Low-Frequency Floppy Modes in $\beta$-Cristobalite

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Inelastic neutron scattering and molecular dynamics simulations provide evidence for the existence of low-frequency floppy modes in the high-temperature phase of cristobalite, which are analogous to those found in network glasses. The behavior is similar to that observed in computer simulations of orientationally disordered crystals.

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The importance of low-frequency modes has long been recognized in glasses. The description of these modes originates from the idea of Phillips [1] of underconstrained and overconstrained glasses, defined as the ratio of the number of constraints, $n_c$, to the number of degrees of freedom, $n_d$. Phillips [1] suggested that glass formation may be expected in the region around $n_c \approx n_d$. Thorpe [2] described the effects expected in a random network by varying the proportion $n_c/n_d$, which may be achieved by the alteration of the mean coordination, $\langle r \rangle$, present in the structure. In these random network structures a phase transition exists with a critical $\langle r_c \rangle = 2.4$ [3]. As $\langle r \rangle$ is increased beyond $\langle r_c \rangle$, the number of constraints is increased, and rigidity percolates through the network. For $\langle r \rangle < \langle r_c \rangle$, the glass is underconstrained and floppy, and a large number of low-frequency modes (called "floppy modes" in this context [2,4]) are found to exist. Even once rigidity has percolated there will still be a finite number of locally floppy regions, so the number of floppy modes is never precisely zero. These arguments have been developed for monatomic and simple binary glasses [4]—the application to more complex systems such as silicate glasses is not straightforward, but there is evidence that in these materials low-frequency floppy modes exist and give rise to similar anomalous transport properties at low temperatures [5,6].

In this Letter we extend these ideas to crystalline materials. We consider the case of cristobalite, which is one of the crystalline structures of silica having an infinite three-dimensional network of corner-sharing $\text{SiO}_4$ tetrahedra, and is often used as an analogy to silicate glass [6]. The possible existence of low-frequency modes in a framework silicate may be seen to arise by the description of the network in terms of a model potential of the form [2]

$$V = \frac{1}{2} \sum_{\langle ij \rangle} \alpha_{ij} (\Delta r_{ij})^2 + \frac{1}{2} \sum_{\langle ijk \rangle} \beta_{ijk} (\Delta \theta_{ijk})^2,$$

where $\alpha_{ij}$ and $\beta_{ijk}$ are the bond-stretching and bond-bending force constants, respectively, and the summations include only interactions between atoms in the same tetrahedron. There are no terms that are dependent on the relative orientations of two neighboring tetrahedra. In this approximation the floppy modes are those in which the tetrahedra can move without any distortion, and these have zero frequency. These floppy modes are called "rigid unit modes" (RUMs) in the crystalline context [7–9]. In a silicate with all the corners of the tetrahedra shared, there is a fine balance between $n_d$ and $n_c$—in a simple counting $n_d = n_c = 6$ per tetrahedron, which implies that there are no floppy modes. However, symmetry allows some of the constraints to be degenerate and hence no longer independent. This creates a small difference between $n_d$ and $n_c$, thereby generating some RUMs. It is possible to determine the number of RUMs for any wave vector [10]: for the high-temperature phase of quartz the RUMs are confined to lines of wave vectors in reciprocal space (i.e., there are of the order of $N^{1/3}$ RUMs, where $N$ is the number of unit cells) [7], whereas in the high-temperature phase of cristobalite there are RUMs in whole planes of wave vectors (i.e., there are of the order of $N^{2/3}$ RUMs) [9]. The number of RUMs in the low-temperature phases of both materials is significantly reduced, owing to the fact that the loss of symmetry breaks the degeneracies of the constraints, so that the ratio $n_c/n_d$ becomes closer to unity.

RUMs have special importance in silicates. For example, they can act as the classical soft modes that give rise to structural phase transitions, as in quartz [7,8]. As reviewed elsewhere [9], the extremely anisotropic nature of RUMs gives rise to small Ginzburg intervals, and RUMs are responsible for other properties such as negative (or anomalously low) thermal expansion.

In this Letter we will present evidence from neutron scattering, infrared experiments, and molecular dynamics simulations that reveal the existence of these modes in the high-temperature ($\beta$) phase. The key point is that the low-frequency dynamics of the $\beta$ phase are very similar to those found in network glasses, indicating that the low-frequency properties of the network glasses are not so much properties of the amorphous structure but of the existence of the network.

Cristobalite undergoes a structural phase transition at ca. 270°C, although this temperature is dependent on the quality of the sample. The high-temperature $\beta$ phase has cubic symmetry, $Fd\bar{3}m$, and the low-temperature $\alpha$ phase is tetragonal, $P4_2\overline{1}2_1$ [11]. The set of RUMs for the $\beta$ phase is given in Table I [9]. The condensation
TABLE I. Rigid unit modes in \( \beta \)-cristobalite.

<table>
<thead>
<tr>
<th>Wave vector</th>
<th>Rigid unit mode$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0, 0, 0 (( \Gamma ))</td>
<td>( ^3 \Gamma_4^- + ^3 \Gamma_5^- )</td>
</tr>
<tr>
<td>0, ( \xi ), 0 (( \Delta ))</td>
<td>( ^2 \Delta_3 )</td>
</tr>
<tr>
<td>( \xi ), ( \xi ), ( \xi ) (( \Lambda ))</td>
<td>( ^2 \Lambda_3 + \Lambda_2 )</td>
</tr>
<tr>
<td>( \xi ), ( \xi ), 0 (( \Sigma ))</td>
<td>( \Sigma_2 )</td>
</tr>
<tr>
<td>( \frac{1}{2}, \frac{1}{2}, \frac{1}{2} ) (( L ))</td>
<td>( ^2 \Lambda_4 + L_2 )</td>
</tr>
<tr>
<td>( \xi ), 1, ( \xi ) (( S ))</td>
<td>( S_2 )</td>
</tr>
<tr>
<td>0, 1, 0 (( X ))</td>
<td>( ^2 X_4 )</td>
</tr>
<tr>
<td>( \xi ), ( \xi ), ( \xi ) (( \Theta ))</td>
<td>( \Theta_2 )</td>
</tr>
</tbody>
</table>

$^a$The superscripts denote the degeneracy of the modes, and the subscripts refer to the modes’ symmetries.

of the \( X_4 \) RUM gives rise to both the translations and the rotations of the tetrahedra required to generate the \( \alpha \) phase \([9,11,12]\). Almost all the RUMs found in the \( \beta \) phase vanish in the \( \alpha \) phase, apart from the RUMs along the lines \{110\} in the tetragonal setting \([13]\).

Our molecular dynamics simulations have been performed on both phases of cristobalite, using samples containing 49152 rigid ions in a constant-volume–constant-energy ensemble \([14]\). The calculations were performed on the Cambridge (U.K.) AMT Distributed Array Processor \([8,15]\), using the interatomic potential model of Tsuneyuki \textit{et al.} \([16]\). The size of the simulation cells were chosen to correspond to approximately zero pressure.

Our initial evidence for the existence of RUMs in \( \beta \)-cristobalite comes from calculations of the phonon density of states, \( g(\nu) \), obtained as the power spectrum of the mass-weighted velocity autocorrelation function. In Fig. 1 we compare \( g(\nu) \) of both phases. The key difference between \( g(\nu) \) for the two phases is at low frequencies. \( g(\nu) \) for the \( \alpha \) phase varies roughly as \( \nu^2 \), as expected for the normal contribution from the acoustic modes. On the other hand, \( g(\nu) \) for the \( \beta \) phase in the low-frequency regime increases nearly linearly, showing significant enhancement of the number of low-frequency modes. This result is similar to measurements of \( g(\nu) \) that have been made on the amorphous Se-Ge system \([4]\). The same behavior has also been found in calculations of \( g(\nu) \) for translational motions in orientationally disordered (plastic) crystals \([17]\), although this point has barely been appreciated \([18]\). In cristobalite, therefore, this behavior may reflect some orientational disorder of the tetrahedra (which is consistent with the observation of characteristic diffuse scattering in the powder diffraction patterns of the \( \beta \) phase \([11]\)).

We have confirmed the prediction of the enhancement of the number of low-frequency modes in \( \beta \)-cristobalite using inelastic neutron scattering from a powder sample of cristobalite. The experiments were performed on the time-focused crystal analyzer (TFXA) spectrometer at the ISIS Spallation Neutron Source \([19]\). TFXA measures \( S(\nu, \delta \nu) \) for a parabolic trajectory in \((Q, \delta Q, \nu) \) space, using a fixed analyzing energy. Although this trajectory does not sample a true density of states, since the \( |Q| \) averaging is not complete, the sampling will be reasonable for modes with frequencies only weakly dependent on wave vector, such as RUMs \([9]\). Measurements of the inelastic spectrum were performed at temperatures of 20 \(^\circ\)C and 320 \(^\circ\)C. The results for energies between 2 and 22 THz are shown in Fig. 2(a), and for energies between 0 and 2.5 THz in Fig. 2(b). The high-frequency spectra are similar, as expected, but the low-frequency spectra are very different—there is a large increase in the number of low-frequency modes in the data from the \( \beta \) phase.

Given the similarities we have noted between \( \beta \)-cristobalite and plastic crystals, we now discuss the issue of the orientational disorder in the \( \beta \) phase. The “ideal” structure of the \( \beta \) phase has the oxygen atoms lying exactly halfway between two silicon atoms. This

![FIG. 1. \( g(\nu) \) for \( \alpha \) phase (line) and \( \beta \) phase (points) calculated by molecular dynamics simulations.](image1)

![FIG. 2. TFXA spectra for (a) wide range of energies (\( \alpha \) phase data are the lower curve) and (b) low-frequency regime.](image2)
gives an unphysically short Si–O bond (1.54 Å, as compared to the value of 1.62 Å in the α phase) and Si–O–Si bond angle (180° rather than the value of 147° in the α phase). A more reasonable model for the structure of the β phase has the tetrahedra rotated by ca. 17° from the “ideal” orientations—this gives a good fit to diffraction data and realistic bond lengths and angles [11,20]. There has, however, been some uncertainty as to whether the β phase is a true dynamically disordered phase, as tacitly assumed in the RUM model, or contains static or dynamic domains of the low-temperature phase [12,20]. We have tackled this issue by measuring the infrared and Raman spectra of cristobalite over a wide range of temperatures in both phases [21]. Figure 3 shows the temperature dependence of the infrared spectra. The peaks at 300 cm\(^{-1}\) (assigned as \(A_2\)), 380 cm\(^{-1}\) (\(E\)), and 620 cm\(^{-1}\) (\(E\)) in the infrared spectra vanish completely on heating into the β phase. The modes at 114 cm\(^{-1}\) (\(A_1\)), 231 cm\(^{-1}\) (\(B_1\)), and 418 cm\(^{-1}\) (\(A_1\)) in the Raman spectra also vanish completely on heating into the β phase. If there were small domains of the ordered phase within the disordered phase these peaks would not completely disappear, as the correlation length sampled by infrared and Raman spectroscopy for modes at these frequencies is no longer than a few unit cell lengths [22]. These results are similar to those obtained in a recent spectroscopic study of the phase transition in quartz [23], and demonstrate (as in the case of quartz) that the disorder in the β phase is dynamic rather than static. Thus we can exclude the Wright and Leadbetter model of β-cristobalite. This conclusion is important in view of the widespread use of that model as an analogy to silicate glasses [6].

Finally we address the question of whether the orientational disorder involves hopping of oxygen atoms between specific sites or whether it is better described by an isotropic precession of the Si–O bonds about (111) [11,20]. Previous dynamically disordered models have tended to assume that the oxygen atoms either rotate about a fixed radius, defining an annulus, or hop between six symmetrically equivalent positions on the annulus. It is difficult to differentiate between these two motions from diffraction data, so we have used molecular dynamics simulations to try to clarify the nature of the disorder in β-cristobalite. We have formed the orientational distribution function (ODF) for Si–O bonds, defining the reference axis as the nearest (111) axis. Figure 4 shows the Si–O ODF averaged over the azimuthal angle. The main feature of this function is the broad peak at 17° consistent with a mean O–Si–O angle of 146°. We have found that, apart from statistical error, the ODF is independent of the azimuthal angle—this means there is no preferred orientation of the Si–O bond in the annulus, and so in the simulations at least the disorder is better described by a random precession of the Si–O bonds rather than the hopping of the O atoms between specific sites. This would be expected from the activity of the large number of RUMs active in the β phase. Flipping between the six sites on the annulus would only be achieved if the soft \(X_4\) RUM dominated the behavior.

This broad distribution is very similar to that obtained from experimental evidence from silica glass [24]. The suggestion [24] that a broad angular distribution is a criterion for the distinction between amorphous silica and its crystalline counterparts would appear to only hold for low-symmetry phases where few RUMs exist, and not for high-symmetry phases where the presence of many RUMs makes the framework flex dynamically.

In conclusion, we have demonstrated that the low-frequency floppy modes found in network glasses have very close analogs in the high-temperature β phase of the
crystalline silicate cristobalite. These modes are not so prominent in the low-temperature α phase because of the loss of symmetry and subsequent increase in the number of independent constraints. The low-frequency dynamics of the β phase are very similar to the low-frequency translational dynamics observed in molecular dynamics simulations of orientationally disordered crystals—only now have we been able to confirm this behavior experimentally.

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[13] The a and b axes in the conventional tetragonal phase are rotated by 45° from those in the cubic phase.
[14] Full details and the results of additional calculations will be presented elsewhere.
[18] The observation of this enhancement of the number of low-frequency translational modes in plastic crystals has never been tested experimentally, since the power spectrum for the rotational modes tends towards a constant value as ν → 0 (the signature of rotational diffusion), so that scattering from rotational modes would dominate any signal in a scattering experiment. In the present case, the tetrahedra are not able to tumble, so there is no rotational diffusion, and we might therefore expect to be able to confirm this prediction experimentally.
[21] The details of these experiments, together with a more complete data analysis, will be reported in more detail elsewhere.