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Quantum saturation of the order parameter and the dynamical soft mode in quartz

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Abstract

The temperature evolution of the static order parameter of α-quartz and its soft-mode frequencies were determined at temperatures below 300 K. While these parameters follow classic Landau theory at higher temperatures, quantum saturation was found below room temperature with a characteristic quantum temperature of 187 K. A quantitative analysis gave a good agreement with the predictions of a Φ^6 model close to the displacive limit and a rather flat dispersion of the soft-mode branch. No indication of any effect of strong mode–mode coupling on the saturation behaviour was observed.

1. Introduction

Two characteristic temperatures are needed for the quantitative description of structural phase transitions. The first is a transition temperature T_c. The second characteristic temperature is the saturation temperature θ_s below which the order parameter becomes independent of temperature. The existence of a finite temperature θ_s is a manifestation of the third law of thermodynamics, which requires that entropy changes, and hence order parameter changes, disappear at absolute zero temperature. The interplay between T_c and θ_s has been investigated theoretically [1] and experimentally [2–6] showing that the phase transition is suppressed by quantum fluctuations for $T_c \ll \theta_s$. Exact limits can easily be derived for specific dispersion relationships of the fluctuations; the case of flat, Einstein mode-type oscillations was discussed in [1]. The importance of quantum saturation was demonstrated in the case of the ferroelastic phase transition in $SrTiO_3$ with $T_c = 105.65$ K and $\theta_s = 60.75$ K where saturation effects are noticeable even at temperatures close to T_c [7, 8].

Soft modes with very weak dispersion are encountered in perovskite structures which often show a flat phonon branch between the R and the M point of the cubic Brillouin zone [9, 10]. The same is expected in the case of the $\beta \rightarrow \alpha$ transition in quartz [11]. In this transition, the strength of the interactions between rotating SiO_4 tetrahedra is also known from atomistic

calculation ($J = 70$–150 cm^{-1}) [12], so a direct comparison between the experimental observations and the theoretical model of Salje *et al* [1] is possible under the condition that all other interactions in this complex crystal structure are ignored. This condition leads to a puzzle, however. Atomistic calculations have shown that the soft mode in quartz couples strongly with other phonon branches, in particular the branch near 149 cm^{-1}. This effect is also borne out by the experimental observation [6] that hard modes in quartz show stronger order parameter coupling than in other silicate structures. In fact, the driving force for the $\beta \rightarrow \alpha$ transition is the collapse of the specific volume (a non-symmetry-breaking process) while the geometrical transition process is obtained by symmetry-breaking tetrahedra rotations which, by themselves, contain little excess enthalpy [13]. The soft mode is expected, therefore, to couple strongly with other degrees of freedom which could, in principle, renormalize θ_s (but not necessarily T_c). These arguments are somewhat counterbalanced by calculations by Pérez-Mato and Salje [14] who showed that couplings with secondary degrees of freedom have little effect on the temperature evolution of the order parameter unless the coupling strength becomes very strong. We will show in this paper that the saturation behaviour in quartz is in full agreement with a soft-mode picture with no observed renormalization by secondary processes. The quantum temperature saturation is found to be the same for the spontaneous strain, the order parameter and the frequency of the soft mode.

2. Experimental details

Part of a natural quartz sample from Brazil was crushed and ground to a fine powder. The powder was mixed with Si as an internal standard and placed in a novel high-resolution diffractometer fitted with a cryostat [15, 16]. A focused and strictly monochromatic Cu Kα_1 beam was diffracted by the powder and registered by a 120° (2θ) position-sensitive detector (120-PSD). The 2θ resolution of the detector was 0.027°. Refinement of the powder data led to temperature-independent uncertainties of ± 0.0006 Å for lattice constants. The measurements were carried out on heating and cooling the sample in the temperature range 30–300 K, in steps of 3 K.

Raman spectra were recorded with a DILOR Z24 spectrometer in single-mode operation, coupled with a Coherent 90-2 argon-ion laser. The incident wavelength was 514 nm; the spectral resolution was 2 cm^{-1}. The temperature control allowed reproducible adjustments within a temperature stability of 1 K.

3. Results and discussion

The temperature evolution of the lattice parameters is shown in figure 1, where we also show the lattice parameters obtained from x-ray and neutron powder diffraction from [13] in the range 10–900 K. Our data agree very well with the previous ones but allow a better characterization of the low-temperature behaviour.

Taking the almost temperature-independent data of the β-phase as the baseline, we find the components of the spontaneous strain e_1 and e_3. In a first test of self-consistency of the two data sets, we show in figure 2 that the two independent components e_1 and e_3 correlate linearly ($e_3 = 0.573 e_1$) over the full temperature interval within experimental errors, so we do not need to distinguish between these components any further.

In order to compare the experimental behaviour and the theoretical one predicted by Salje *et al* [1], the analytical description of the temperature dependence of the spontaneous strain was obtained by fitting the above model, taking into account the nearly tricritical behaviour of quartz and considering that the spontaneous strain scales with the square of the order parameter:

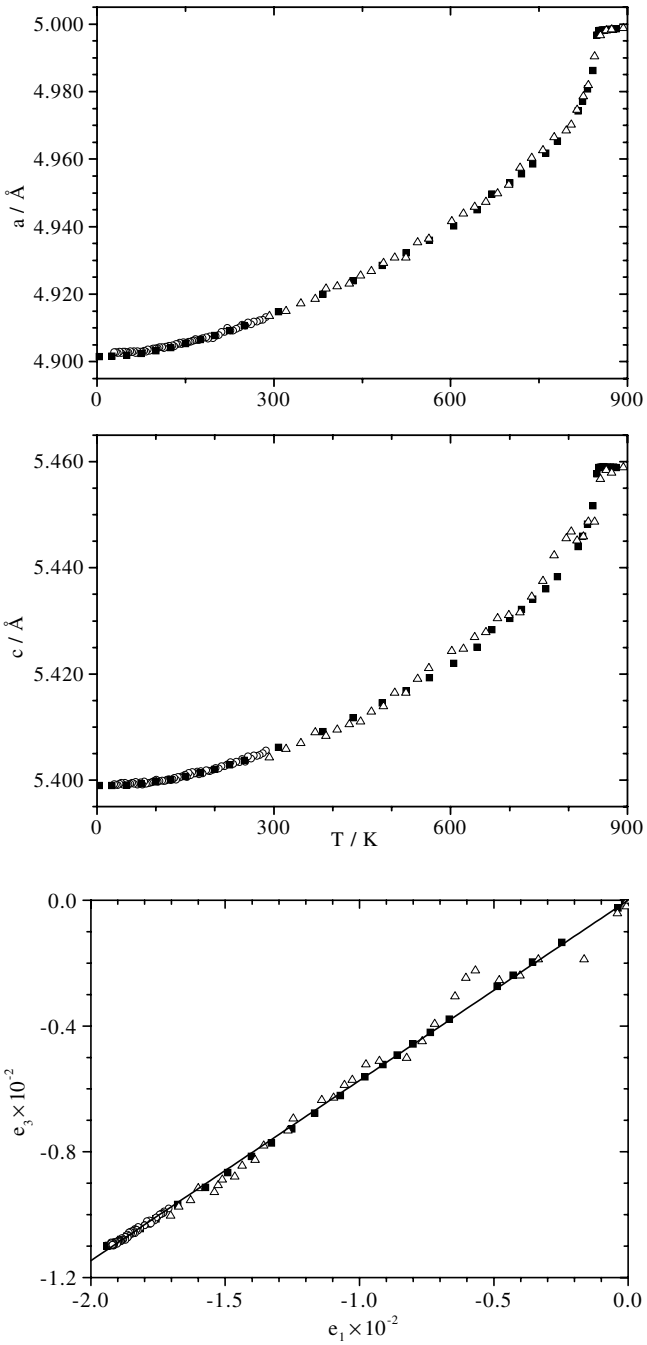

Figure 1. The temperature dependence of the lattice parameters of quartz from our data (circles) and from [13]: neutron data (squares) and x-ray data (triangles).

Figure 2. The linear correlation between the components of the spontaneous strain e_1 and e_3 from our data (circles) and from [13]: neutron data (squares) and x-ray data (triangles).

$$e^2 \propto Q^4 \propto \left(\coth\frac{\theta_s}{T_0} - \coth\frac{\theta_s}{T}\right) \tag{1}$$

where T_0 is the fitted transition temperature which, in principle, can differ very slightly from T_c as discussed in [1]. A standard least-squares fitting procedure yielded the value $\theta_s = 187$ K (figure 3).

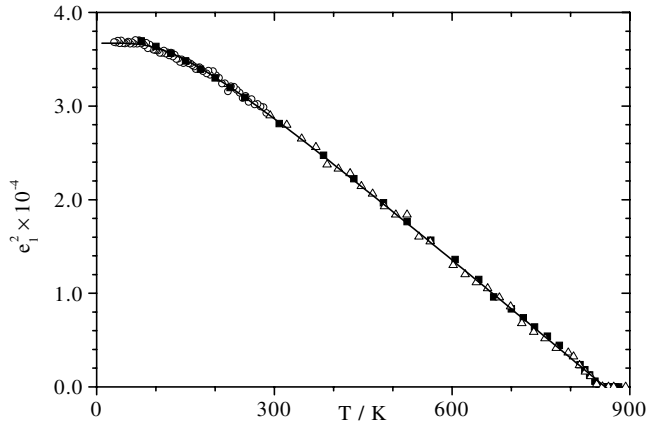

Figure 3. The evolution of e_1^2 as determined from our data (circles) and from [13]: neutron data (squares) and x-ray data (triangles). The line is the fit of the Salje *et al* model [1]. The quantum temperature saturation is $\theta_s = 187$ K.

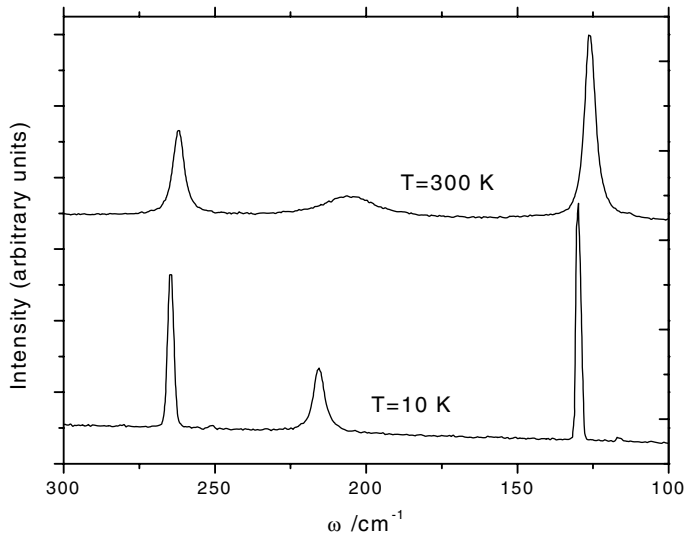

Figure 4. Raman spectra of quartz at $T = 10$ and 300 K.

The soft-mode frequency was obtained from the Raman spectroscopy study (figure 4). Due to the mode coupling which occurs in quartz, the soft-mode frequency had to be determined indirectly. Scott [17–19] identified the 207 cm^{-1} mode as the soft optic mode which is considered to go to zero frequency at T_c. The peak at 147 cm^{-1} is seen as an excitation of two-edge acoustic phonons and it is assumed to be temperature independent. The soft optic mode couples anharmonically to the two-phonon continuum.

The coupled-mode equation is given by [17, 18]

$$\omega_{\pm} = \tfrac{1}{2}(\omega_1 + \omega_2) \pm \tfrac{1}{2}[(\omega_1 - \omega_2)^2 + 4|W_{12}|^2]^{1/2} \tag{2}$$

where $\omega_1(T)$ is the soft-mode frequency, ω_2 is the temperature-independent two-acoustic-phonon state whose value is 160 cm^{-1} [17] and W_{12} is the off-diagonal matrix element in the anharmonic Hamiltonian connecting the two states. Scott found that W_{12} varies linearly with the temperature in quartz [18, 20].

From our Raman data in the region 10–300 K and taking the values of ω_2 and W_{12} determined by Scott, we obtain the temperature dependence of the squared soft-mode frequency associated with the phase transition (figure 5(a)). In the same figure, we have

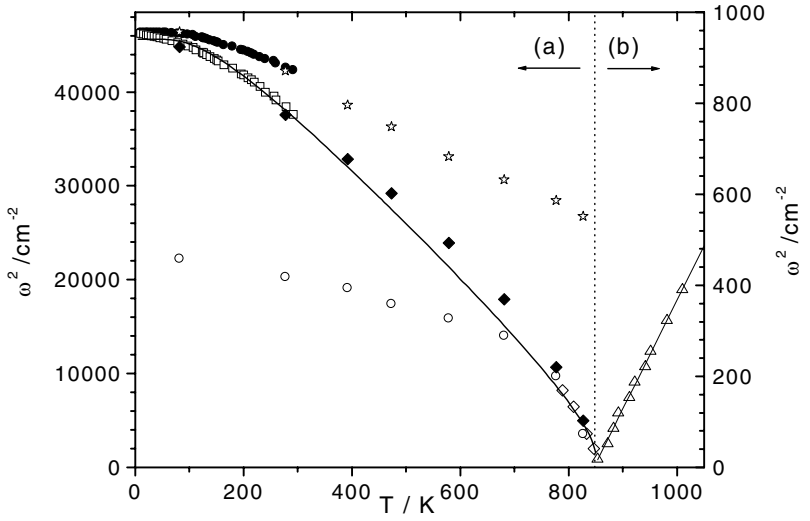

Figure 5. (a) ω_+^2 from [19] (open stars), ω_-^2 from [19] (open circles), ω_1^2 from [19] (full diamonds), ω_1^2 from [20] (open diamonds), ω_+^2 as measured in this study (full circles), ω_1^2 as deduced in this study (open squares). The continuous line is the prediction for $T < T_c$ from the inverse unrelaxed order parameter susceptibility with $F = 0.8\ \mathrm{J}^{-1}\ \mathrm{cm}^{-2}$ mol. Note that all the data for $T < T_c$ are referred to the left axis; (b) experimental data for the squared soft-mode frequency (open triangles, from [21]). The continuous line is the prediction from the calculated susceptibility for $T > T_c$ with $F = 0.24\ \mathrm{J}^{-1}\ \mathrm{cm}^{-2}$ mol. Note that the data for $T > T_c$ are referred to the right axis.

also represented values of the squared soft-mode frequency and the squared coupled-mode frequencies determined previously [17, 19, 20]. Our data allow us to study the low-temperature behaviour of the soft mode and to determine whether the quantum saturation temperature determined previously is in agreement with these data. Note that the details of the mode–mode coupling analysis have little to do with the determination of the saturation behaviour at low temperatures; in all scenarios the phonon frequency remains temperature independent below the saturation point.

To see whether the saturation behaviour in quartz is in agreement with the soft-mode picture, we compare the soft-mode frequency with the predictions of the Landau behaviour for quartz using the quantum saturation temperature obtained from the strain measurements.

The frequency of a classical soft mode for $T > T_c$ is expected to be proportional to the order parameter susceptibility:

$$\omega^2 = F\chi^{-1} \tag{3}$$

where F is the inverse effective mass and χ^{-1} is given by $a(T - T_c)$, where $a = 9.8$ J mol^{-1} K^{-1} [13]. As Carpenter *et al* [13] showed for the soft mode in β-quartz [21], the agreement in this case is very good. We obtain a value of $F = 0.24\ \mathrm{J}^{-1}\ \mathrm{cm}^{-2}$ mol (figure 5(b)).

Below the transition temperature a similar behaviour is expected but we have to take into account that the coupling between strain and order parameter provides the dominant stabilization energy for α-quartz and it is also responsible for the first-order character of the transition [13]. As has been found in [13], when phonon coordinates operate on a much faster timescale than the strain, the phonon susceptibility is given by the unrelaxed susceptibility [13]:

$$\chi^{-1} = a\theta_s\left(\coth\frac{\theta_s}{T} - \coth\frac{\theta_s}{T_0}\right) + (2b + b^*)Q^2 + \frac{1}{3}(8c + 7c^*)Q^4 + (4d + 3d^*)Q^6 \tag{4}$$

where $a = 9.8$ J mol^{-1} K^{-1}; b^*, c^*, d^* are the renormalized values of the fourth-order, sixth-order and eighth-order coefficients in the Landau expansion, whose values are $b^* = -1921$ J mol^{-1}, $c^* = 10\,190$ J mol^{-1} and $d^* = 0$; and b, c and d are respectively the bare fourth-, sixth- and eighth-order coefficients of the Landau expansions whose values are $b = 4900$ J mol^{-1}, $c = 17\,200$ J mol^{-1} and $d = 1600$ J mol^{-1}. The order parameter Q is obtained from the Landau potential determined by Carpenter *et al* [13], but considering the quantum saturation temperature $\theta_s = 187$ K determined previously.

The previously obtained soft-mode frequency data could be fitted to the unrelaxed order parameter susceptibility taking a value of the inverse effective $F = 0.8\,\mathrm{J}^{-1}\,\mathrm{cm}^{-2}\,\mathrm{mol}$, obtaining a good description of the low-temperature data. This model is the continuous line in figure 5(a).

The different values of the inverse effective mass for $T > T_c$ and $T < T_c$ can be explained in terms of other degrees of freedom which play an important role for $T > T_c$ [22]. In fact, one could speculate that the observed 'soft mode' at $T > T_c$ is not the thermodynamically relevant excitation as concluded from results in [22], but that strong coupling exists with other low-frequency modes. A detailed analysis is difficult but our results lend credence to the idea that a simple soft-mode picture is not adequate for the description of the dynamics of the β-phase of quartz.

In conclusion, we find that the temperature evolution of the spontaneous strain, the soft mode and the structural order parameter in the α–β phase transition in quartz are well described by the model of Salje *et al* [1] near the displacive limit. Only one quantum saturation temperature ($\theta_s = 187$ K) is needed to describe the observations.

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