Calculation of the soft-mode frequency for the alpha – beta transition in quartz

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ABSTRACT

The $\alpha - \beta$ structural transition occurs in quartz at $T_C = 846$ K. The frequency of the soft mode associated with the volume increase, decreases with increasing temperature as the transition temperature is approached.

In this study, we calculate the soft-mode frequency as a function of temperature using the volume data by means of the mode Grüneisen parameter for the $\alpha - \beta$ transition in quartz.

Our calculated frequencies of the soft-mode agree with the observed data from the literature. This shows that the method of calculating the soft mode frequency from the crystal volume is adequate, which can explain the soft mode behavior associated with the $\alpha - \beta$ transition in quartz.

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1. Introduction

Quartz exhibits a phase transition by lowering the symmetry from the high-temperature hexagonal β phase to the low-temperature trigonal α phase at 847.5 K [1]. It was found some years ago that a weak mode of symmetry A$_1$ with room-temperature Raman shift of 147 cm^{-1} grows in intensity by moving toward zero Raman shift as the $\alpha - \beta$ transition is approached [2]. It was stated that this soft mode plays the fundamental role in the $\alpha - \beta$ transition in quartz [2,3]. Since the incommensurate (INC) phase occurs in a narrow temperature range of ~1.3 K between the α and β phases, its occurrence has been attributed to the coupling of the soft mode with TA modes in quartz [4]. As the symmetry changes between the phases, many low-frequency high-amplitude modes of vibration are excited, which causes orientational disorder of the SiO$_4$ tetrahedra in quartz [5]. The soft mode associated with the phase transitions in quartz propagates as a phonon that moves the SiO$_4$ tetrahedra as rigid units [6]. The soft mode behavior of the $\alpha - \beta$ transition in quartz has been studied extensively [7–9], which is associated with the SiO$_4$ rotation – vibration [10] as stated above. Using the temperature dependence of the observed Raman frequencies for the soft mode (147 cm^{-1}) and also the 207 cm^{-1} mode [2], we have calculated the Raman linewidths of those lattice modes close to the $\alpha - \beta$ transition in quartz [11]. In another study [12], we have calculated the temperature dependence of the

Raman frequency shifts and the linewidths for the optical lattice vibrations (128 cm^{-1} and 466 cm^{-1}) in the α phase of quartz using the anharmonic self energy model.

Temperature [10,13,14] and pressure [15,16] dependences of the volume have also been calculated using the molecular dynamics (MD) for the $\alpha - \beta$ transition in quartz, as measured experimentally [17–21].

Vibrational frequencies can be calculated from the crystal volume through the mode Grüneisen parameter. This calculation can also be performed for the $\alpha - \beta$ transition in quartz. Using the observed volume data (neutron diffraction and the unit-cell volume of the average structure) [20], we have calculated the Raman frequency of the 207 cm^{-1} mode at various temperatures for the $\alpha - \beta$ transition in quartz [22] and also for the Raman frequency of an internal mode for SiO$_2$-moganite [23] using the unit cell volume [24]. Very recently, we have calculated [25] the resonant frequency from the neutron diffraction [26] and variation of volume [20] with the temperature in the vicinity of the $\alpha - \beta$ transition in quartz.

In this study, the soft mode frequency (147 cm^{-1}) is calculated as a function of temperature using the volume data [7–9] through the mode Grüneisen parameter close to the $\alpha - \beta$ transition in quartz.

Below, in Section 2 we give our calculations and results. In Section 3, we discuss our results. Conclusions are given in Section 4.

2. Calculations and results

We calculated the soft-mode frequency using the volume data through the mode Grüneisen parameter for the $\alpha - \beta$

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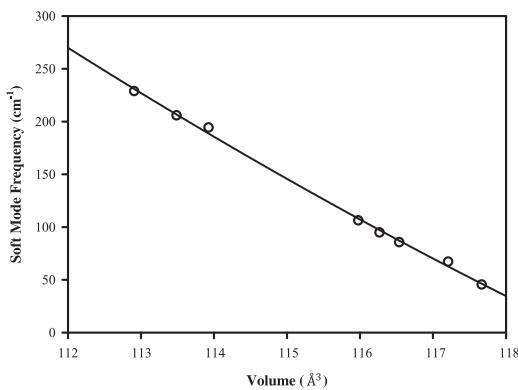 E-mail address: hamit@metu.edu.tr (H. Yurtseven).

Fig. 1. Observed soft-mode frequency [7–9] as a function of volume [17,19] extracted from Eq. (1), as also given previously [10] in terms of the volume increment (%) for the α – β transition in quartz.

transition in quartz. The volume increment can be defined as [10],

$$\delta = \frac{V - V_\alpha}{V_\beta - V_\alpha} \tag{1}$$

where, V_α is the equilibrium α-quartz with cell volume and V_β is the unit cell volume at the α – β transition in quartz. Using the observed values of $V_\alpha(T=0)$ and $V_\beta(T=T_C)$ [19], the volume values were extracted from the values of the volume increment (%) [10] according to Eq. (1), as given in Table 1. As the observed [7–9] soft-mode frequency plotted as a function of the volume increment (%) previously [10], we plot here the soft-mode frequency as a function of volume for the α – β transition in quartz in Fig. 1. From our plot, we obtained the soft-mode frequency with the volume as

$$\nu = a + bV + cV^2 \tag{2}$$

where, a, b and c are constants, which are given in Table 1. Thus, using the observed values of $V_\alpha(T=0)$ and $V_\beta(T=T_C)$ as given above, the corresponding values of the soft-mode frequency were obtained through Eq. (2) as $\nu_\alpha (T = 0)$ and $\nu_\beta (T = T_C)$ for the α – β transition in quartz, as given in Table 1.

The mode Grüneisen parameter γ of the soft mode can be determined from the frequency shifts and volume change by defining

$$\gamma = -\frac{V}{\nu} \frac{d\nu}{dV} \tag{3}$$

According to the variation of the frequency with the volume (Eq. (2)) using the observed data for the soft-mode frequency [7–9] and for the volume data extracted from Eq. (1) (Fig. 1), the γ value can be determined for the soft mode frequency in the α-phase of quartz. By defining the frequency alteration δ' similar to the volume increment δ in Eq. (3) as,

$$1 - \delta' = \frac{\nu - \nu_\alpha}{\nu_\beta - \nu_\alpha} \tag{4}$$

or

$$\delta' = \left(\nu_\beta - \nu \right) / \left(\nu_\beta - \nu_\alpha \right) \tag{5}$$

values of the mode Grüneisen parameter γ can be determined as a ratio,

$$\gamma = \frac{V}{\nu} \cdot \frac{\delta'}{\delta} \tag{6}$$

The values of the mode Grüneisen parameter γ were determined at various temperatures from the volume and frequency data at the temperatures of $T = 0$ and $T = T_C$ according to Eq. (6). The temperature dependence of γ is plotted in Fig. 2 for the α-phase of quartz. Once we determined the mode Grüneisen parameter from the variation of the soft-mode frequency and the volume change according
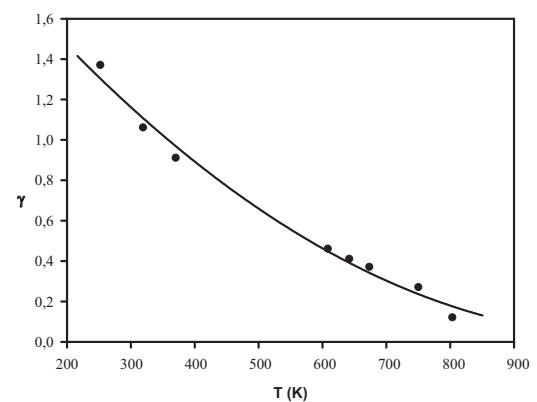

Fig. 2. Variation of the mode Grüneisen parameter γ with the temperature for the α phase of quartz according to Eq. (6).
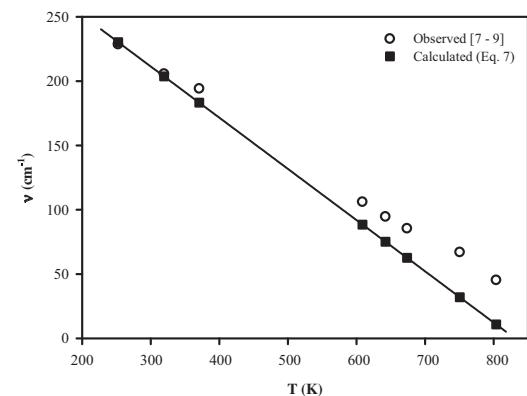

Fig. 3. The Raman frequencies calculated (Eq. (7)) for the soft mode as a function of temperature for the α – β transition in quartz.

to Eq. (6), the soft-mode frequency can then be calculated at various temperatures using the volume data through the mode Grüneisen parameter γ according to the relation

$$\nu = A(T) + \nu_0 \exp \left[-\gamma \ln \left(V(T)/V_0 \right) \right] \tag{7}$$

which can be obtained from Eq. (3) with the additional temperature-dependent $A(T)$ term. This term can be assumed as

$$A(T) = a_0 + a_1 T \tag{8}$$

where, a_0 and a_1 are constants. Values of those coefficients were determined by fitting Eq. (7) to the observed frequencies [7–9] as given in Table 1.

Finally, using the observed data [10], values of the mode Grüneisen parameter γ was generated (Fig. 2), $V_0 = V_\beta$ and $\nu_0 = \nu_\beta$ with the values of the coefficients a_0 and a_1 (Table 1), the soft-mode frequencies were predicted as a function of temperature according to Eq. (7) for the α – β transition in quartz, as plotted in Fig. 3.

3. Discussion

The soft-mode frequency was predicted as a function of temperature using the observed volume data [10] for the α – β transition in quartz, as plotted in Fig. 3. By fitting Eq. (7) to the observed data for the soft-mode frequency [7–9], the fitted parameters of a_0 and a_1 for the temperature-dependent term $A(T)$ were determined (Table 1). The temperature dependence of the mode Grüneisen parameter (γ) was obtained to predict the soft mode frequencies, as plotted in Fig. 2. It decreases as the temperature increases up to the transition temperature ($T_C = 846.5$ K) in quartz, as expected. Since the soft-mode frequency decreases with the increase in

Table 1
Values of the coefficients a, b and c (Eq. (2)), and the coefficients of a_0 and a_1 (Eq. (8)) for the variation of the soft-mode frequency with the volume for the $\alpha - \beta$ transition in quartz (see Fig. 1). Values of the volume and the soft mode frequency at $T = 0$ and $T = T_C$ are also given here.

a (cm^{-1})	b (cm^{-1}/Å^3)	c (cm^{-1}/Å^6)	V_α (Å^3) ($T=0$)	V_β (Å^3) ($T=T_C$)	ν_α (cm^{-1}) ($T=0$)	ν_β (cm^{-1}) ($T=T_C$)	a_0 (cm^{-1})	a_1 (cm^{-1}/K)
13,669.82	−196.02	0.68	110.73	118.03	269.45	34.58	292.95	−0.394

volume (Fig. 1), this decrease in the mode Grüneisen parameter γ with the temperature (Fig. 2), leads to the soft mode frequency decreasing according to Eq. (7) toward the transition temperature T_C, as also observed experimentally [7–10]. As seen from this figure, our calculated Raman frequencies of the soft mode get lower in comparison with the observed data [7–9] as the transition temperature is approached above about 600 K in the α phase of quartz. So, the agreement with the experimental data is much better at low temperatures. This discrepancy near T_C may be due to the critical behavior of the soft mode frequency, which is also reflected on the anomalous change in volume. However, this anomalous behavior is not taken into account in Eq. (7) to predict the soft mode frequency from the volume data. A power-law analysis of the soft mode frequency and the volume might be needed near T_C to describe the anomalous behavior with the critical exponent.

Calculation of the mode Grüneisen parameter γ for the soft mode as a function of temperature was performed basically by using the observed values of the volume (V_α and V_β) and the soft mode frequency $\left(\nu_\alpha \text{ and } \nu_\beta\right)$ at the minimum ($T=0$) and maximum ($T_C = 846.5$ K) temperatures. Between the two extreme temperatures, using the volume and soft mode frequency data, the temperature dependence of the mode Grüneisen parameter γ was generated.

Our γ values which decrease between 1.37 and 0.14 as the temperature increases from about 250 K up to 800 K, respectively, can be compared with our value of $\gamma_P = 0.75$ as the isobaric mode Grüneisen parameter of the Raman internal mode of 501 cm^{-1} for the $\alpha - \beta$ transition in SiO$_2$-moganite [23]. However, for the soft mode of 207 cm^{-1} (at room temperature) we obtained in our recent study [22] the values of $\gamma_P = 5.5$ using the neutron diffraction data for the volume [20] and $\gamma_P = 2.5$ using the unit-cell volume data of the average structure of quartz [20]. Those γ_P values are much higher than the temperature-dependent $\gamma(T)$ values varying from 1.37 to 0.14 as stated above, for the soft mode of 207 cm^{-1}, which we also studied here. There might be two reasons for this discrepancy regarding the values of the mode Grüneisen parameter of the same soft mode (207 cm^{-1}) for the $\alpha - \beta$ transition in quartz. Firstly, for our recent study [22], we used constant values of γ_P to predict the Raman frequencies of the 207 cm^{-1} mode using the observed volume data [8] from two different sources. Secondly, we used the observed frequency data [2] to determine the γ_P values for the 207 cm^{-1} mode in our previous study [22].

In this study, differently from our earlier studies [22,23], we calculated the Raman frequency of the soft mode (207 cm^{-1}) by considering the temperature dependence of the mode Grüneisen parameter for this soft mode (Fig. 2) using the different sources of the observed volume data [17,19] and the soft-mode frequency data [7–10]. There is also contradiction in the literature whether the room-temperature renormalized soft mode is at 147 cm^{-1} [2] or at 208 cm^{-1} [3]. Overall, the method of predicting the soft-mode frequency using the volume data through the mode Grüneisen parameter as given in our earlier studies [22,23] and also in this study, leads to predict the observed behavior of this mode adequately for the $\alpha - \beta$ transition in quartz. Calculating the soft mode frequencies by considering the temperature dependence of the soft-mode Grüneisen parameter as we studied here, can give better insight into the mechanism of the $\alpha - \beta$ transition in quartz.

4. Conclusions

The soft-mode frequency was predicted from the volume data by regarding the temperature dependence of the mode Grüneisen parameter γ for the $\alpha - \beta$ transition in quartz. Our results show that the γ values vary from 1.37 to 0.14 as the transition temperature ($T_C = 846.5$ K) is approached from the low-temperature α-phase in quartz. Using the γ values determined, the soft-mode frequencies were predicted from the volume data by means of the fitting procedure.

The Raman frequencies of the soft mode which we obtained, indicate that the order – disorder transition ($\alpha - \beta$ transition) in quartz is associated with the critical behavior of the soft mode studied here. The method of calculating the Raman frequencies from the volume data through the mode Grüneisen parameter at various temperatures as presented here for the $\alpha - \beta$ transition in quartz, can also be applied to some other molecular crystals exhibiting the soft mode behavior.

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