

Spontaneous strain energies associated with orientational order-disorder phase transitions

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(Received 28 November 1989; accepted 8 March 1990)

The contributions to the excess free energies of the orientational order-disorder phase transitions from the associated lattice distortions (spontaneous strains) in SF_6 and calcite have been calculated. These contributions are about one-third of the total excess free energies in both cases.

1. Introduction

Although the properties of orientationally disordered (OD) phases have been studied in considerable detail, comparatively little attention has been paid to the corresponding order-disorder phase transitions. This may be due in part to the fact that most transitions are strongly first-order and therefore appear to be of little interest for the study of phase-transition phenomena [1]. However, it is nevertheless important to understand the phase transition behaviour in these systems. This paper poses a simple question: how important energetically are the lattice distortions, or spontaneous strains, that invariably accompany such transitions? The bilinear coupling between strain and orientational order has been studied in the case of the alkali cyanides [2], but in this paper we shall tackle some of the more general aspects of this question from a detailed consideration of the orientational order-disorder phase transitions in SF_6 and the calcite form of $CaCO_3$.

To lowest order, the strain ϵ enters the ordinary excess free energy via a coupling to the orientational order parameter Q and the normal harmonic elastic energy:

$$F_{\text{strain}} = \eta \epsilon Q^n + \frac{1}{2} C \epsilon^2, \quad (1)$$

where η is the coupling constant, C is the elastic constant and $n = 1$ or 2 , depending on the symmetry of the phase transition. The equilibrium condition

$$\frac{\partial F_{\text{strain}}}{\partial \epsilon} = \eta Q^n + C \epsilon = 0 \quad (2)$$

gives the equilibrium relation between ϵ and Q . Substitution of (2) into (1) gives the equilibrium value of the strain free energy:

$$F_{\text{strain}}(\text{equilibrium}) = -\frac{1}{2} C \epsilon^2. \quad (3)$$

In both SF_6 and $CaCO_3$ we know the temperature dependences of the spontaneous strains ϵ and approximate values for the elastic constants C .

2. The phase transition in SF_6

SF_6 undergoes an orientational order-disorder phase transition at 96 K [3-5]. The low and high temperature structures are C-centred monoclinic and body-

centred cubic respectively (space groups $C2/m$, $Z = 6$, and $Im\bar{3}m$, $Z = 2$). The transition has been discussed in some detail elsewhere [5]. Although there is only the one transition, there are very good reasons for believing that the transition mechanism involves an intermediate trigonal structure (space group $P\bar{3}m1$, $Z = 3$) [6, 7].

The monoclinic unit cell vectors \mathbf{a} , \mathbf{b} and \mathbf{c} are simply related to the basis vectors of the cubic phase by

$$\left. \begin{aligned} \mathbf{a} &= a_c[\bar{1}, 2, \bar{1}], \\ \mathbf{b} &= a_c[\bar{1}, 0, 1], \\ \mathbf{c} &= \frac{1}{2}a_c[1, 1, 1], \end{aligned} \right\} \quad (4)$$

where a_c is the cubic unit-cell parameter. Figure 1(a) shows the temperature dependences of $a/6^{1/2}$, $b/2^{1/2}$, $2c/3^{1/2}$ and a_c , and highlights the lattice distortions associated with the transition. Another lattice distortion can be described by the monoclinic β angle, and this is shown as a function of temperature in figure 1(b).

These lattice distortions can be formally described in terms of the strain tensor defined with axis 1 along \mathbf{a} , axis 2 along \mathbf{b} and axis 3 along \mathbf{c}^* , following Schlenker

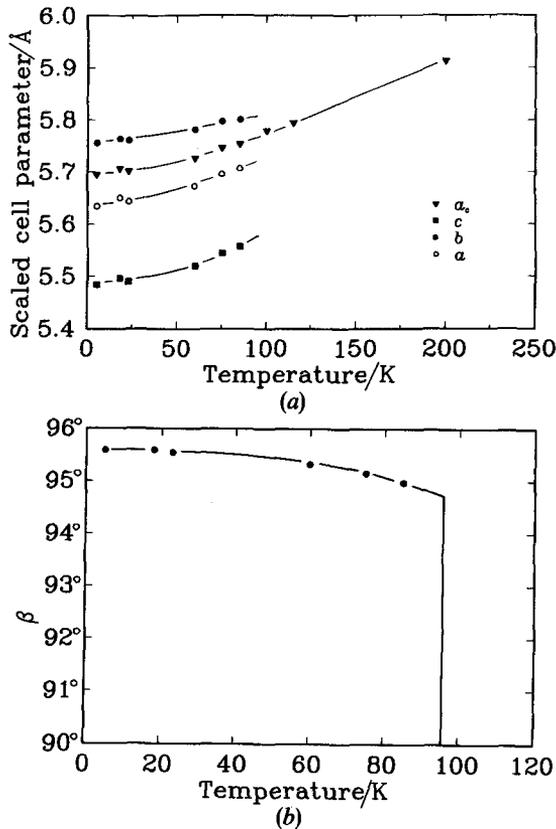


Figure 1. (a) Temperature dependence of the unit-cell lengths of SF_6 above and below the monoclinic-cubic transition temperature 96 K. The parameters have been scaled for easy comparison: \circ , $a/6^{1/2}$; \bullet , $b/2^{1/2}$; \blacksquare , $2c/3^{1/2}$; \blacktriangledown , a_c . The curves are given as guides to the eye. Data are from [3-5, 8]. (b) Temperature dependence of the monoclinic cell angle β of SF_6 . Data are from [4, 5]. The curve is given as a guide to the eye.

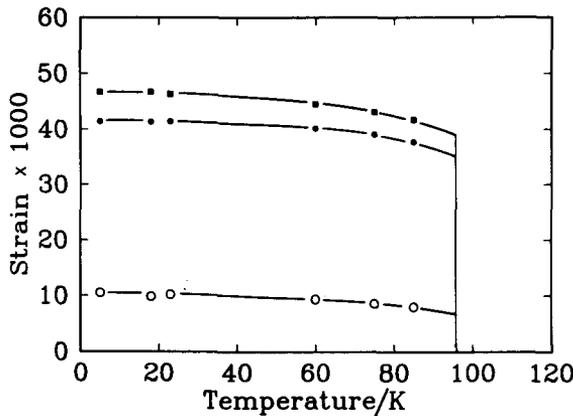


Figure 2. The spontaneous strains in the monoclinic phase of SF_6 as functions of temperature: ○, ϵ_1 ; ●, ϵ_3 ; □, ϵ_5 . The curves are given as guides to the eye.

et al. [9] and Redfern and Salje [10]:

$$\begin{aligned} \epsilon_1 &= \frac{a - a_0}{a_0}, & \epsilon_2 &= \frac{b - b_0}{b_0}, & \epsilon_3 &= \frac{c \sin \beta^* - c_0}{c_0}, \\ \epsilon_4 &= 0, & \epsilon_5 &= \frac{c \cos \beta^*}{c_0}, & \epsilon_6 &= 0, \end{aligned} \quad (5)$$

where the subscript 0 implies the value in the absence of the phase transition, as obtained from the extrapolations of a_c below 96 K in figure 1(a). The splitting of a and b below 96 K indicates that the extrapolation of a_c can be approximated reasonably well by

$$a_c(T < 96 \text{ K}) = \frac{1}{2}(a + 3^{1/2}b)/6^{1/2}. \quad (6)$$

The quantities a_0 , b_0 and c_0 can be taken as $6^{1/2}a_c$, $2^{1/2}a_c$ and $3^{1/2}a_c/2$ respectively. The strain components (5) are shown in figure 2.

The only strain component that would be non-zero in the intermediate trigonal phase would be ϵ_3 —in principle ϵ_1 and ϵ_2 could also be non-zero and equal in the trigonal phase, but figure 1 shows that $\epsilon_1 = -\epsilon_2$ at all temperatures in the monoclinic phase, implying that these strains are mostly associated with the monoclinic deformation. The monoclinic distortion primarily involves the shear strain ϵ_5 . The secondary strain $\epsilon_1 - \epsilon_2$ defines an orthorhombic shear strain. We have shown elsewhere [5] that $\epsilon_1 - \epsilon_2$ is proportional to ϵ_5^2 . ϵ_3 is not simply related to either $\epsilon_1 - \epsilon_2$ or ϵ_5 , which is consistent with the identification of ϵ_3 with the cubic–trigonal transition and ϵ_5 and $\epsilon_1 - \epsilon_2$ with the subsequent trigonal–monoclinic transition.

3. Strain energy of SF_6

The axes transformation (4) can also be applied to the elastic-constant tensor, giving new components \tilde{C}_{ij} from the normal cubic elastic constants C_{11} , C_{12} and

C_{44} [11]:

$$\begin{aligned}\tilde{C}_{11} &= \tilde{C}_{22} = \frac{1}{2}(C_{11} + C_{12} + 2C_{44}), & \tilde{C}_{33} &= \frac{1}{3}(C_{11} + 2C_{12} + 4C_{44}), \\ \tilde{C}_{44} &= \tilde{C}_{55} = \frac{1}{3}(C_{11} - C_{12} + C_{44}), & \tilde{C}_{66} &= \frac{1}{6}(C_{11} - C_{12} + 4C_{44}), \\ \tilde{C}_{12} &= \frac{1}{6}(C_{11} + 5C_{12} - 2C_{44}), & \tilde{C}_{13} &= \tilde{C}_{23} = \frac{1}{3}(C_{11} + 2C_{12} - 2C_{44}), \\ \tilde{C}_{15} &= -\tilde{C}_{25} = -\tilde{C}_{46} = \frac{1}{3}(C_{11} - C_{12} - 2C_{44})/2^{1/2},\end{aligned}\quad (7)$$

and the remaining components are zero. The elastic constants have been measured at high temperatures [12], and values have been calculated across the whole temperature range of the disordered phase [13]. Figure 3 shows the experimental and calculated elastic constants defined by (7), and the calculated values have been used to extrapolate the experimental data to 96 K. The best estimates for the elastic constant at 96 K are then

$$\begin{aligned}\tilde{C}_{11} &= \tilde{C}_{22} \approx \tilde{C}_{33} \approx 6.5 \times 10^9 \text{ N m}^{-2}, \\ \tilde{C}_{12} &= \tilde{C}_{23} \approx \tilde{C}_{13} \approx 3.25 \times 10^9 \text{ N m}^{-2}, \\ \tilde{C}_{44} &= \tilde{C}_{55} \approx \tilde{C}_{66} \approx 1.75 \times 10^9 \text{ N m}^{-2}, \\ \tilde{C}_{15} &= -\tilde{C}_{25} = -\tilde{C}_{46} \approx 0.\end{aligned}$$

The spontaneous strains at 96 K taken from figure 2 are

$$\varepsilon_1 = -\varepsilon_2 = 0.007,$$

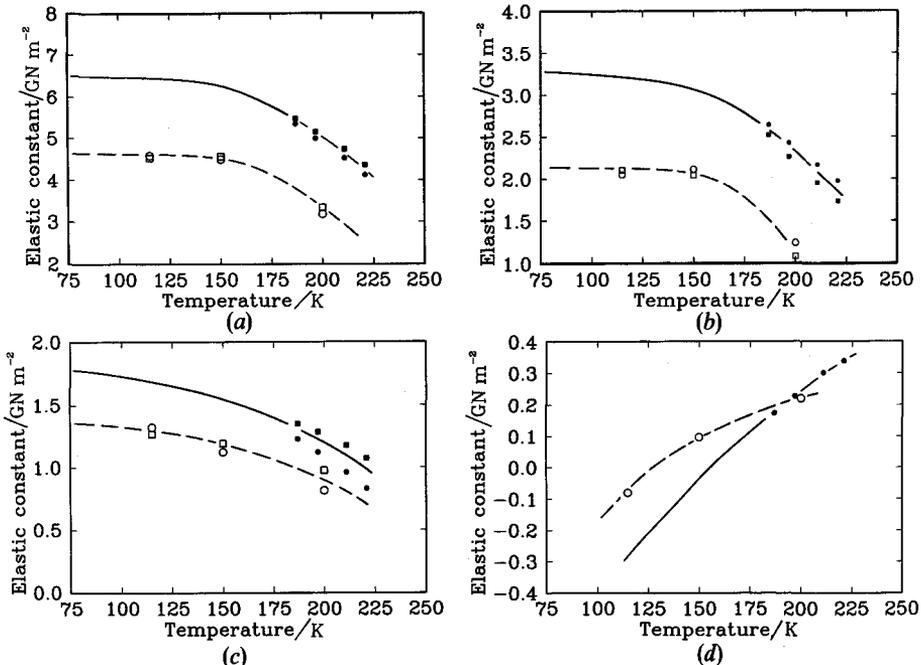


Figure 3. The elastic constants of SF₆ for $T > 96$ K in the pseudo-orthorhombic coordinate setting of the monoclinic phase: (a) \tilde{C}_{11} (●, ○) and \tilde{C}_{33} (■, □); (b) \tilde{C}_{12} (●, ○) and \tilde{C}_{13} (■, □); (c) \tilde{C}_{44} (●, ○) and \tilde{C}_{66} (■, □); (d) \tilde{C}_{46} (●, ○). The filled symbols are the experimental data [12], and the open symbols are simulation calculations [13]. The broken lines indicate the trend shown by the simulations, and the continuous lines give the extrapolations of the experimental data obtained by comparison with the simulation results.

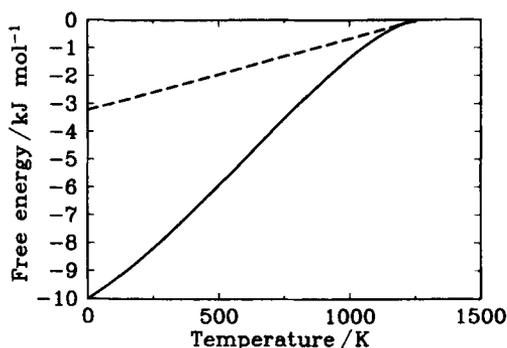


Figure 4. The excess free energy associated with the orientational order-disorder phase transition in calcite. The continuous curve is the total excess free energy given by the Landau expansion (9), while the broken curve is the harmonic strain energy (3).

$$\varepsilon_3 = 0.036, \quad \varepsilon_5 = 0.040.$$

$\varepsilon_1 - \varepsilon_2$ is almost an order of magnitude smaller than ε_3 or ε_5 because it arises from a higher-order coupling in the free energy than ε_3 and ε_5 ; recall that $\varepsilon_1 - \varepsilon_2 \propto \varepsilon_5^2$. Therefore the largest components of the strain energy are $-\frac{1}{2}C_{33}\varepsilon_3^2$ and $-2C_{55}\varepsilon_5^2$. (Note that the extra factor of four in the latter case arises because ε_5 denotes two equivalent strains, e_{13} and e_{31} , which can be combined in four ways in the strain energy.) These two quantities are approximately 0.23 and 0.31 kJ mol⁻¹ respectively. These values should be compared with the measured value of the latent heat of the transition of 1.6 kJ mol⁻¹ [14]. The relative contributions of the strain energies for ε_3 and ε_5 are approximately 14% and 19%; about 33% of the latent heat is strain energy. This is a significant contribution, and shows that the spontaneous strains are important for the thermodynamics of the orientational order-disorder phase transition in SF₆.

4. The phase transition and strain energy in calcite

Calcite has an orientational order-disorder phase transition at 1260 K. The space groups below and above the transition are R3c ($Z = 2$) and R3m ($Z = 1$). The transition is continuous, with the order parameter Q having the temperature dependence [15]

$$Q = \left(1 - \frac{T}{T_c}\right)^{1/4}. \quad (8)$$

In the orientationally disordered phase the CO₃ molecular ions are disordered by rotations about the molecular threefold axis (which is parallel to the crystal threefold axis in both phases). The transition is accompanied by a large negative strain ε_3 , involving contraction along the direction of the threefold axis, on cooling. It is found experimentally that $\varepsilon_3 \propto Q^2$ [15].

The transition behaviour is accurately described by a Landau free-energy function of the form

$$F = \frac{1}{2}a(T - T_c)Q^2 + \frac{1}{6}cQ^6, \quad (9)$$

where $a = 24(\pm 3)$ J mol⁻¹ K⁻¹ and $c = 30(\pm 3)$ kJ mol⁻¹ [15, 16]. Thus at $T = 0$, where by definition $Q = 1$, the excess free energy is 10 kJ mol⁻¹. This value may be a

slight overestimate because of the neglect of saturation effects in (9), but, since we know that $Q = 0.93$ at $T = 300$ K, these effects will be relatively small.

The elastic constant C_{33} has been measured at 300 K, with a value of $8.4 \times 10^{10} \text{ N m}^{-2}$ [17]. The Landau free energy (9) is shown as a function of temperature in figure 4. The neglect of saturation effects leads to a non-zero value for the entropy at $T = 0$. The strain energy calculated from (3) using the experimental data for ϵ_3 [15] is also shown in figure 4. Any temperature dependence of C_{33} has been neglected, but, since the coupling of the strain to the order parameter Q is not bilinear, it is not expected that there will be a significant renormalization of C_{33} . It can be seen from figure 4 that the strain energy is a significant fraction of the total excess free energy of the transition, and is approximately 30% at low temperatures.

5. Conclusions

Although the calculations presented in this paper are rather rough, we can still draw the conclusion that the energies associated with the spontaneous strains at orientational order-disorder transitions make substantial contributions to the total excess free energies associated with at least some of these transitions. This conclusion transcends the details of the rough calculations given in this paper.

There are few reported measurements of the temperature dependence of lattice parameters of orientationally disordered crystals in the literature. It is hoped that one result of this paper will be to encourage such measurements. Consider again the case of SF_6 . Although the transition is strongly first-order, the temperature dependences of the cell parameters below 96 K primarily reflect the temperature dependence of residual disorder. The cell parameters therefore contain important information concerning the phase transition. Ideally, therefore, the cell parameters should be measured as functions of temperature for all systems of interest (e.g. N_2 , CBr_4 , KCN, adamantane). So too should the elastic constants. For it is probable that, despite their first-order character, many orientational order-disorder phase transitions can be described by a Landau-like free-energy function, and the contribution of the strain energy will be an integral part of such a description.

Some of the experimental results discussed in this paper were obtained from collaborative work with Dr Brian Powell (Chalk River) and Professor Stuart Pawley (Edinburgh). I am grateful to Dr Ekhard Salje (Cambridge) for encouraging this work through a speaking invitation.

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