



# Landau mean-field model with the cubic term for the $\alpha$ - $\beta$ transition in quartz

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**Abstract.** Thermodynamic quantities are calculated as a function of temperature by using Landau mean-field model for the  $\alpha$ - $\beta$  transition in quartz. By expanding the Gibbs free energy in terms of the order parameter ( $Q$ ) with the cubic term ( $Q^3$ ), the temperature dependence of the relevant thermodynamic quantities are predicted using the heat capacity ( $C_p$ ), which is fitted to the experimental data from the literature for the  $\alpha$ - $\beta$  transition in quartz. Our results indicate that the Landau mean-field model is adequate to describe the first-order  $\alpha$ - $\beta$  transition in quartz.

**Keywords.** Landau model;  $\alpha$ - $\beta$  transition; quartz.

## 1. Introduction

Crystalline quartz exhibits a first-order transition from the hexagonal  $\beta$  phase (high temperature) with the space group  $D_6^4$  to the trigonal  $\alpha$  phase (low temperature) with the space group  $D_3^4$  at about 846 K.

The  $\alpha$ - $\beta$  transition including the incommensurate (INC) phase ( $\sim 1.3$  K) in quartz has been extensively studied in the literature. Its thermal properties in particular, have been investigated by various experimental and theoretical techniques. Measurements of the heat capacity  $C_p$  exhibit a sharp peak close to the INC phase [1–5]. Some elastic properties of quartz close to the  $\alpha$ - $\beta$  transition have been studied [6–10]. The elastic constants [6] have been related, as we have related the resonant frequency shifts to the order parameter [11,12] and to the elastic constants [13] near the  $\alpha$ - $\beta$  transition in quartz.

Regarding the INC phase in quartz, spectroscopic studies by differential scanning calorimetry (DSC) [1,2], elastic neutron scattering [2,14] and Brillouin scattering [3] have been reported. Also Raman and infrared [15], time resolved triple-axis [16] and the electric field dependent neutron scattering [17] experiments have been performed for the INC phase of quartz. Theoretically, molecular dynamics calculations have been carried out, in particular, on the temperature and pressure dependence of volume near the  $\alpha$ - $\beta$  transition including INC phase in quartz [18–21].

Mean-field theory can be employed to study various physical properties close to the  $\alpha$ -INC- $\beta$  transitions in quartz. Following Landau, one can introduce an order parameter  $\eta$  due to the orientation of  $\text{SiO}_4$  tetrahedra, which is zero in the  $\beta$ -phase and which can take two opposite values in the  $\alpha$ -phase corresponding to Dauphiné twins [1]. In terms of  $\eta$  and

elastic deformations, the gradient interaction model of Aslanian and Levanyuk [22] has been introduced. On the basis of the experimental data, Landau mean-field model has been studied previously [6,8,23,24]. Temperature dependence of the fourth power of the average  $\text{SiO}_4$  tetrahedral tilt angle  $\delta$  was taken as the order parameter of the  $\alpha$ - $\beta$  transition in quartz [25]. We have also studied recently the Landau phenomenological model to calculate the temperature dependence of the tilt angle and susceptibility for the  $\alpha$ - $\beta$  transition in quartz [26]. Very recently, we have applied the Landau phenomenological model as used for the  $\alpha$ - $\beta$  transition in quartz [8], to the metal organic frameworks; in particular, magnetic and thermal properties of chiral  $\text{HyFe}$  and  $\text{HyMn}$  [27].

The thermodynamic properties such as heat capacity ( $C_p$ ), order parameter ( $Q$ ), entropy ( $S$ ) and susceptibility ( $\chi$ ) can be studied as a function of temperature using the Landau mean-field model and they can be compared with the experimental data. Previously, by expanding the Gibbs ( $G$ ) free energy in terms of the even powers of the order parameter ( $Q$ ) up to the sixth order, some thermodynamic quantities have been derived and the excess heat capacity ( $\Delta C_p$ ) in particular was calculated in comparison with the measurements for the first-order  $\alpha$ - $\beta$  transition in quartz using the Landau theory [8]. Also by expanding  $G$  with the cubic term ( $Q^3$ ) the order parameter ( $Q$ ) was predicted and the strain variations were calculated using the neutron diffraction data [8]. As we have calculated the tilt angle (order parameter) and susceptibility in the Landau mean-field model in our earlier study [26], in the present study we calculate some thermodynamic quantities by using the Landau mean-field model with the cubic term ( $Q^3$ ) in the free energy expansion for the first-order  $\alpha$ - $\beta$  transition in quartz. Thermodynamic quantities of interest are

derived from the Gibbs free energy with the cubic term and using the observed data for the excess heat capacity  $\Delta C_p$  [8], their temperature dependences are calculated close to the  $\alpha$ - $\beta$  transition in quartz.

Below in section 2 Landau mean-field model is introduced with the thermodynamic quantities studied. Section 3 includes our calculations and results. Discussion and conclusions are given in sections 4 and 5, respectively.

## 2. Theory

Thermal properties of the  $\alpha$ - $\beta$  transition in quartz can be studied by the Landau phenomenological model. By expanding the Gibbs free energy in terms of the order parameter  $Q$  of the  $\alpha$  phase including cubic term [8],

$$G = \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{3}u|Q|^3 + \frac{1}{4}bQ^4 \quad (1)$$

The  $\alpha$ - $\beta$  transition in quartz can be described with the odd order term (cubic) appearing due to fluctuations [28], which makes the  $\alpha$ - $\beta$  transition a first order. In equation (1),  $T_c$  is the critical temperature with the constants  $a > 0$ ,  $u < 0$  and  $b > 0$ . The order parameter  $Q$  in equation (1) defines the discontinuous variation of the thermodynamic quantities such as thermal expansion, elastic constant, piezoelectric constant, etc. (macroscopic level) with a typical hysteresis at the  $\alpha$ - $\beta$  transition in quartz. It is associated with the large temperature variation of those quantities mostly proportional to  $Q^2$ , as also indicated previously [24]. Temperature dependence of the fourth power of the average  $\text{SiO}_4$  tetrahedral angle  $\delta$  also defines the macroscopic order parameter ( $Q \propto \delta^4$ ) of the  $\alpha$ - $\beta$  transition in quartz [8], as stated above. As a symmetry-breaking order parameter described by Landau theory [23], the change of the symmetry at the  $\alpha$ - $\beta$  transition introduces microscopic order parameter ( $\eta$  and  $\delta$ ) due to a tilt angle of  $\text{SiO}_4$  tetrahedra [2].

As there is no order in the  $\beta$  phase ( $Q = 0$ ), the condition for the first-order transition states that

$$G_\alpha(Q) = G_\beta(0) \quad (2)$$

which gives

$$3bQ^2 + 4u|Q| + 6a(T - T_c) = 0 \quad (3)$$

The two roots of the quadratic equation can be solved as

$$Q_{1,2} = -\frac{2u}{3b} \left\{ 1 \pm \left[ 1 - \frac{9ab}{2u^2} (T - T_c) \right]^{1/2} \right\} \quad (4)$$

Equation (4) gives that at  $T = T_c$  the nonzero  $Q$  solution with the positive root square represents the  $\alpha$ -phase ( $Q \neq 0$ ) with

nonzero  $a$ ,  $u$  and  $b$ , whereas the solution with the negative root square describes the  $\beta$  phase ( $Q = 0$ ). For the first-order  $\alpha$ - $\beta$  transition in quartz, the transition temperature ( $T_{tr}$ ) can be defined as the temperature where the two phases ( $\alpha$  and  $\beta$ ) have the same free energy, which can also be named as the first-order temperature [23]. Owing to the fact that there exists nonzero order parameter ( $Q \neq 0$ ) at the transition temperature ( $T_{tr} > T_c$ ), we can assume that the square root in the  $Q$  solution (equation 4) becomes zero, which then gives

$$T_{tr} - T_c = \frac{2u^2}{9ab} \quad (5)$$

This defines the difference between the transition ( $T_{tr}$ ) and critical ( $T_c$ ) temperatures for the first-order  $\alpha$ - $\beta$  transition in quartz. This temperature difference implies that the first-order transition starts at the critical temperature ( $T_c$ ) and ends up at the transition temperature ( $T_{tr}$ ) with the nonzero order parameter ( $Q$ ). A constant value of  $Q$  can be calculated at  $T_c$  and  $T_{tr}$ . By inserting equation (5) into equation (4), we have

$$Q = -\frac{3a}{u}(T_{tr} - T_c) \left\{ 1 \pm \left[ 1 - \frac{(T - T_c)}{(T_{tr} - T_c)} \right]^{1/2} \right\} \quad (6)$$

At the transition temperature ( $T_{tr}$ ) and the critical temperature ( $T_c$ ), the order parameter  $Q$  becomes

$$Q(T = T_{tr}) = Q_0 = -\frac{3a}{u}(T_{tr} - T_c), \quad Q(T = T_c) = 2Q_0 \quad (7)$$

Thus we find that a constant order parameter ( $Q_0$ ) at  $T = T_{tr}$  is twice as much ( $2Q_0$ ) at  $T = T_c$  (equation 7) where the first-order  $\alpha$ - $\beta$  transition has just started.

In equilibrium, by minimizing the Gibbs free energy ( $\partial G/\partial Q = 0$ ), we get from equation (1)

$$a(T - T_c) + u|Q| + bQ^2 = 0 \quad (8)$$

Equation (8) has the roots of

$$Q_{1,2} = -\frac{u}{2b} \left\{ 1 \pm \left[ 1 - \frac{4ab}{u^2} (T - T_c) \right]^{1/2} \right\} \quad (9)$$

By inserting equation (5) into equation (9) with equation (7), we find the temperature dependence of the order parameter given by

$$Q = \frac{3}{4}Q_0 \left\{ 1 + \left[ 1 - \frac{8}{9} \frac{(T - T_c)}{(T_{tr} - T_c)} \right]^{1/2} \right\} \quad (10)$$

The temperature dependence of the inverse susceptibility ( $\chi^{-1}$ ) of the order parameter  $Q$  can also be derived from

the Gibbs free energy (equation 1) by using the definition  $\chi^{-1} = \partial^2 G / \partial Q^2$ ,

$$\chi^{-1} = a(T - T_c) + 2u|Q| + 3bQ^3 \quad (11)$$

This equation can then be used to describe the inverse susceptibility below ( $Q \neq 0$ ) and above ( $Q = 0$ ) the critical temperature ( $T_c$ ) for the  $\alpha$ - and  $\beta$ -phases, respectively, in quartz. By considering the tilt angle ( $\phi$ ) due to the rotational motion of  $\text{SiO}_4$  tetrahedral which can be related to the macroscopic order parameter ( $Q$ ) according to

$$\phi^4 \propto Q \propto \omega^2 \quad (12)$$

with the soft mode frequency ( $\omega$ ) for the  $\alpha$ -phase of quartz [2,15], the inverse susceptibility  $\chi^{-1}$  can be expressed in terms of the soft mode frequency as

$$\chi^{-1} = a(T - T_c) + 2u^*\omega^2 + 3b^*\omega^6 \quad (13)$$

where  $u^*$  and  $b^*$  are the renormalized second and sixth order coefficients.

Regarding the thermal properties of  $\alpha$ - $\beta$  transition in quartz, some other thermodynamic functions such as heat capacity, entropy, etc. can also be derived from the Gibbs free energy (equation 1) as given below:

Starting from the enthalpy ( $H$ ) and entropy ( $S$ ) associated with the  $\alpha$ - $\beta$  transition in quartz, they can be obtained by using the definitions  $H = \partial(G/T)/\partial(1/T)$  and  $S = -(\partial G/\partial T)_P$ , respectively. From the Gibbs free energy (equation 1), this gives

$$H = \frac{1}{2}aT_cQ^2 + \frac{1}{3}u|Q|^3 + \frac{1}{4}bQ^4 \quad (14)$$

and

$$S = -\frac{1}{2}aQ^2 \quad (15)$$

Also, at a constant pressure, the difference in the entropy at the transition temperature ( $T_{tr}$ ) gives the latent heat ( $L$ ) by using the definition  $L = \Delta S T_{tr}$  as

$$L = -\frac{1}{2}aT_{tr}Q_0^2 \quad (16)$$

where the difference in the entropy ( $\Delta S$ ) defines the order parameter ( $Q_0$ ) at the transition temperature ( $T_{tr}$ ) for the  $\alpha$ - $\beta$  transition in quartz. By using equations (15), (16) and (10) the entropy ( $S$ ) becomes in the form of

$$S = \frac{9}{16} \frac{L}{T_{tr}} \left\{ 1 + \left[ 1 - \frac{8}{9} \frac{(T - T_c)}{(T_{tr} - T_c)} \right]^{1/2} \right\}^2 \quad (17)$$

The excess entropy  $\Delta S$  defines the excess heat capacity  $\Delta C_P$ . According to the definition  $C_P = T \left( \frac{\partial S}{\partial T} \right)_P$ , the heat capacity can be obtained from the entropy (equation 17) in the form of

$$\left( \frac{T}{C_P} \right)^2 = \frac{16(T_{tr} - T_c)^2}{a^2 Q_0^4} \left\{ 1 + \left[ 1 - \frac{8}{9} \frac{(T - T_c)}{(T_{tr} - T_c)} \right]^{-1/2} \right\}^{-2} \quad (18)$$

We can also obtain the temperature dependence of the spontaneous strain  $V_s$  by defining

$$V_s = \frac{V - V_0}{V_0} = \frac{\Delta V}{V_0} \quad (19)$$

where  $V$  is the lattice parameter (volume) of  $\alpha$ -quartz and  $V_0$  represents the reference parameter extrapolated down to the same temperature from the stability field of  $\beta$ -quartz [8]. The temperature dependence of the spontaneous strain ( $V_s$ ) can then be obtained by relating it to the order parameter ( $Q$ ) according to [8]

$$V_s \propto Q^2 \quad (20)$$

for the  $\alpha$ - $\beta$  transition in quartz. Using equation (6) we have

$$V_s = \frac{9}{16} V_{s,0} \left\{ 1 + \left[ 1 - \frac{8}{9} \frac{(T - T_c)}{(T_{tr} - T_c)} \right]^{1/2} \right\}^2 \quad (21)$$

where  $V_{s,0}$  represents the  $V_s$  value or the magnitude of the discontinuity at  $T = T_{tr}$ . The proportionality constant between  $V_s$  and  $Q^2$  cancels out from both sides of equation (20) [8], as  $V_{s,0} \propto Q_0^2$  by the definition in equations (10) and (21). Additionally, regarding the temperature dependence of the anomalous strain  $\Delta L$  defined as

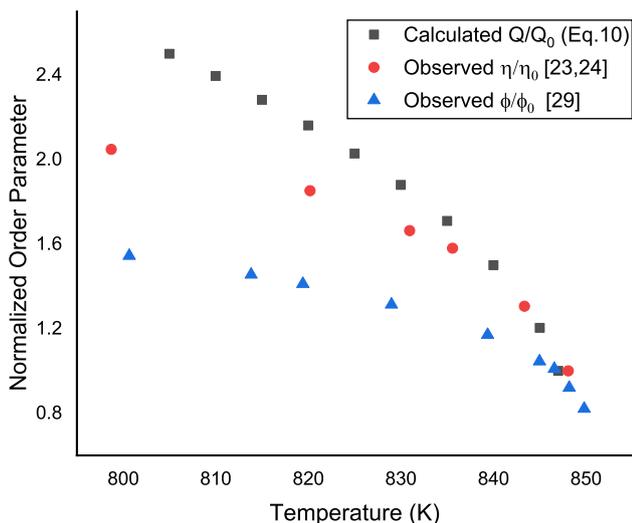
$$\Delta L(T) = L(T) - L_B(T) \quad (22)$$

where  $L_B(T)$  is the background elastic strain,  $\Delta L$  can also be related to the order parameter  $\eta$  according to [6]

$$\Delta L \propto \langle \eta^2 \rangle \quad (23)$$

### 3. Calculations and results

We calculated the temperature dependence of the order parameter ( $Q$ ), inverse susceptibility ( $\chi^{-1}$ ), heat capacity ( $C_P$ ), entropy ( $S$ ) and the spontaneous strain ( $V_s$ ) for the  $\alpha$ - $\beta$  transition in quartz by using the Landau phenomenological model with the cubic term ( $Q^3$ ) according to the Gibbs free energy (equation 1). For this calculation, the expressions derived from the Gibbs free energy were used and they were fitted to the experimental data from literature for comparison.



**Figure 1.** Normalized order parameter calculated as a function of temperature according to equation (10) for the  $\alpha$ - $\beta$  transition in quartz by using the Landau phenomenological model with the cubic term (equation 1). Observed data [23,24,29] are also shown.

### 3.1 Calculation of the order parameter ( $Q$ )

Temperature dependence of the order parameter  $Q$  was calculated according to equation (10) for the  $\alpha$  phase in quartz, as plotted in figure 1. The order parameter  $Q$  was normalized with respect to  $Q_0$  at  $T = T_{tr}$ . In this figure we also show the observed data for the order parameter  $\eta$  (normalized) [2,23,24] and  $\phi$  (normalized) [29] for the  $\alpha$ - $\beta$  transition in quartz. The coefficients  $a$ ,  $b$  and  $u$  as given in the Gibbs free energy (equation 1), were calculated through equations (9) and (10) as provided in table 1. The value of  $Q_0 = 0.117$  was determined from equation (10) in the  $\alpha$ -phase of quartz since  $Q = 1$  (fully ordered) at the absolute temperature ( $T = 0$  K).

Correlation between the macroscopic order parameter ( $Q$ ) and the soft mode frequency ( $\omega$ ) was established according to equation (12) for the  $\alpha$ -phase of quartz. A linear variation of the order parameter  $Q$  with the square of the soft mode frequency ( $\omega^2$ ) was obtained (equation 12) in the form of

$$Q/Q_0 = a' + b'\omega^2 \tag{24}$$

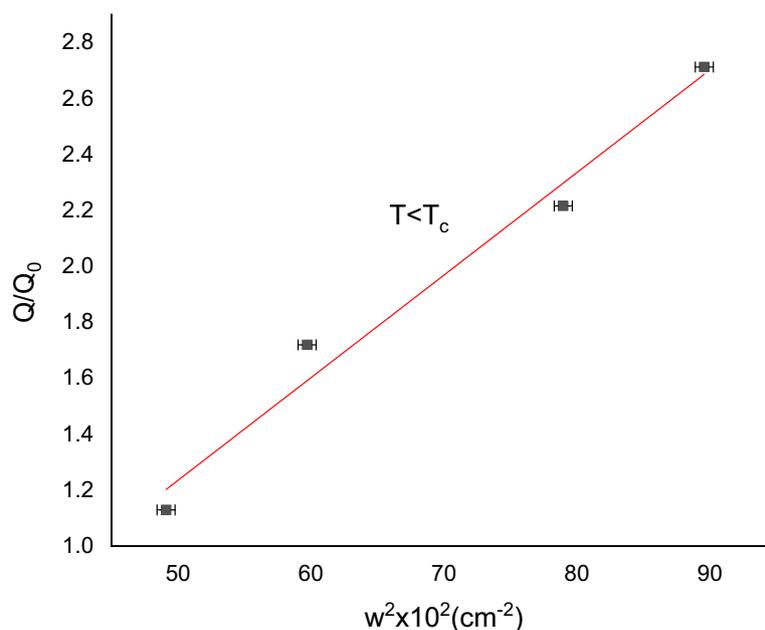
with the coefficients  $a'$  and  $b'$ . Our calculated values of  $Q/Q_0$  (equation 10) were fitted below  $T_c$  to the observed Raman data for the soft mode with the uncertainties [29] which are associated with the  $\alpha$ - $\beta$  transition in quartz as plotted in figure 2 and the coefficients  $a'$  and  $b'$  (equation 24) were determined (table 2).

### 3.2 Calculation of the inverse susceptibility ( $\chi^{-1}$ )

The inverse susceptibility ( $\chi^{-1}$ ) was calculated as a function of temperature in the mean-field model (equation 1) through equation (11) in the  $\alpha$  ( $T < T_c$ ) and  $\beta$  ( $T > T_c$ ) phases of

**Table 1.** Values of the parameters  $a$ ,  $u$  and  $b$  (equation 1);  $u^*$  and  $b^*$  (equation 13); and the values of the order parameter  $Q_0$  (at  $T = T_{tr}$ ) (equation 7), latent heat  $L$  (equation 16) and the observed entropy  $S_\beta$  (in the  $\beta$ -phase) [31] for the  $\alpha$ - $\beta$  transition in quartz. Observed values of the transition temperature ( $T_{tr}$ ) and the critical temperature ( $T_c$ ) [18].

Quartz	$T_{tr}$ (K)	$T_c$ (K)	$a$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )	$-u \times 10^3$ ( $\text{J mol}^{-1}$ )	$b \times 10^3$ ( $\text{J mol}^{-1}$ )	$-u^*$ ( $\text{J mol}^{-1} \text{cm}^{-2}$ )	$b^*$ ( $\text{J mol}^{-1} \text{cm}^6$ )	$Q_0$	$-L$ ( $\text{J mol}^{-1}$ )	$S_\beta$ ( $\text{J K}^{-1} \text{mol}^{-1}$ )
$\alpha$ - $\beta$ Transition	847	840	101.8	18.27	104.1	0.237	0.292	0.117	590.2	105.079



**Figure 2.** Normalized order parameter (equation 10) as a function of the observed Raman soft-mode frequency  $\omega$  (squared) ( $\sim 100 \text{ cm}^{-1}$  at  $500^\circ\text{C}$ ) with the uncertainties [29] according to equation (24) in the  $\alpha$ -phase ( $T < T_c$ ) close to the  $\alpha$ - $\beta$  transition in quartz.

**Table 2.** Values of the parameters  $a'$  and  $b'$  (equation 24);  $a_0$  and  $a_1$  (equation 27) for the  $\alpha$ - $\beta$  transition in quartz. Observed values of the transition temperature ( $T_{tr}$ ) and the critical temperature ( $T_c$ ) [8].

Quartz	$T_{tr}$ (K)	$T_c$ (K)	$-a'$	$b'$ ( $\text{cm}^2$ )	$a_0 \times 10^5$ ( $\text{K}^4 \text{ J}^{-2} \text{ mol}^2$ )	$-a_1$ ( $\text{K}^3 \text{ J}^{-2} \text{ mol}^2$ )
$\alpha$ - $\beta$ Transition	847	840	0.5998	0.0367	1.73	200.3

quartz as plotted in figure 3. For this calculation we used the values of the coefficients  $a$ ,  $u$  and  $b$  (table 1) as we determined for the order parameter  $Q$  (equation 9) below  $T_c$ , whereas  $\chi^{-1} = a(T - T_c)$  was used since  $Q = 0$  above  $T_c$  (figure 3). In this figure, calculated  $\chi^{-1}$  due to the Landau mean-field model with the even power ( $Q^4$ ) [8] is also plotted. Additionally, inverse susceptibility  $\chi^{-1}$  (per atom) calculated by using molecular dynamics simulations in the case of two different system sizes of  $N = 1080$  and  $2060$  ( $N$  is the number of atoms) [16] are shown here for comparison.

Variation of the inverse susceptibility ( $\chi^{-1}$ ) with the square of the silent soft phonon frequency ( $\omega$ ) was also evaluated for the  $\beta$ -phase of quartz. For this calculation, according to equation (13), we used the observed data below [29] and above [30]  $T_c$  for the frequency of the soft mode which can be associated with the mechanism of the  $\alpha$ - $\beta$  transition in this crystalline system. By fitting equation (13) to the observed data for the soft mode frequency above  $T_c$  [30], we determined the values of the renormalized coefficients  $u^*$  and  $b^*$  as given in table 1. Figure 4 shows a plot of  $\chi^{-1}$  vs.  $\omega^2$  in the  $\beta$ -phase ( $T > T_c$ ) of quartz. We were not able to fit equation (13) to the observed data below  $T_c$  [29] for the  $\alpha$ -phase of quartz.

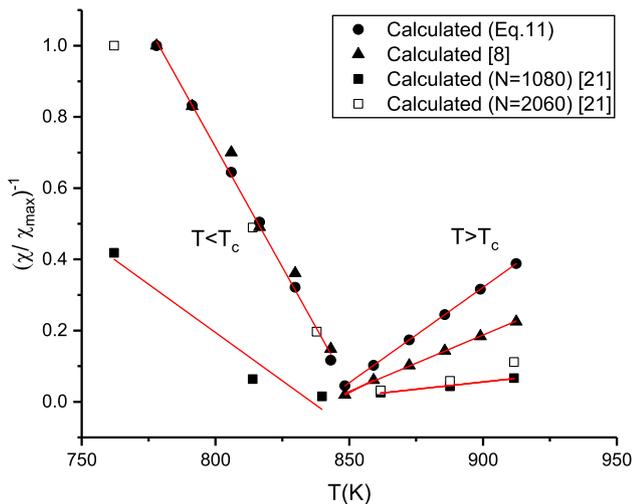
### 3.3 Calculation of the excess heat capacity ( $\Delta C_P$ )

Using the Gibbs free energy with the cubic term (equation 1), the excess heat capacity  $C_P(T)$  was calculated in the form of  $(T/C_P)^2$  (equation 18) for the  $\alpha$ -phase ( $T < T_c$ ). We plot the heat capacity  $C_P$  in the form of  $(T/C_P)^2$  as a function of temperature in figure 5. In this figure, observed data [8] are also plotted for the  $\alpha$ -phase of quartz. Linear variation of  $(T/C_P)^2$  with  $T$  was restricted to the temperature interval of  $720 < T$  (K)  $< 860$  with  $T_{tr} = 847$  K and  $T_c = 840$  K [8] in the  $\alpha$ -phase of quartz. We find from equation (18) the excess heat capacity ( $\Delta C_P$ ) as

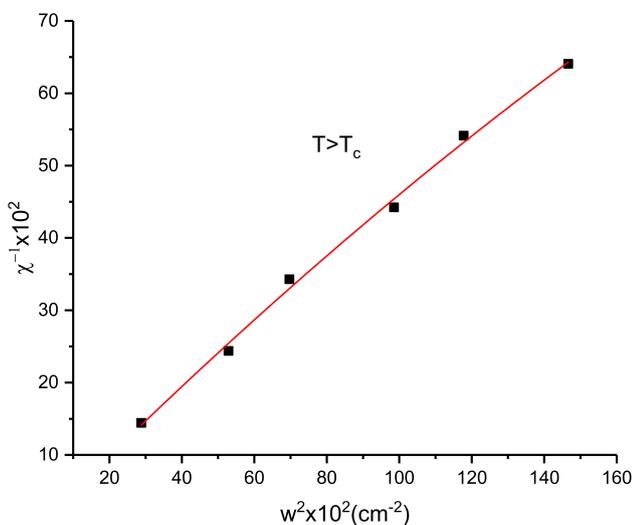
$$\frac{T}{\Delta C_P} = \frac{2(T_{tr} - T_c)}{aQ_0^2} \quad \text{at } T = T_c \quad (25)$$

and

$$\frac{T}{\Delta C_P} = \frac{(T_{tr} - T_c)}{aQ_0^2} \quad \text{at } T = T_{tr} \quad (26)$$



**Figure 3.** Normalized inverse susceptibility  $\chi^{-1}$  calculated as a function of temperature according to equation (11) through equation (10) below and above  $T_c$  for the  $\alpha$ - $\beta$  transition in quartz by using the Landau phenomenological model with the cubic term (equation 1). Calculated values by using the Landau model with the fourth power ( $Q^4$ ) [8] and those from the molecular dynamics simulations [21] are also shown.

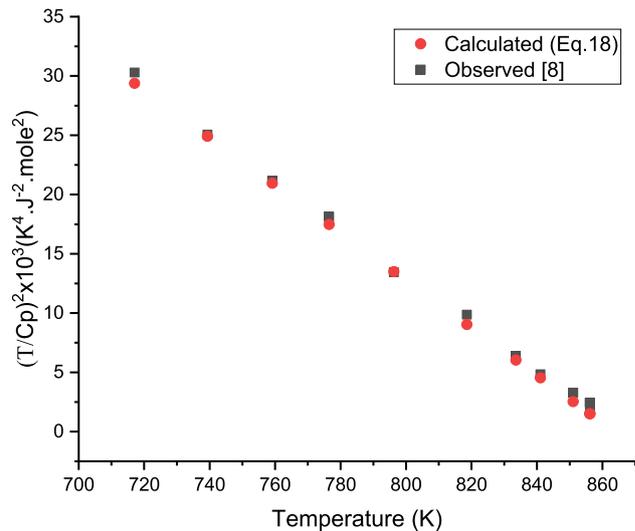


**Figure 4.** Variation of the inverse susceptibility ( $\chi^{-1}$ ) calculated (equation 13) with the square of the observed Raman frequency  $\omega$  (squared) of the silent soft phonon in the  $\beta$ -phase [29] for the  $\alpha$ - $\beta$  transition in quartz.

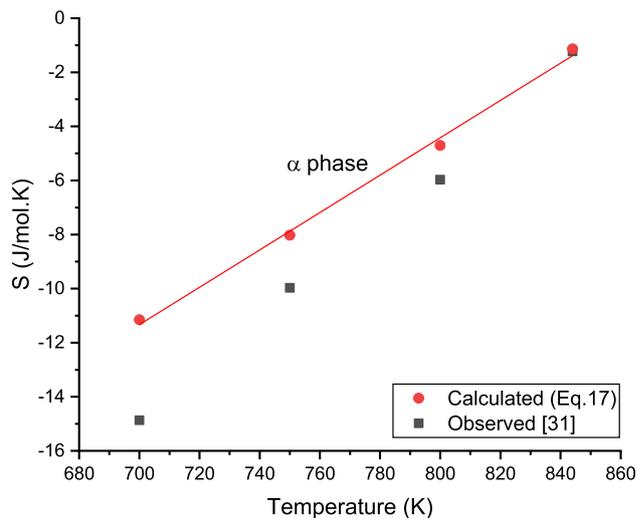
From the linear variation of  $(T/C_p)^2$  with the temperature according to

$$(T/C_p)^2 = a_0 + a_1 T \quad (27)$$

by using the observed data [8], the coefficients  $a_0$  and  $a_1$  were determined as given in table 2.



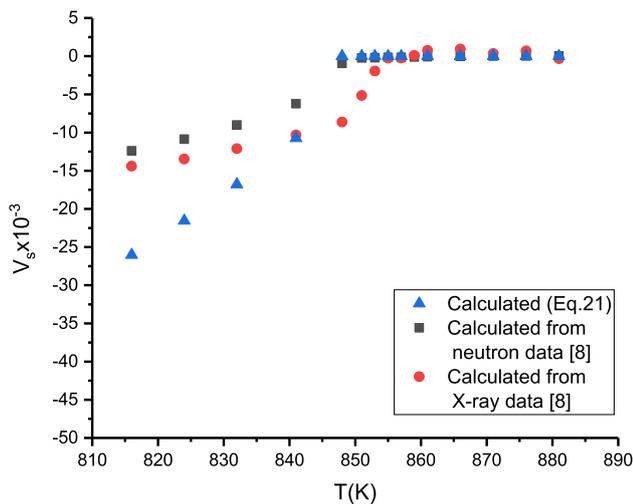
**Figure 5.** Calculated heat capacity  $C_p$  in the form of  $(T/C_p)^2$  as a function of temperature according to equation (18) in the  $\alpha$ -phase of quartz. Observed data [8] are also shown.



**Figure 6.** Calculated entropy  $S$  as a function of temperature according to equation (17) in the  $\alpha$ -phase of quartz. Observed data [31] are also shown.

### 3.4 Calculation of the excess entropy ( $\Delta S$ )

The temperature dependence of the entropy  $S(T)$  was also calculated according to equation (17) for the  $\alpha$ - $\beta$  transition in quartz as plotted in figure 6. For this calculation, equation (17) was fitted to the observed data [31] by defining  $\Delta S = S_\alpha - S_\beta$  where  $S_\alpha$  and  $S_\beta$  are the entropies of the  $\alpha$  and  $\beta$  phases, respectively, in quartz. We used the observed data [31] for  $S_\alpha$  and constant  $S_\beta$  at  $T = 850$  K (table 1), then we calculated  $S$  as a function of temperature for the  $\alpha$ -phase of quartz (figure 6). Observed data [31] are also shown in the figure.



**Figure 7.** Spontaneous strain  $V_s$  calculated as a function of temperature according to equation (21) for the  $\alpha$ - $\beta$  transition in quartz.  $V_s$  values calculated from the neutron and X-ray data [8] are also shown.

### 3.5 Calculation of the spontaneous strain ( $V_s$ )

Temperature dependence of the spontaneous strain was calculated according to equation (21) for the  $\alpha$ - $\beta$  transition in quartz as plotted in figure 7. In this figure, we also show the calculated  $V_s$  by the Landau mean-field model with the even powers in the order parameter ( $Q^4$ ) using the experimental X-ray and neutron diffraction data [8]. Note that when the temperature dependence of  $V_s$  as obtained from the fourth power ( $Q^4$ ) mean-field model, was fitted to the neutron data in the temperature interval of 308–341 K with  $T_c$  as the only variable, it was found that  $T_c = 843.9\text{K}$  [8]. So, we shifted the temperature by about  $\Delta T_c = 3.9\text{K}$  according to the critical temperature ( $T_c = 840\text{K}$ ) which we used in our calculation. For the calculation of the spontaneous strain  $V_s$  (equation 21) we first used the temperature dependence of the reference volume  $V_0$  (equation 19) as obtained previously [8] from linear least squares fits to the combined X-ray and neutron data [8] above  $T_{tr}$  according to the relation

$$V_0 = c_0 + c_1 T \tag{28}$$

where  $c_0$  and  $c_1$  are constants (table 3).  $V_0$  value of  $\sim 118.15 \text{ \AA}^3$  was used as a reference volume at the temperature of  $T_c = 1138\text{K}$  as the stability field of the  $\beta$ -quartz [8]. By using the

observed  $V$  value [8] at  $T_{tr} = 847\text{K}$  (equation 19)  $V_{s,0}$  value was determined (equation 21) (table 3). The spontaneous strain  $V_s$  was then calculated as a function of temperature according to equation (21) for the  $\alpha$ - $\beta$  transition in quartz.

Our calculated order parameter  $Q$  (equation 10) was also related to the strains  $V_s$  and  $\Delta L$  at various temperatures in the  $\alpha$ -phase close to the  $\alpha$ - $\beta$  transition in quartz. Square of the order parameter in the normalized form  $(Q/Q_0)^2$ , which was calculated (equation 10) is plotted in figure 8a as a function of the spontaneous strain  $V_s$  (equation 21) for the  $\alpha$ -phase of quartz according to

$$(Q/Q_0)^2 = c'_0 + c'_1 V_s \tag{29}$$

with constants  $c'_0$  and  $c'_1$  as determined (table 3). Also, by defining the temperature dependence of the elastic strain (equation 22),  $(Q/Q_0)^2$  is plotted as a function of  $\Delta L(T)/L_B(T)$  close to the  $\alpha$ - $\beta$  transition in quartz (figure 8b). In this figure, the observed data for the elastic strain  $\Delta L$  with the temperature dependence of the background elastic strain  $L_B(T)$  according to

$$L_B(T) = b_0 + b_1 T \tag{30}$$

where the values of the coefficients  $b_0$  and  $b_1$  [6] were used (table 4). A nonlinear relation between  $(Q/Q_0)^2$  and  $\Delta L/L_B$  was also obtained by using

$$(Q/Q_0)^2 = b'_0 + b'_1 (\Delta L/L_B) \tag{31}$$

for the INC (incommensurate)- $\beta$  phase transition in quartz. The coefficients  $b'_0$  and  $b'_1$  were determined in two different temperature regions as given in table 4. As the values  $T_0 = T_{tr} = 845.7\text{K}$  and  $T_c = 838.7\text{K}$  ( $T_0 - T_c = 7\text{K}$ ) were obtained experimentally [6], we shifted the temperature difference ( $T_{tr} - T_c$ ) with respect to the observed values of  $T_{tr} = 847\text{K}$  and  $T_c = 840\text{K}$  [8] which were used in our plot (figure 8b).

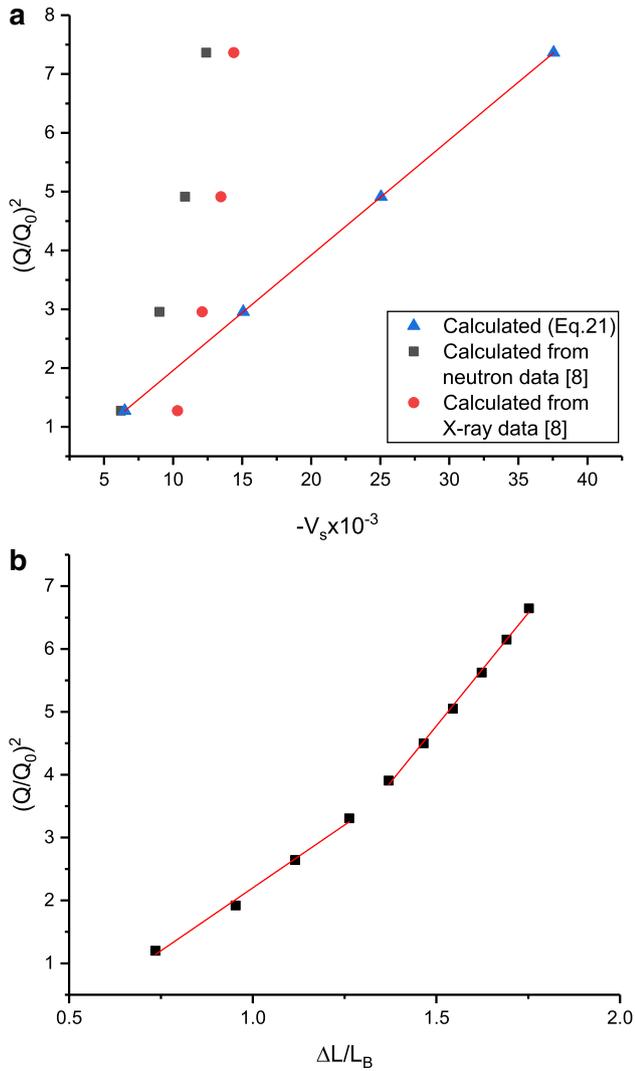
## 4. Discussion

Normalized order parameter ( $Q/Q_0$ ) calculated (equation 10) at various temperatures, exhibits anomalous behaviour as shown for the observed  $\eta/\eta_0$  and  $\phi/\phi_0$  when the transition temperature ( $T_{tr} = 847\text{K}$ ) is approached (figure 1) close to the  $\alpha$ - $\beta$  transition in quartz. Our calculated  $(Q/Q_0)$  values are

**Table 3.** Values of the observed spontaneous strain  $V_0$  and  $V_{s,0}$  (at  $T = T_{tr}$ ) [8]; coefficients  $c_0$  and  $c_1$  (equation 28) with the observed critical temperature ( $T_c$ ); and the values of the coefficients  $c'_0$  and  $c'_1$  (equation 29) for the  $\alpha$ - $\beta$  transition in quartz.

Quartz	$V_0$ ( $\text{\AA}^3$ ) at 1138 K	$c_0$ ( $\text{\AA}^3$ )	$-c_1 \times 10^{-5}$ ( $\text{\AA}^3\text{K}^{-1}$ )	$T_c$ (K)	$-V_{s,0} \times 10^3$ ( $\text{\AA}^3$ )	$c'_0$	$c'_1 \times 10^{-3}$
$\alpha$ - $\beta$ Transition	118.15	118.15	3.64	843.9	5.1	0	5.1

relatively higher in magnitude with increasing slope than those observed  $\eta/\eta_0$  [23,24] and  $\phi/\phi_0$  [29] data towards  $T_{tr}$  (figure 1). As seen in figure 2, the macroscopic order parameter ( $Q/Q_0$ ) varies linearly with the square of the



**Figure 8.** (a) Variation of the normalized order parameter  $Q$  (equation 10) with the spontaneous strain (equation 21) through equation (29) for the  $\alpha$ - $\beta$  transition in quartz.  $V_s$  values calculated from the neutron and X-ray data [8] are also shown. (b) Variation of the normalized order parameter  $Q$  (equation 10) with the observed [6] elastic strain  $\Delta L$  normalized (equation 22) through equation (31) for the  $\alpha$ - $\beta$  transition in quartz.

Raman frequency ( $\omega^2$ ) in the  $\alpha$  phase ( $T < T_c$ ) of quartz. This indicates that the square of the frequency of the soft mode can be associated with the order parameter in regard to the mechanism of the  $\alpha$ - $\beta$  transition in quartz.

A linear decrease ( $T < T_c$ ) and increase ( $T > T_c$ ) was obtained for the variation of the inverse susceptibility ( $\chi^{-1}$ ) with the temperature close to the  $\alpha$ - $\beta$  transition in quartz (figure 3). Our calculated  $\chi^{-1}$  according to equation (11) which was derived from the Gibbs free energy with the cubic term  $Q^3$  (equation 1) was compared with those calculated from the free energy with the  $Q^4$  term [8] in the Landau phenomenological model and also with those calculated by the molecular dynamics simulation for two different system sizes ( $N = 1080$  and  $2060$ ) [21]. Our calculated  $\chi^{-1}$  shows similar critical behaviour (below and above  $T_c$ ) with relatively higher values above  $T_c$  as compared with those calculated, whereas below  $T_c$ ,  $\chi^{-1}$  calculated with the  $Q^3$  (equation 11) matches with those values due to the  $Q^4$  term [8].

We also examined the variation of the inverse susceptibility ( $\chi^{-1}$ ) with the square of the Raman frequency ( $\omega^2$ ) for the soft mode ( $\sim 100 \text{ cm}^{-1}$  at  $500^\circ\text{C}$ ) above  $T_c$  [30] according to equation (13) as stated above (figure 4). A linear variation of  $\chi^{-1}$  was obtained with the  $\omega^2$  above  $T_c$  as expected within the temperature interval studied close to the  $\alpha$ - $\beta$  transition in quartz. A nonlinear variation which occurs can be attributed to the cubic term in  $\omega^2$  (or the third term) in equation (13). However, its contribution to the  $\chi^{-1}$  is almost insignificant so that the  $\chi^{-1}$  essentially varies linearly with the  $\omega^2$  of the soft mode accompanied with the mechanism of the  $\alpha$ - $\beta$  transition in quartz. This also indicates that the square of the soft mode frequency ( $\omega^2$ ) can be considered as an order parameter (equation 12) and the Gibbs free energy (equation 1) can be expanded in terms of the  $\omega^2$  as the macroscopic order parameter  $Q$  from which the  $\chi^{-1}$  can be obtained (equation 13) for the  $\alpha$ - $\beta$  transition in quartz.

Regarding the temperature dependence of the excess heat capacity  $\Delta C_p$ , a linear variation of  $(T/C_p)^2$  with the temperature was obtained within the temperature interval of  $720 < T \text{ (K)} < 860$  (figure 5) as stated above whereas for a much wider range of temperature well below  $T_c$  in the  $\alpha$ -phase,  $(T/C_p)^2$  varies nonlinearly with the temperature according to equation (18). This linear variation of  $(T/C_p)^2$  with  $T$  which we obtained from the Gibbs free energy with the cubic  $Q^3$  term (equation 1), is close to that obtained from the free

**Table 4.** Values of the coefficients  $b_0$  and  $b_1$  (equation 30);  $b'_0$  and  $b'_1$  (equation 31) within the temperature intervals indicated with the observed transition temperature  $T_0$  for the elastic strain  $\Delta L$  [6] close to the INC- $\beta$  transition in quartz.

Quartz	$T_0$ (K)	$b_0$ (cm)	$b_1 \times 10^{-5}$ (cm K $^{-1}$ )	Temperature interval (K)	$-b'_0$	$b'_1$	Temperature interval (K)
INC- $\beta$ transition	845.7	1.00834	1.5386	$842.23 < T < 846.7$	6.002	7.185	$801.1 < T < 826.8$
					1.803	4.002	$831.9 < T < 846.2$

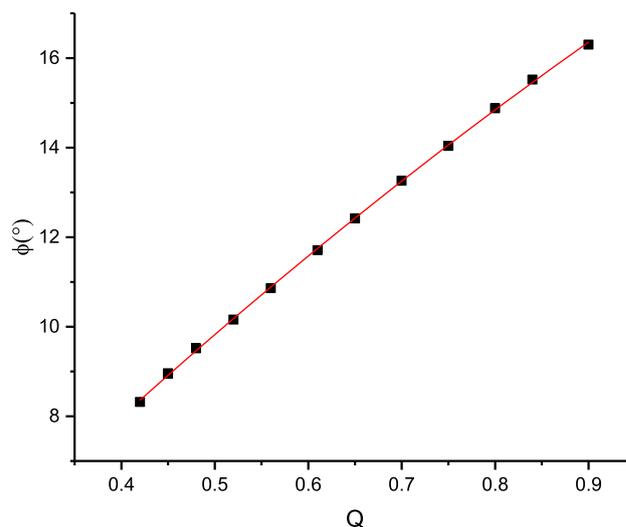
energy with the  $Q^4$  term, according to

$$(T/C_p)^2 = 1.47 \times 10^5 - 173.0T \tag{32}$$

within the temperature interval we studied, as compared to equation (27) with the values of  $a_0$  and  $a_1$  (table 2). Thus, we conclude that the similar critical behaviour is obtained within almost the same temperature interval for both the temperature dependence of the linear  $(T/C_p)^2$  (equation 27 through equation 18) as derived from the Gibbs free energy with the cubic  $Q^3$  term and with the  $Q^4$  term (equation 32) [8] in the Landau phenomenological model. Similarly, we can interpret the behaviour of the entropy ( $S$ ) increasing with increase in temperature which agrees with the experimental data [31] as obtained for the  $\alpha$ -phase according to equation (17), as shown in figure 6. This indicates that motions of the nearest-neighbour  $\text{SiO}_4$  tetrahedra are highly correlated with the large nearest-neighbour coupling constant. In the temperature interval studied, this increase is nearly linear as the variation of  $(T/C_p)^2$  with  $T$  (decreasing) and we expect that well above  $T_c$  the entropy saturates in the stabilized  $\beta$ -phase.

The spontaneous strain ( $V_s$ ) exhibits anomalous behaviour, which increases with increase in temperature in the  $\alpha$ -phase towards the transition temperature ( $T_{tr}$ ) whereas it stabilizes in the  $\beta$ -phase as we calculated (equation 21) using the Landau phenomenological model as plotted in figure 7. The  $V_s$  calculated (equation 21) from the Gibbs free energy with the cubic  $Q^3$  term (equation 1) agrees with the similar plot which was obtained by calculating  $V_s$  from the free energy with the  $Q^4$  term on the basis of the observed neutron and X-ray data for the volume  $V$  [8], as also plotted in figure 7. In relation to the macroscopic order parameter an almost linear correlation was obtained between  $(Q/Q_0)^2$  and  $V_s$  (figure 8a). Values of the slope ( $c'_1$ ) and intercept ( $c'_0$ ) for the  $(Q/Q_0)^2$  vs.  $V_s$  graph were determined according to equation (29) within the temperature intervals of  $793.9 < T \text{ (K)} < 845.9$  in the  $\alpha$ -phase of quartz. On the contrary  $(Q/Q_0)^2$  varied nonlinearly with the normalized elastic strain  $\Delta L/L_B$  (figure 8b) for the  $\alpha$ - $\beta$  transition in quartz. Linear variations of  $(Q/Q_0)^2$  with  $\Delta L/L_B$  were obtained in the two different temperature regions (figure 8b) with the values of slopes ( $b'_1$ ) and intercepts ( $b'_0$ ) according to equation (31) (table 4).

Regarding the tilt angle ( $\phi$ ), anomalous behaviour of the macroscopic order parameter  $Q$  was directly related to the tilt angle ( $\phi$ ) due to the rotational motion of  $\text{SiO}_4$  tetrahedral in



**Figure 9.** Tilt angle  $\phi$  as a function of macroscopic order parameter  $Q$  according to equation (33) in the  $\alpha$  phase close to the  $\alpha$ - $\beta$  transition in quartz. Observed data [23,32] are also shown.

quartz previously [8] according to the quadratic equation

$$\phi = A Q + B Q^2 \tag{33}$$

where  $A$  and  $B$  are constants. We also fitted those values of  $\phi$  extracted from structure refinements [32] and data of Young in [23] to our calculated  $Q$  (equation 10) values according to equation (33), as plotted in figure 9 and we determined the coefficients  $A$  and  $B$  (table 5). We find a linear variation of  $\phi$  with  $Q$  (equation 33), which indicates that the measured tilt angle ( $\phi$ ) can also be considered as the macroscopic order parameter ( $Q$ ).

It has been pointed out that at the macroscopic level the order parameter  $\eta$  is associated with the new physical properties appearing in the  $\alpha$  phase such as piezoelectric constant, elastic constant, etc. [24], as we have also studied previously [13]. Close to the transition, nonlinear variations are observed for several physical properties as the elastic constants due to thermal fluctuations [24]. At high temperatures in the  $\beta$  phase ( $Q = 0$ ), many thermodynamic quantities have smaller linear variations whereas near the transition temperature due to nonlinear variations of the thermodynamic quantities as observed experimentally, our calculations from the Landau mean-field model agree with the experimental results in a

**Table 5.** Values of the coefficients  $A$  and  $B$  (equation 33) within the temperature interval indicated for the  $\alpha$ - $\beta$  transition in quartz. Observed values of the transition temperature ( $T_{tr}$ ) and the critical temperature ( $T_c$ ) [8].

Quartz	$T_{tr}$ (K)	$T_c$ (K)	$A$ ( $^\circ$ )	$-B$ ( $^\circ$ )	Temperature interval (K)
$\alpha$ - $\beta$ Transition	847	840	22.009	4.058	$273 < T < 823$

limited range. So, the mean-field theory we used here to calculate mainly the macroscopic order parameter, heat capacity and entropy is restricted to, as compared to the observed data, the temperature interval close to the  $\alpha$ - $\beta$  transition in quartz. As seen from figure 1, the macroscopic order parameter ( $Q$ ) calculated (equation 10) agrees with the experimental data [23,24,29] within the temperature interval of about 830 to 847 K [23,24] nearly 7 K close to the transition temperature ( $T_{tr}$ ) and from 845 to 850 K [29] for the  $\alpha$ - $\beta$  transition in quartz. The temperature interval where the mean-field theory holds is  $720 < T \text{ (K)} < 850$  for the heat capacity as stated above in the form of  $(T/C_p)^2$  calculated as a function of temperature according to equation (18) through equation (27), which agrees with the observed data [8] as given in figure 5. However calculated entropy  $S$  (equation 17) seems to agree with the experimental data [31] in a very short temperature interval (most likely in a couple of degrees) close to the transition temperature ( $T_{tr} = 847 \text{ K}$ ), as plotted in figure 6. As the temperature decreases (away from the  $T_{tr}$ ), calculated  $S$  is diverted significantly from the observed data [31] (figure 6). This indicates that the mean-field theory for the entropy  $S$  is valid in the vicinity of the transition temperature ( $T_{tr}$ ) as approached from the  $\alpha$  phase. Also, it has been stated that the INC phase can occur when the order parameter couples with the degrees of freedom such as acoustic phonons [28,33]. Regarding the coupling between the strain and the order parameter, energy is stabilized for the  $\alpha$ -quartz and it is responsible for the first-order transition [1]. A large spontaneous strain generated due to the coupling of the phonon coordinates and the lattice distortion causes the  $\alpha$ - $\beta$  transition [29]. In this study, we have not considered coupling between the macroscopic order parameter ( $Q$ ) and phonons associated with the  $\alpha$ - $\beta$  transition in quartz. Also, we have not considered coupling between strain ( $V_s$ ) and the order parameter ( $Q$ ) for the first-order transition. Without any coupling terms in the free energy (equation 1) of the Landau phenomenological model, we were able to explain the thermodynamic properties of quartz close to the first-order  $\alpha$ - $\beta$  transition, as we studied here. Undoubtedly, coupling terms can be added to the free energy (equation 1) to investigate some changes if any for the first-order  $\alpha$ - $\beta$  transition in quartz by using the Landau phenomenological model which we introduced here.

## 5. Conclusions

The mean-field model with the cubic term ( $Q^3$ ) expanded in the free energy was used to describe the first-order  $\alpha$ - $\beta$  transition in quartz. Thermodynamic quantities were calculated from the free energy by using the observed data for the excess heat capacity ( $\Delta C_p$ ) from the literature for the  $\alpha$ - $\beta$  transition in quartz.

Our calculations show that the Landau mean-field model is satisfactory to describe the first-order  $\alpha$ - $\beta$  transition in quartz.

This also indicates that the mean-field model can be applied to some other crystalline systems to describe their thermal properties close to the phase transitions.

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