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A theoretical consideration of the intermediate phase in α-β transition of quartz

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Abstract. Recently, a thermodynamically stable phase between α (low) and β (high) phases of quartz has teen found. This paper explains the three phases by a statistical theory of Bragg-William's type by assuming three states of SiO_4 tetrahedron along a-axis. Adjusting the interaction parameters one can predict the successive transitions of the first-order (T_C) and the nearly second-order (T_Q). Also with an assignment of $T_C = 573°C$, one obtains $T_Q = T_C + 1{\cdot}2$ degree which fits to the experiment. The difference in energy between Dauphiné twin bonding and the normal bonding is estimated to be 0·525 eV.

Keywords. Phase transition theory; quartz.

1. Introduction

Recently, we found an intermediate phase between α (low) and β (high) phases of quartz (Gouhara *et al* 1983). Figure 1 is the most direct illustration of the new phase. The figure is an x-ray oscillating topograph* (Schuttky 1965) near the transition temperature ($T_C = 573°C$) and under a small thermal gradient. The differences in the intensity of different phases are mainly due to the difference in the degree of extinction. The details of the contrasts are given in Gouhara *et al* (1983).

The temperature region of the intermediate phase (IP) is about 2 degrees above T_C. Several evidences show that the transition between α and IP is of first-order and the transition between IP and β is of second-order. Recently, distinct satellite spots were also observed near the strong Laue spots (Gouhara *et al* 1983). Analysis shows that IP has a character of incommensurate phase**.

This paper intends to show that the successive phase transitions can be understood by statistical mechanics assuming three energy states of SiO_4 tetrahedron. Historically, Wannier (1959) proposed a theory of Bragg-William's type assuming two energy states but the transition was predicted to be of the second-order. Recent experimental evidences favour the first-order transition. The present theory can predict that the transition between α and IP is of first-order whereas the transition between IP and β can be of second-order or at least a weak first-order. Our experimental results agree with this prediction.

2. Free energy of the system

Let us consider the structure of quartz in figure 2, which illustrates only Si atoms in β-phase. Si locates in the middle of three equivalent a-axes of a unit cell. The crystal has

* This is essentially equivalent to the traverse pattern of Lang's technique.

** Recently, a similar result obtained by means of neutron diffraction is reported (Dolino and Bachheimer 1983). Since no experiment curve is published we cannot compare their results with ours.

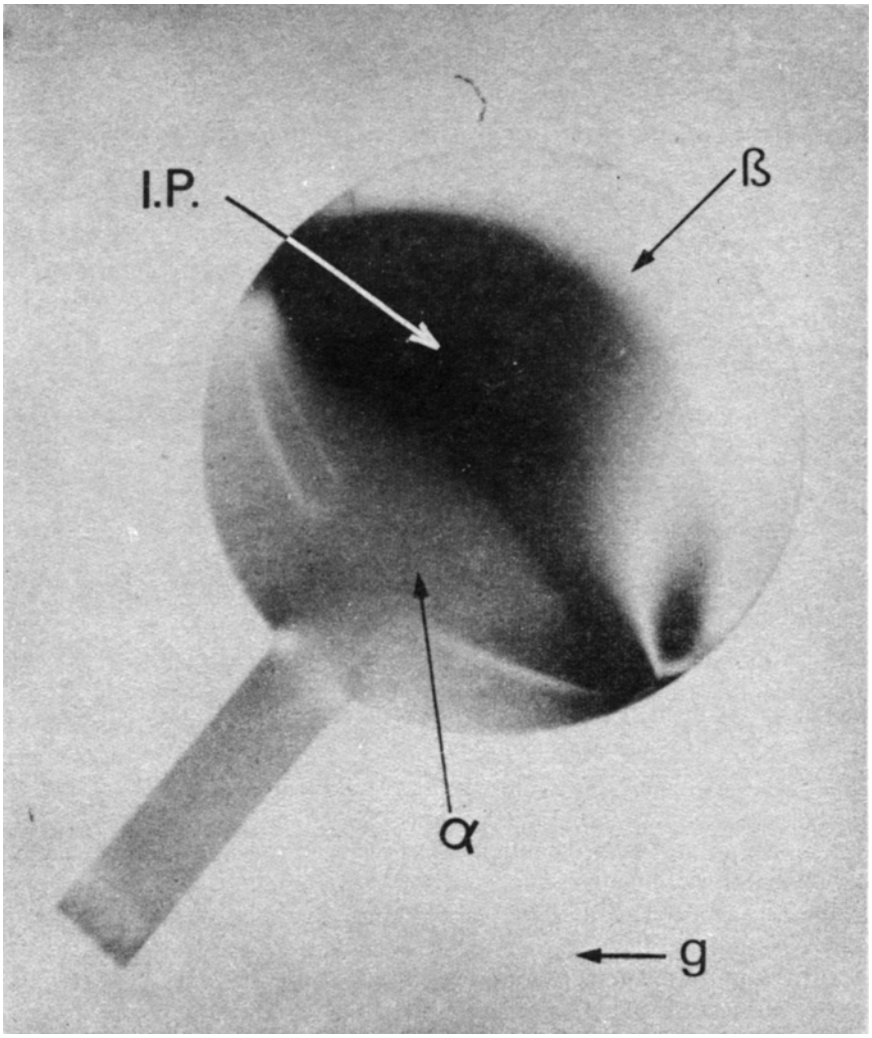

Figure 1. Three phases of quartz in x-ray diffraction topograph taken near 573°C.

six-fold axes. In α-phase, Si is displaced by $\pm u$ along **a**-axis. The crystal then transforms to the structure of three-fold symmetry. The phases corresponding to $\pm$ are referred to α_1 and α_2, which are mutually equivalent. The macroscopic coexistence is traditionally called Daupine twin. Incidentally, the separation by faint white curves in the α phase of figure 1 can be interpreted to be the twinning of this sort, which was caused by thermal strain when the temperature of the specimen was decreased from β phase.

In the present theory, it is assumed that Si can take three positions on **a**-axis; $u = 0$ and $\pm u$. The oxygen tetrahedron is associated to each Si. They also take three states corresponding to the positions of Si. Henceforth, the three states are denoted by the suffixes 0, 1 and 2.

Since Si–O bonding is homopolar, it is reasonable to take into account only the interaction between the nearest neighbours of tetrahedron units. The interaction

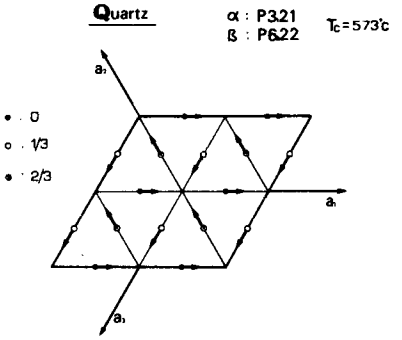

Figure 2. Static models of β-quartz (Si only).

energy is listed in table 1. Besides, we assume the intrinsic energy of the unit, which are denoted by ε_0 and $\varepsilon_1 = \varepsilon_2 \equiv \varepsilon$.

Assuming the mean-field approximation (Bragg–William's approximation), one can write the total energy in the form

$$U/N = \bar{u}_0 + \bar{\varepsilon} n_0 + 2\bar{\tau} n_0^2 + 4\bar{\mu} n_1 n_2. \tag{1a}$$

In the special case of $n_1 = n_2$, it has the form

$$U/N = \bar{u}_0 + \bar{\mu} + (\bar{\varepsilon} - 2\bar{\mu}) n_0 + (2\bar{\tau} + \bar{\mu}) n_0^2. \tag{1b}$$

Here, N is the total number of the tetrahedron unit, and n_i is the population ratio in the state i. Obviously, the condition

$$n_0 + n_1 + n_2 = 1 \tag{2}$$

must be satisfied. The (reduced) energy parameters $\bar{u}_0$, $\bar{\varepsilon}$ etc. are given by

$$\bar{u}_0 = \varepsilon + 2\tau, \tag{3a}$$

$$\bar{\varepsilon} = \varepsilon_0 - \varepsilon - 4\tau + 4\mu_0, \tag{3b}$$

$$\bar{\tau} = \tau_0 + \tau - 2\mu_0, \tag{3c}$$

$$\bar{\mu} = \mu - \tau. \tag{3d}$$

Since α-phase is stable at a sufficiently low temperature, $U(n_0 = 1, n_1 = n_2 = 0)$ must be larger than $U(n_0 = 0, n_1 = 1, n_2 = 0)$. This implies that

$$\bar{\varepsilon} + 2\bar{\tau} > 0. \tag{4}$$

Table 1. Interaction energy of the nearest neighbours of SiO_4 tetrahedron. Symmetry is taken into account.

	0	1	2
0	τ_0	μ_0	μ
1	μ_0	τ	μ
2	μ	μ	τ

Also, one can anticipate the right pair ($i = j$) has less interaction energy than the wrong pair ($i \neq j$). Then, the following inequalities must be fulfilled.

$$\bar{\varepsilon} > 0,\ \bar{\tau} < 0,\ \bar{\mu} > 0 \tag{5a, b, c}$$

The entropy S is the mixing entropy of Nn_0, Nn_1 and Nn_2 in N sites. Therefore, it has the expression

$$S = k \log\left((1/N)^N \frac{N!}{n_0!\, n_1!\, n_2!} \right), \tag{6a}$$

$$= -kN[n_0 \log n_0 + n_1 \log n_1 + n_2 \log n_2], \tag{6b}$$

where k is the Boltzmann constant and Stirling's approximation is used in the last expression.

In the theormodynamical equilibrium the Helmholtz-free energy $[F = U - TS]$ must be minimum with respect to two independent variables of n_0, n_1 and n_2. Various expressions are available as the equilibrium conditions. For example,

$$n_0 \exp[\{(\bar{\varepsilon} - 4\bar{\mu}) - 4(|\bar{\tau}| - \bar{\mu})n_0\}/kT] = n_1 \exp[-4\bar{\mu}n_1/kT], \tag{7a}$$

$$= n_2 \exp[-4\bar{\mu}n_2/kT]. \tag{7b}$$

Wannier's two-state theory (Wannier 1959) ($i = 1, 2$) is a special case of $\bar{\varepsilon} \gg 4\bar{\mu}$. In this case, the equilibrium condition reduces to the last relation (7b). The phase transition occurs at

$$T_W = 2\bar{\mu}/k. \tag{8}$$

The present theory is more versatile. Depending on the energy paramters, the various types of the phase transitions are described. Since this paper intends to show the possibility of the successive transitions (α-IP-β), we shall not discuss the details and present only some numerical results in the next section. As to the formal discussion, it is worth referring to the paper of Nakano (1964) which dealt with a statistical system of unity spin.

3. Numerical analysis

Figure 3 is a series of the contour diagram of the free energy. Here, we shall define a normalized temperature

$$R = T/T_W. \tag{9}$$

At low temperature ($R = 0{\cdot}65$), a large minimum A and a small minimum $B1$ are expected. Increasing temperature ($R = 0{\cdot}71$), the minimum A becomes shallow and $B1$ becomes deep. Further, by increasing the temperature, A and $B1$ disappear and another minimum $B2$ appears.

To understand more precisely the behaviour of $B1$ and $B2$, the minimum and maximum positions of n_0 are plotted against R under the condition of $n_1 = n_2$. One example is shown in figure 4. The minimum below the line of $n_0 = 1/3$ is not a real minimum but a saddle point. A phase transition is expected between $T1$ and $T2$ with hysteresis. In this sense, the transition is of first-order. If $T1$ and $T2$ are very close, it is nearly of second-order. This is the case of quartz.

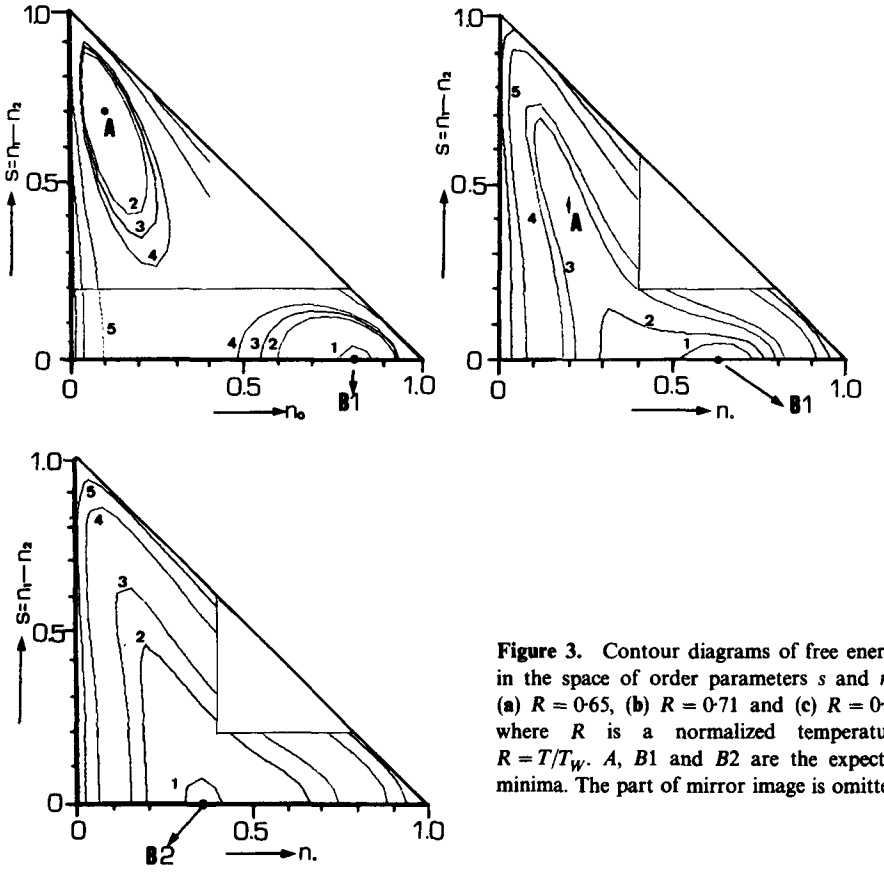

Figure 3. Contour diagrams of free energy in the space of order parameters s and n_0. (**a**) $R = 0{\cdot}65$, (**b**) $R = 0{\cdot}71$ and (**c**) $R = 0{\cdot}75$ where R is a normalized temperature $R = T/T_W$. A, $B1$ and $B2$ are the expected minima. The part of mirror image is omitted.

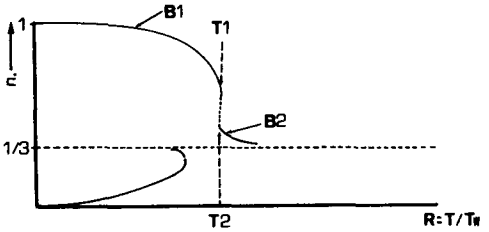

Figure 4. Temperature dependence of n_0 at the minima (solid curve) and the maxima (broken curve) of free energy.

In figure 3 and 4, for the sake of clear illustration, the energy parameters used are not real ones ($\bar{\varepsilon}/\bar{\mu} = 3{\cdot}925$; $|\tau|/\bar{\mu} = 1{\cdot}96$). Nevertheless, one can identify the minima of A, $B1$ and $B2$ to the α, IP and β phases, respectively.

After several trials, we finally obtained a set of parameters, which are realistic in the sense that the phase transitions occur successively. The parameters employed are

$$\bar{\varepsilon}/\bar{\mu} = 3{\cdot}817,\ |\tau|/\bar{\mu} = 1{\cdot}890. \qquad (10a, b)$$

Then the transition occurs at

$$\alpha \rightarrow IP: \quad R_C = 0{\cdot}6937, \tag{11a}$$

$$IP \rightarrow \beta : \quad R_Q = 0{\cdot}69465. \tag{11b}$$

If R_C is assigned to the temperature $T_C = 573°C$, we shall see

$$T_Q - T_C = 1{\cdot}2 \text{ degree}, \tag{12}$$

which is slightly less than the experimental value (Gouhara *et al* 1983).* By the definitions of T_W and R (equations (8) and (9)), we also see

$$T_W = 946{\cdot}5°C, \tag{13}$$

and

$$\bar{\mu} = 0{\cdot}525 \text{ eV}. \tag{14}$$

4. Discussion

The present theory is no more than a parameter theory, although it is microscopic. The parameters employed, therefore, must be regarded merely as "effective ones". Nevertheless, it is worth discussing their physical implications, particularly of the numerical figures given by (10) through (14).

First, although the intrinsic energies (ε_0 and ε) were formally introduced, they must be practically null. Secondly, the main part of the interaction energies (IE) listed in table 1 is the bonding energy of Si–O–Si. Thirdly, the deformation of tetrahedron units is negligible. This is justified to some extent by the structural study of Young (1962).

The figures of IE were sought under the requirements given by (4) and (5). From these figures, with the use of a reasonable working hypothesis ($\sigma = 0$), one can obtain

$$\mu = \bar{\mu}, \quad \mu_0 = 0{\cdot}954\bar{\mu}, \quad \tau_0 = 0{\cdot}018\bar{\mu}, \tag{15a,b,c}$$

The modification with a finite τ comparable with τ_0 does not change the sequential order of the magnitudes in (15) which is quite reasonable. Incidentally, μ is the bonding energy per bond of the interface between α_1 and α_2 states.

Very little information is available for criticizing the $\bar{\mu}$ values of (14). It is reported (Klassen–Neklyudova 1964) that indentation with a steel ball bearing can produce twinning even at room temperature. A rough estimation of the required pressure P was 1000 kg/mm^2 or more. The elastic energy absorbed per unit cell divided by six (the number of bonding) will trigger the twinning. Here again the deformation of the tetrahedron is neglected. Based on this model, one can estimate μ by $\alpha^2/12(1/C)P^2v$ (C: elastic constant, 10^{11} dyne/cm^2; v: volume of unit cell), which amounts to $\alpha^2 \times 6{\cdot}24 \times 10^{-2}$ eV. Here, α is introduced as a multiplication factor to the pressure mentioned above. Since $\alpha = 3 \sim 5$ is not unrealistic, the figure given by (14) is satisfactory at the present state of the art.

A question may arise for any theory of the present type; namely whether the state 0 is really stable in the potential curve. The present author believes that the physical reality is a continuous distribution of the tetrahedron unit along **a**- axis under a self-consistent

* It is not difficult to improve the calculation.

potential field. Thus, the problem of whether the potential curve has double or triple minima is not significant. The double minimum theory of Wannier (1959) cannot predict properly the intermediate phase. The success of the present theory implies that the sojourn of the tetrahedron unit within a limited range of **a**-coordinate is significant. The physical interpretation of the present theory, therefore, must be different from that for the statistical system of unity spin.

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