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Correlations between the resonant frequency shifts and the thermodynamic quantities for the α-β transition in quartz

M.C. Lider, H. Yurtseven*

Department of Physics, Middle East Technical University, 06531 Ankara Turkey

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ABSTRACT

The resonant frequency shifts are related to the thermodynamic quantities (compressibility, order parameter and susceptibility) for the α-β transition in quartz. The experimental data for the resonant frequencies and the bulk modulus from the literature are used for those correlations. By calculating the order parameter from the mean field theory, correlation between the resonant frequencies of various modes and the order parameter is examined according to the quasi-harmonic phonon theory for the α-β transition in quartz. Also, correlation between the bulk modulus in relation to the resonant frequency shifts and the order parameter susceptibility is constructed for the α-β transition in this crystalline system.

1. Introduction

Transition between α and β phases of quartz ($T_c = 847$ K) has been studied extensively using various experimental and theoretical techniques. In particular, measurements of heat capacity [1–3], elastic constants [4], Raman spectroscopy [5,6], neutron scattering [7], light scattering [8] and resonant ultrasound spectroscopy [9] have been reported in the literature.

α-β transition in quartz has also been studied theoretically by molecular dynamic simulations [10–13]. Regarding the thermodynamic properties for the α-β transition in quartz, we have analyzed the heat capacity [14] using the observed data [1] and have examined the Pippard relations [15]. Very recently, we have calculated the tilt angle and susceptibility using the Landau phenomenological model [16]. As spectroscopic studies, we have calculated the Raman frequencies [17] and, we have also calculated variations in the resonant frequency [18] and the soft mode frequency [19] for the α-β transition in quartz.

α-quartz with the low symmetry, changes to the high symmetry in the β-phase ($T_c \sim 847$ K) as the temperature is increased [20]. α-quartz belongs to the trigonal (rhombohedric) – hexagonal system with a 3-order symmetry axis, whereas β-quartz as a hexagonal system has a 6-order symmetry axis [21]. Although α-quartz (trigonal form) and β-quartz (hexagonal) exhibit dielectric properties [22], their crystal structures do not give rise to pyroelectricity because of the symmetry of quartz [23]. It exhibits piezoelectric behavior.

An intermediate phase (IP) also called the incommensurate (INC) phase has been found experimentally between α (low) and β (high) phases of quartz [24]. In the α-phase, the temperature variation of most physical properties can be related to the variation of the order parameter (η) as described by the Landau theory of first order phase transitions [25,26]. Temperature dependence of the fourth power of the average SiO_4 tetrahedral tilt angle (δ) has been taken as the order parameter of the α-β transition [26,27]. An order parameter (η) related to the orientation of SiO_4 tetrahedra is zero in the β phase and it can take two opposite values in the α phase corresponding to Dauphine twins [25].

In the present study, we consider the temperature dependence of the resonant frequency as an order parameter, which is associated with the orientation of SiO_4 tetrahedra in quartz. With increasing temperature toward the transition (α→β), resonant frequencies of various modes exhibit anomalous behavior, as observed experimentally in quartz [9]. Similarly, bulk modulus (K) measurements give this anomalous behavior in the vicinity of the α-β transition in quartz [9]. On that basis, we investigate the correlations between the resonant frequency shifts and the thermodynamic quantities such as order parameter, density difference, susceptibility and the bulk modulus for the α-β transition in quartz. Quasi-harmonic phonon theory in relation to the Landau mean field model is used for those correlations.

Below, we give our calculations and results in Section 2. Our

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

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discussion and conclusions are given in Sections 3 and 4, respectively.

2. Calculations and results

The resonant frequency shifts can be related to some of thermodynamic quantities such as the order parameter, susceptibility and the bulk modulus (isothermal compressibility) close to the phase transitions in molecular crystals. Here, we correlate between the resonant frequency shifts and those thermodynamic quantities near the α-β transition in quartz. Those correlations are given by using a mean field approximation to anharmonic phonon theory [28,29] by deriving the order parameter and the susceptibility from the free energy within the Landau phenomenological model.

2.1. Temperature dependence of the order parameter and susceptibility

Considering the Landau phenomenological model to describe the α-β transition in quartz, the free energy can be expanded in terms of the order parameter Q as

$$G = G_0 + \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6 \quad (1)$$

where the coefficients a>0, c > 0 and b < 0 for the first order transition. By minimizing the free energy with respect to the order parameter ($\partial G/\partial Q = 0$), one finds the temperature dependence of the order parameter as

$$Q^2 = \frac{-b \pm \sqrt{b^2 - 4ac(T - T_c)}}{2c} \quad (2)$$

The inverse susceptibility χ^{-1} can also be derived from the free energy according to

$$\chi^{-1} = \partial^2 G/\partial Q^2 = a(T - T_c) + 3bQ^2 + 5cQ^4 \quad (3)$$

Using the temperature dependence of the order parameter (Eq. (2)), χ^{-1} can be calculated by determining the coefficients through the order parameter Q for the α-β transition in quartz.

2.2. Anharmonic phonon theory

Any phonon frequency ω_k (k is the wave vector and phonon branch) can be modified by anharmonic coupling to the order parameter Q according to [28].

$$\omega_\kappa'^2 = \omega_\kappa^2 + \frac{1}{2}\alpha_k Q^2 \quad (4)$$

where ω_k is the phonon frequency in the absence of any ordering and ω_k' is the frequency modified (renormalized) by coupling to the ordering. α_k is a fourth-order anharmonic coupling coefficient.

Bulk modulus K of the α-quartz can also be related to the $Q^2\chi$ according to the relation [9].

$$K = K^0 + \mu Q^2 \chi \quad (5)$$

where K^0 is the bulk modulus in the absence of ordering (Q = 0 in the β-phase) and μ describes the order parameter coupling coefficient. By assuming that the resonant frequency (ω) is considered as an order parameter (Q) of the α-phase, we can calculate the temperature dependence of the $Q^2\chi$ (=$\omega^2\chi$) for the various modes studied.

Finally, the resonant frequency shifts, $(1/\omega)(\partial\omega/\partial T)$, of the modes can be related to the isothermal compressibility κ_T which is the inverse of the bulk modulus for the α phase of quartz.

In this study, we analyzed the observed resonant frequency data [9] for quartz according to

$$\omega = a_0 + a_1 T + a_2 T^2 \quad (6)$$

where a_0, a_1 and a_2 are constants. Table 1 gives the values of the coefficients a_0, a_1 and a_2 for those observed modes from the resonant ultrasound spectra [9]. From our analysis, those observed resonant frequencies [9] of the modes studied are plotted as a function of temperature in Fig. 1.

The density difference (Δd) between the two phases (α-β transition in quartz) can also be considered as an order parameter Q. We calculated the density difference (Δd) which is essentially the unitcell volume using the observed data from the x-ray diffraction [4] at various temperatures for the α-β transition in quartz, as plotted at various temperatures in Fig. 2. According to Eq. (4), the resonant frequencies (ω_k') considered as the order parameter (Q) as stated above, were compared with the density difference (Δd). Fig. 3 gives our plot of $\omega_k'^2$ versus $(\Delta d)^2$ of the modes studied for the α-β transition in quartz. From those plots, the values of ω_k^2 and the fourth-order anharmonic coupling coefficient α_k (Eq. (4)) were determined in the temperature intervals where the linear variation of ($\omega_k'^2$) with Q^2(or $(\Delta d)^2$) was obtained. As an example, we determined for the 318×10^3 Hz mode the values of $\omega_k^2 = 4.39 \times 10^{10}$ Hz^2 and $\alpha_k = 1.36 \times 10^7$ Hz^2 m^6/kg^2 within the temperatures between 549.9 < T (K) < 839.7 for the α-β transition in quartz (T_c = 847 K).

The inverse susceptibility (χ^{-1}) was also calculated using the order parameter Q according to Eq. (3) for the α-β transition in quartz, as plotted in Fig. 4. Using the values of Q^2 as ω^2 (Eq. (4)) of the resonant frequencies for various modes studied and the χ

Table 1
Values of coefficients according to Eq. (6) for the observed resonant frequencies [9] (at T = 300 K) of various modes indicated for the α-β transition in quartz.

Resonant frequency × 10^3(Hz)	$a_0 \times 10^3$ (Hz)	a_1 (Hz/K)	-a_2 (Hz/K^2)
649	513.4	758.97	1.09
598	477.8	673.15	0.97
558	468.5	487.71	0.81
400	328.6	402.64	0.59
318	273.8	322.57	0.47

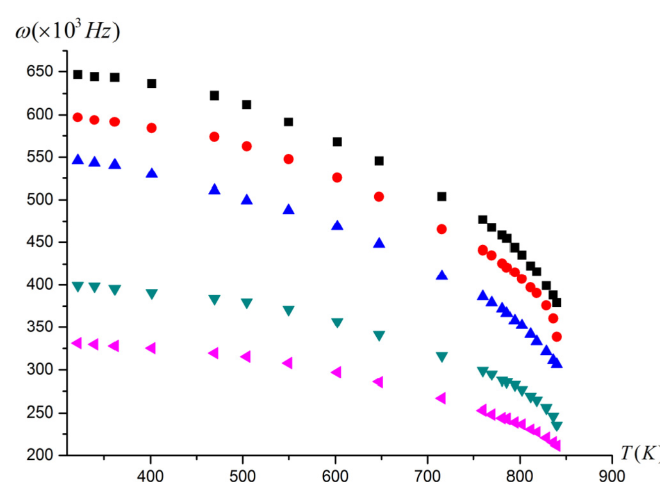

Fig. 1. Temperature dependence of the observed resonant frequencies [9] for various modes according to Eq. (6) for the α-β transition in quartz.