

On the displacive character of the phase transition in quartz: a hard-mode spectroscopy study

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Abstract. The temperature evolution of the frequencies and absorption cross section of the infrared-active phonons near 795 cm^{-1} and 695 cm^{-1} and the Raman-active mode near 355 cm^{-1} follow that of the symmetry-breaking order parameter of the α - β phase transition in quartz. The IR signal at 695 cm^{-1} and the Raman signal at 355 cm^{-1} are symmetry forbidden in the β phase. The experimental results show that these signals do, indeed, disappear at $T > T_c + 10\text{ K}$. No signal related to microdomains of the α phase was found at these temperatures. Transition models based on the β phase being a time-averaged structure with local α states and lifetimes of clusters being much longer than phonon times are incompatible with these observations. The experimental results affirm the displaciveness of the phase transition although the existence of small amounts of α or INC phase in a matrix of β structure cannot be ruled out.

1. Introduction

Controversy exists about the transition mechanism of the α -INC- β phase transition in quartz. The discussion may be focused on two questions:

(i) What is the physical nature of the β phase? From the studies of electron diffraction (van Tendeloo *et al* 1976), neutron scattering (Wright and Lehmann 1981) and computational molecular dynamics simulations (Tsenuyuki *et al* 1988, Tautz *et al* 1991), there appears to be evidence that the β phase is either a disordered form of the α phase or that a matrix of a rather uniform β phase contains clusters of the α phase. These results are in apparent contrast to the results of x-ray diffraction studies (Kihara 1990) and the observation of soft modes below and above the transition point (Scott 1974, Tezuka *et al* 1991, Axe and Shirane 1970, Dolino *et al* 1989). The evidence from this second set of experiments is fully compatible with a displacive type of phase transition. (For the sake of this argument, we may first ignore the existence of the INC phase over a small temperature interval of 1.5 K.) The phase transition α - β is then co-elastic (i.e. a large spontaneous strain is generated) and Ginzburg fluctuations at temperatures very close to the transition point are irrelevant (Cowley 1976, Folk *et al* 1979, Salje 1990). The effect of INC states is less clear in so far as the soft mode in the β phase is extremely low energy ($d\omega^2/dT = 0.0025\text{ THz}^2\text{ K}^{-1}$) and

diffuse neutron scattering near the β -INC transition point (Dolino *et al* 1991) may be related to heterogeneous states.

(ii) The second riddle concerns the observation that macroscopic measurements of the order parameter in quartz using different experimental techniques lead to quantitatively different answers. For example, the step in the order parameter at the transition point varies between 25% and 40% of the value at room temperature (see the review by Dolino 1990, Bachheimer and Dolino 1975, Kihara 1990, Gervais and Piriou 1975). A key to the understanding of these inconsistencies may be observations of Barron and Pasternak (1987) who found that structural changes at low temperatures are largely due to changes of Si-O and O-O distances, whereas Boysen *et al* (1980) report that the Si-O₄ tetrahedra remain essentially rigid near the transition point. It is, of course, difficult at this point to distinguish between the real local deformations (i.e. at a fixed, immobile complex) and the apparent deformations due to thermal excitations. Some information can be gained by pressure experiments at constant temperature. In fact, structure analyses under pressure by Levien *et al* (1980), Jorgensen (1978) and D'Amour *et al* (1979) do show that the tetrahedral O-O distances and inter-tetrahedral O-Si-O bond angles change significantly when the pressure is increased, in addition to the inter-tetrahedral rotations. Guided by these observations, one might speculate that rigid unit motions (RUMs) of the tetrahedra and intra-unit deformations couple non-linearly and that macroscopic observations reflect these two features with different sensitivity. Such non-linearities related to rather high energy phonon excitations are certainly compatible with the observation of a high saturation temperature ($T_s = 167$ K) below which the order parameter in quartz becomes independent of temperature (Salje *et al* 1991).

The two questions, namely of the displaciveness and the hidden non-linearities of the transition, are not independent of each other because the dynamic formation of clusters in the β phase could account for non-linear response functions close to the transition point. The inverse conclusion (i.e. that the absence of large scale clusters in the β phase does not exclude other non-linearities in the α phase) is obviously false. The questions we wish to answer in this paper are simply whether or not the β phase is a time-averaged, disordered form of α -quartz, and to what extent α clusters may exist in β -quartz. We define α 'clusters' as spatially extended areas of the crystal with α structure and lifetimes which are long on a phonon time scale (longer than 10^{-9} s, say).

2. Experimental and results

The experimental techniques used in this study are hard-mode Raman and infrared spectroscopy (reviews by Salje 1991, Bismayer 1990, Petzelt and Dvorak 1976). In the case of the IR spectroscopy, there are two phonon branches which are optimal for this type of investigation, namely the E symmetry modes near 695 cm^{-1} and those near 795 cm^{-1} . Both modes have small LO-TO splitting and do not overlap with other phonon branches (Gervais and Piriou 1975). Their dispersion is small with correlation lengths below 5 \AA (Salje 1991). Both the infrared absorption intensity (integrated absorption cross section) and the TO frequencies are direct functions of the order parameter as measured on a phonon time scale. The very short time scale and the small correlation length mean that these modes are ideally suited to detect clusters in the β phase. The Raman spectroscopic work concentrated on the

355 cm^{-1} frequency which was already shown by Shapiro (1969) to depend sensitively on the α -type deformation of the quartz structure.

Crystals of optically clear (natural mineral) quartz were cut and polished with surfaces parallel to the (0001) plane. Three types of experiments were performed: (i) powder IR spectroscopy to determine the frequency shifts and the integral intensity changes; (ii) single-crystal absorption and reflectivity for the high-sensitivity intensity measurements; (iii) Raman spectroscopy (at temperatures close to the transition point) to determine the first-order character of the phase transition. We now describe some experimental details.

(i) *Powder IR spectroscopy.* Powders were prepared by the conventional pellet technique (0.37 mg quartz in 300 mg CsI). The pellets were then heated inside a Bruker V113V Fourier Transform Spectrometer. The slit function was set to 2 cm^{-1} and typically 512 runs were integrated per spectrum. The temperature evolution of the powder spectrum is shown in figure 1. The disappearance of the 695 cm^{-1} mode in the β phase is clearly observed.

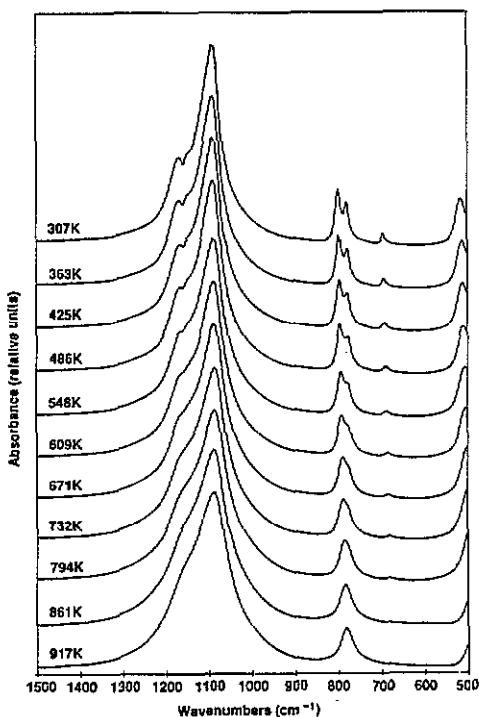


Figure 1. Temperature evolution of the infrared absorption spectrum of a powder sample of quartz.

(ii) *Single-crystal absorption and reflectivity.* In two separate experiments, the single crystals were mounted in a furnace with KBr windows. The metal support of the sample was optimized for large thermal contact with the sample in order to reduce thermal gradients in the crystal. The furnace was mounted on the stage of a Bruker IR microscope which allows the measurement of absorption and reflection spectra with a

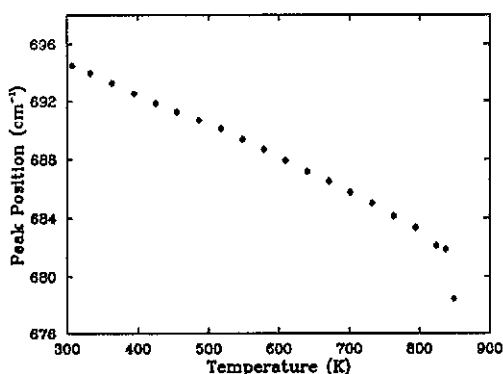


Figure 2. Temperature dependence of the phonon frequency of the 695 cm^{-1} mode in quartz. This phonon signal disappears at $T > T_c$.

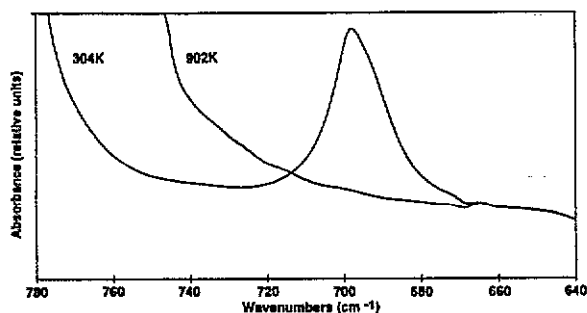


Figure 3. Absorption spectra of a thin slab of quartz with surfaces parallel to the (0001) plane at room temperature and at 902 K. No phonon absorption signal was found near 690 cm^{-1} in the high temperature spectrum.

low frequency cut-off at 550 cm^{-1} . The reflection spectra confirmed the temperature evolution of the mode frequencies already observed in the powder spectra (figure 2).

Again, no signal was observed for the 695 cm^{-1} mode in the β phase. In order to test this observation with a higher degree of sensitivity, the absorbance of the crystal was measured with the IR beam propagating along the crystallographic c axis. Only E symmetry modes are seen in this arrangement. The signal of the 695 cm^{-1} mode appears in a spectral region which is not greatly affected by the absorption of other phonons and can serve as an IR window for quartz. A typical absorption spectrum is shown in figure 3. The maximum of the absorption peak corresponds well with the frequency obtained in the powder experiment (note that the TO-LO splitting is small for this phonon). With increasing temperature, the integral absorption cross section decreases and we observe a slightly smeared-out step at the transition point. At higher temperatures no signal was found (figure 4).

(iii) *Raman spectroscopy*. The details of the scattering experiments were reported by Berge (1984). Here we concentrate on the temperature evolution of the 355 cm^{-1} line which is symmetry forbidden in the high symmetry phase (Shapiro 1969). The integrated Raman scattering intensities for a heating and a cooling run (figure 5) show clearly the step-like character of the phase transition. At temperatures above the transition point, the observed signal was very weak and could hardly be distinguished

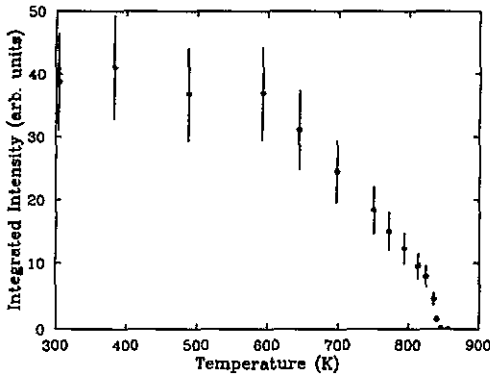


Figure 4. Temperature dependence of the integral absorption cross section of the 695 cm^{-1} mode.

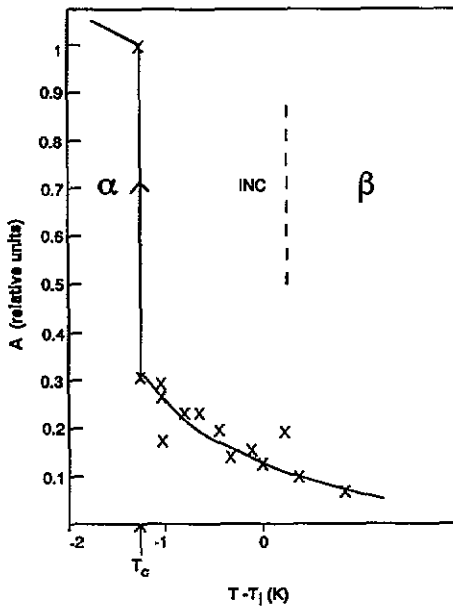


Figure 5. Raman scattering cross section of the 355 cm^{-1} mode at temperatures near the β -INC phase transition. The intensity is normalized to unity in the α phase at the temperature closest to T_c . The intensity decreases rapidly in the INC phase. No signal was found at higher temperatures.

from the background. At still higher temperatures, this signal disappeared completely.

3. Discussion

The temperature evolution of all the phonon signals reported in this paper show the typical order parameter dependence. The microscopic features of the coupling between the phonon coordinates and the lattice distortion will be analysed and presented in a separate paper; here it suffices to argue that the direct coupling between the order parameter, Q , and the intensity, A , and frequency shift, $\Delta(\omega^2)$ are, for symmetry reasons (Salje 1991), of fourth order— $\Delta A \propto \Delta(\omega^2) \propto Q^4$. Additional cross terms might be superimposed with a Q^2 dependence. These cross terms would increase our experimental sensitivity for small values of the order parameter. As we

wish to establish the upper bound of the possible degree of low symmetry distortions in β -quartz, we may ignore these cross terms and find, as lowest order coupling, the typical Q^4 dependence. As additional support for this Q^4 dependence, we find that the data in the low temperature phase are in agreement with this proportionality (Salje *et al* 1991).

The disappearance of the phonon signal of the 695 cm^{-1} mode and the temperature independence of the 795 cm^{-1} mode in the β phase clearly indicate that we do not see α clusters in the β phase. In particular, the step in order parameter at the transition point is also observed in the change in the infrared absorption and Raman scattering signal intensities. This experimental result, at face value, excludes any model of a phase transition which is based on the β phase being a time-averaged structure of α clusters (as defined above). Our results are, on the other hand, fully compatible with the picture of a displacive phase transition driven by dynamical soft modes.

We are not in a position to reconcile our present observations with the results of the computational studies performed in our group (Tautz *et al* 1991) which find heterogeneous states in the β phase. There are two relevant limitations to the interpretation of the experimental results. One concerns the correlation length of the hard-mode experiment, which is calculated using the fluctuation-dissipation theorem in the harmonic limit. Longer correlation lengths might occur for highly coupled modes—this would increase the minimum diameter of a cluster to be seen in the experiment. The second limitation is related to the possibility of having minority α clusters in a matrix of β phase. The upper bound of the volume proportion of such clusters can be estimated from the lower bound of our experimental sensitivity. The Q^4 dependence of the integral absorption cross section leads to the following volume proportions: let the experimental resolution of the intensity measurement be 10^{-4} compared with the intensity at room temperature. The equivalent resolution in Q^2 (relevant for local strain etc) is then 1% and that of Q is about 10%. This means that if clusters exist with a volume proportion of less than 10%, then they would not be observable in our experiment. As they form inhomogeneous states, they would also not change the macroscopic soft-mode behaviour of the phase transition as observed by Axe and Shirane (1970) and Tezuka *et al* (1991). Neither our present results nor these earlier observations of soft modes can exclude the existence of α clusters as a minority state in a non-uniform β phase. What we can exclude, however, is the idea that the β phase itself is simply the time average of resonating clusters of α -quartz on time scales which are longer than phonon times.

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