation (e.g. Blinc and Zeks 1974).

We have performed a calculation of these quantities using a large grid in reciprocal space (1000 points, giving 27000 contributions to the sums in the expression of $\tilde{\alpha}$ and $\tilde{\omega}^2$), and with two values of Q (0 and $Q_0/20$). For each mode α_k was calculated by subtracting the values of ω_k^2 calculated for the two values of Q. We obtained the value T_c=1700 K. We consider the agreement with experiment to be satisfactory given the approximations inherent in this calculation which we now comment on.

We should comment that the molecular dynamics simulations of quartz using the same potentials found T_c for the α–β phase transition to be around the same as the experimental value (Tsuneyuki et al. 1990). Thus the discrepancy between our calculations and the experimental value for T_c is due to the approximations in our calculation. The first of these is that the values of κ_2 and κ_4 should be the same in our calculation for the low-temperature phase as seen in the high-temperature phase. These quantities can easily be renormalised by the anharmonic interactions that are relevant in the high-temperature phase, and will certainly be modified as a result of dynamic coupling to strain (a static coupling has been taken into account in the calculation of $V(Q)$ above). The second approximation is that the values of α_k and ω_k will also be renormalised by anharmonic interactions neglected in our calculation, although the effects on the averages may not be as severe. All the other approximations are inherent to the renormalised phonon theory, which is outlined in the review by Dove (1997a). Taking account of these approximations, we do not consider that the differences between our calculations and experiment are significant.

As we have noted above, our aim is not simply to achieve agreement with experiment but to understand why the transition temperature has the value it has, and why the full phonon calculation gives a result close to that of the one branch model. The question of the value of T_c can now be rephrased. Given that the anharmonic coupling coefficient is weakly correlated with the phonon frequency, and that the average phonon frequency is directly related to the interatomic potentials and well-understood, the important question concerns why $\tilde{\alpha}$ has the appropriate size. A larger value would give a significantly smaller value of T_c, whereas a smaller value would increase T_c to well-above the melting point.

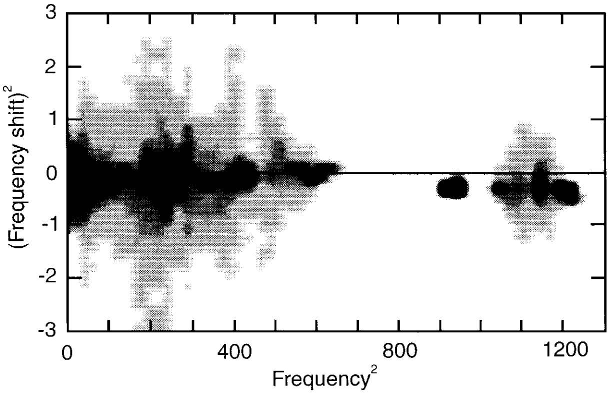

Fig. 5 A shaded contour map showing the values of the frequency shifts $\Delta\omega_k^2$ of the normal modes of 1000 **k**-points ie. 27000 modes. The non linear scale highlights those regions of the plot which have the greatest density of points. Note the approximately even distribution of positive and negative values. The average squared frequency shift is $3.71 \cdot 10^{-2}$(rad/s)^2

We have constructed a map showing the distribution of the values of α_k that contribute to $\tilde{\alpha}$, Fig. 5. There are two features to note. The first is that the individual values of α_k are much larger in magnitude than the final average $\tilde{\alpha}$. The second is that there is an almost equal distribution of positive and negative values, which means that to a first approximation $\tilde{\alpha}$ has a value close to zero. A zero value will give rise to an infinite value for T_c: the system will stay in the low-temperature phase for all values of temperature. It might seem therefore that the existence of the phase transition is sensitively dependent on summation of a large number of near-cancelling terms. We will explain now why this is not so.

Why does the simple model work?

The relation of Eq. 20 to Eq. 29 can be seen, if κ_4 simply replaces $\tilde{\alpha}/2$, and $\tilde{J}$ replaces $\tilde{\omega}^2$. In this case κ_4 is the fourth-order anharmonic coefficient, but in the Fourier transform to reciprocal space κ_4 transforms as a constant value independent of k, so that α_k=κ_4 for all k. Since in this model there is only one phonon branch, whereas in the general case (Eq. 29) there are 3 n branches, where n is the number of atoms in the unit cell, the question is whether the remaining (3 n–1) branches are important – we will show that they are not.

The fact that the simple theory gives a result for T_c that is close to the value obtained from the calculation in the previous section, with all 27 branches but with a lot of cancelling terms, suggests that the two models are closely connected. The case of a general rigid unit structure has already been shown to map onto the simple theory. We will now show how this mapping provides an explanation for the small but non-zero value of $\tilde{\alpha}$ that determines the value of T_c in Eq. 29.

The simple theory expressed in reciprocal space (Eq. 16) can be solved for non-zero temperatures using renormalised phonon theory. The phonon frequencies using the nomenclature of Eq. 16 are then given as

$$\omega_{\mathbf{k}}^2 = \frac{1}{m}(J_{\mathbf{k}} - \kappa_2) - \frac{1}{m^2}(3\kappa_4 k_{\mathrm{B}} T)\sum_{\mathbf{k}'} \omega_{\mathbf{k}'}^{-2}. \tag{30}$$

The whole phonon branch changes uniformly in ω^2 as the temperature changes, since the anharmonic coefficient κ_4 is independent of $\mathbf{k}$, as discussed above. This point is crucial to our discussion, since it now ensures that the coupling coefficient averaged over all $\mathbf{k}$ does not vanish in the same way that we found in the full phonon calculations for quartz.

Validity of Landau theory

In recent years Landau theory has been successfully used to describe the phase transitions in a number of aluminosilicates (Putnis 1992; Salje 1990, 1991; Salje et al. 1991) particularly for the important but complicated feldspar series. We can now use the arguments we have developed to firmly underpin the application of Landau theory to displacive phase transitions in aluminosilicates.

In the displacive limit of the ϕ^4 model ($s \rightarrow 0$), the application of mean field theory to the system becomes more accurate (e.g. Bruce and Cowley 1981; Dove 1997a; Padlewski et al. 1992) and the evolution of the order parameter over a wide range of temperature adheres closely to the law

$$Q^2(T) \propto (T_{\mathrm{c}} - T). \tag{31}$$

Since the simplest form of Landau theory is a variant of the mean field idea, which assumes the order parameter is homogeneous over the system, it describes the displacive case well. In this limit the entropy comes almost entirely from the phonons. The absence of configurational entropy comes from the fact that the large nearest-neighbour coupling constant ensures that the motions of nearest-neighbour atoms are highly correlated, and indeed the correlation lengths due to the large force constant will be quite large. Our deduction that the displacive phase transitions in aluminosilicates fall into the displacive limit as a consequence of the stiffness of the tetrahedra leads to the conclusion that Landau theory is expected to be applicable.

This is not however the complete general picture. In many aluminosilicates the phonon branch that contains the soft mode is not soft only at a single wave vector, but may also be soft along certain directions in reciprocal space, as in quartz, or in planes in reciprocal space, as in cristobalite. We have carried out a theoretical study of phase transitions in these situations and have found the applicability of Landau theory also depends on the variation of the phonon frequency along the soft directions or within the soft planes (Sollich et al. 1994). Away from the transition temperature we found that the temperature dependence of the order parameter Q followed the classical prediction of Landau theory, namely that $Q^2(T_{\mathrm{c}}' - T)$, where T_{c}' is a temperature slightly above the actual transition temperature. However, at temperatures close to T_{c} the effects of critical fluctuations may be important – these define the *Ginzburg interval* (Bruce and Cowley 1981). Due to the lack of experimental data it was not possible to pin down the size of the Ginzburg interval for silicates. But for the feldspars this is not an issue. We know from general considerations that the $C2/m - C\bar{1}$ phase transition in alkali feldspars is driven by a soft acoustic mode which from theory quarantees that the Ginzburg interval is absent in three dimensions. We also know that in the $I\bar{1} - P\bar{1}$ phase transition in the plagioclase feldspars the soft mode is restricted to a single point in reciprocal space, validating our previous arguments.

Conclusions

The discussion of this paper has led us to understand the origin of the transition temperatures associated with displacive phase transitions in aluminosilicates. We have shown that the transition temperature is primarily dependent on two quantities, the maximum amount the structure can distort owing to short-range steric repulsions, and the stiffness of the tetrahedra. This result relied on the application of the simple theory, and to validate it we showed how the phase transition of any aluminosilicate can be mapped onto this model, and why the complicated detail ignored by this mapping is self-cancelling and therefore irrelevant. From this discussion we have been able to show why the simplest form of Landau theory, which assumes long range interactions, is expected to work over a wide range of temperatures.

Our application of these ideas is particularly well suited to systems such as the feldspars, as discussed above. In the case of quartz it is not reasonable to push the quantitative analysis too far as the transition is actually weakly-first-order, and in the case of cristobalite it is strongly first-order. For quartz the first-order discontinuity arises owing to an incommensurate instability that occurs at a temperature that is 1.5 K higher that the transition into the α phase. Thus it is unlikely that the basic picture will be significantly changed given the considerable uncertainty on the parameter values used in the quantitative analysis. On the other hand, the origin of the large first-order discontinuity in cristobalite is not yet understood.

Appendix A

Definition of the order parameter

The order paramter for a phase transition in a material as complex as quartz is not straightforward to define. In principle it might be defined as the rotations of the SiO_4 tetrahedra, but this may not capture the whole picture if there are also significant translations of the tetrahedra.

The positions of the oxygen and silicon atoms as given by the International tables for X-Ray Crystallography for

$P\,6_222$ β quartz and $P\,3_221$ α_+ and α_- quartz (right handed) or $P\,6_422$ β and $P\,3_121$ α_+ and α_- quartz (left handed) are given as fractional coordinates found by operating upon a general position (x, y, z) with the symmetry elements of the group. By comparing the fractional coordinates of equivalent atoms in the α and β phases it is possible to find linear combinations of the x, y and z values, which take a specific value for the α_+ phase and the same, but negative, value for the α_- phase and monotonically decrease to zero as a continuous transformation from α to β occurs. The order parameter we used depended upon the oxygen position. It is found that in the β phase all oxygens have fractional coordinates in the z direction which are multiples of $\frac{1}{6}$. The oxygens we were concerned with moved away from this z fractional coordinate in proportion to how far the simulation sample had changed from the β to α phase. Hence, we assigned this change in the z coordinate as our order parameter (Q).

Appendix B

Analysis of the energy scale of lattice vibrations in quartz

We are concerned here with three matters. Firstly, we need to find an experimentally determined value for the coefficient κ_2 of ϕ_i^2 of Eq. 11. Secondly, following on naturally from this, we calculate a value for the constant J of Eq. 11 in order to estimate the displacive/order disorder measure, s using Eq. 14. Thirdly, the dispersion measure d (section on calculation of T_c for quartz) must be estimated.

The constant κ_2

In the review by Dove (1997a) the free energy contribution of a complete set of normal modes, each with frequency renormalised by the soft mode and all other modes, is added to the lattice energy as a function of the order parameter to give a total free energy function:

$$F(Q)=F_0(T)+\frac{1}{2}\left(\frac{3RT\tilde{\alpha}}{2\tilde{\omega}^2}-\kappa_2\right)Q^2+\frac{\kappa_4}{4}Q^4 \qquad (32)$$

where all symbols have the same meaning as in the main text. Above the transition temperature, it can be seen that the soft mode frequency squared is given by the coefficient of the Q^2 term. This coefficient is linear in T and reduces simply to κ_2 at T=0. Therefore, by extrapolating a soft mode frequency versus temperature plot to zero temperature should yield an estimate for this constant (actually κ_2 divided by the inertia constant m mentioned in the text). The extrapolated data of Dolino et al. (1992), which plots the frequency squared against temperature, provides a value for the soft mode frequency squared at T=0 of -1.7 THz^2.

This quantity may also be found from calculations using interatomic potentials. Employing the Tsuneyuki potentials (Tsuneyuki et al. 1988) for this purpose yields a soft mode frequency squared value of -4.5 THz^2 in the α phase at T=0. The constant κ_2 itself is equal to the absolute values of these squared frequencies divided by the mass m.

The displacive measure s

The quantities required for the calculation of the displacive measure s defined in Eq. 14 are κ_2, which has now been calculated, and J – the coupling constant between sites in the ϕ^4 model. The constant J may be found by considering the highest frequency of the phonon branch containing the soft mode at the Γ-point. The value of J is seen (from e.g. Sollich et al. 1994) to be equal to half of the sum of this maximum frequency squared and κ_2. Calculated frequencies in the soft mode phonon branch were searched using a lattice dynamics program and the maximum frequency squared found was 12 THz^2. The constants necessary for the calculation of s have thus been found and, with reference to Eq. 14 its value is calculated as follows (Z, the number of nearest neighbours is 4):

$$s=\frac{\kappa_2}{2ZJ}=\frac{4.5}{4\times 12}\approx 0.09. \qquad (33)$$

The dispersion measure d

The dispersion measure is the quantity governing the depth of the RUM valleys in the phonon dispersion surface for quartz constructed in the section on calculation of T_c for quartz. This measure lies between 0 and 1: when d=0 the valley's frequencies are zero and when d=1 there are no RUM valleys. In order to estimate d the data of Dolino et al. (1992) are referred to again and it is observed that dispersion surface plots of the β-phase at 1250 K resolve the soft mode frequency at 1 THz and the maximum points of the dispersion curve lies at around 4 THz. The dispersion measure implied by these values is $1/4^2$=0.06. In the main text, the calculations assume d=0.1 – estimating the non soft mode RUM points to be at slightly greater frequencies than the soft mode point itself.

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