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LETTER TO THE EDITOR

Comment on the quasi-harmonic treatment of the structural phase change in s-triazine

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Abstract. Contrary to the statement in a recent publication by A I M Rae, we demonstrate that both the quasi-harmonic lattice approximation and orientational strain order parameter approach to the phase transition in sym-triazine give identical results. Both treatments rely on a Landau mean field expansion of the free energy in the vicinity of the phase transition. The usefulness of one theoretical treatment over the other is a function of the details of the experimental findings and just which properties are chosen to be modelled.

In a recent article, Rae (1982) described a theoretical approach to the structural phase change in s-triazine. Using the quasiharmonic approximation together with a fit of the strain dependence of the optical phonon frequencies, he obtained numerical results of the temperature dependences of the shear and molecular rotation angle as well as the c_{44} elastic constant. A number of features of a previous Landau mean field description of this ferroelastic transition by Raich and Bernstein (1980) were criticised. The purpose of this note is to respond to these criticisms as well as to point out the similarities and differences of the two approaches.

The derivation of a phenomenological free energy, expressed in terms of the orientational and strain order parameters on the basis of symmetry arguments, is given by Raich and Bernstein (1980). If one assumes that the strain $e_1 - e_2$ is always small compared to e_5 one obtains

$$\begin{aligned} F = {} & \tfrac{1}{2}a(R_x^2 + R_y^2) + \tfrac{1}{3}b(R_y^3 - 3R_x^2R_y) \\ & + \tfrac{1}{4}c(R_x^2 + R_y^2)^2 + \tfrac{1}{2}c_{44}^0 e_5^2 - Ae_5R_y \\ & - \tfrac{1}{2}Ce_5(R_x^2 - R_y^2) + \tfrac{1}{2}Ee_5^2R_y + \tfrac{1}{4}He_5^2(R_x^2 - R_y^2) + \dots . \end{aligned} \tag{1}$$

It should be re-emphasised that R_x and R_y are orientational order parameters, i.e. average rotation angles about the x and y axes respectively and not optical phonon coordinates. Because the s-triazine molecule is not located at a centre of inversion of the crystal, the four optical phonon modes at $\boldsymbol{q} = 0$ contain both molecular rotations and translations. At $\boldsymbol{q} \neq 0$ there is an additional mixing of rotations and translations as a result of the bilinear coupling term in equation (1).

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The bilinear coupling term in the free energy can be removed by the transformation

$$R_y = Q + (A/a)e_5$$
$$R_x = Q'. \tag{2}$$

The result is

$$\begin{aligned} F = {} & \tfrac{1}{2}a(Q^2 + Q'^2) + \tfrac{1}{3}b(Q^3 - 3Q'^2Q) \\ & + \tfrac{1}{4}c(Q^2 + Q'^2)^2 + \tfrac{1}{2}c^{(2)}e_5^2 + \tfrac{1}{3}c^{(3)}e_5^3 \\ & + \tfrac{1}{4}c^{(4)}e_5^4 1\, \beta e_5^2 Q + \tfrac{1}{2}\gamma e_5(Q^2 - Q'^2) \\ & + \tfrac{1}{2}\delta_1 e_5^2 Q^2 + \tfrac{1}{2}\delta_2 e_5^2 Q'^2 + \ldots \end{aligned} \tag{3}$$

where

$$\begin{aligned} c^{(2)} &= c_{44}^0 - A^2/a \\ \beta &= b(A/a)^2 + CA/a + \tfrac{1}{2}E \\ \gamma &= 2bA/a + C \\ \delta_1 &= 3c(A/a)^2 - \tfrac{1}{2}H \\ \delta_2 &= c(A/a)^2 + \tfrac{1}{2}H. \end{aligned} \tag{4}$$

Rather than exhibit the temperature dependence of the free energy (3) directly, such as $a = a_0(T - T_0)$ or $c^{(2)} = c_0^{(2)}(T - T_0)$, one can treat a as temperature-independent and use an Einstein approximation to write, in units of $k_B = \hbar = 1$,

$$F = V + T\sum_j \ln[2\sinh(\omega_j/2T)] \tag{5}$$

where V is a static potential energy, which has the same form as equation (3). The second term of equation (5) represents the contribution of a set of Einstein oscillations approximately representing the librational modes of the crystal. It should be noted that, Rae's criticism notwithstanding, this free energy (equations (3) and (5)) is identical to that used by Rae.

The frequencies ω_j can be approximately calculated from

$$\begin{aligned} \omega_1^2 &\approx \partial^2 F/\partial Q^2 = \Omega_0^2 + 2bQ + 3cQ^2 + \gamma e_5 + \delta_1 e_5^2 \\ \omega_2^2 &\approx \partial^2 F/\partial Q'^2 = \Omega_0^2 - 2bQ + cQ'^2 - \gamma e_5 + \delta_2 e_5^2. \end{aligned} \tag{6}$$

In equation (6) the molecular moment of inertia has been incorporated in the definition of Ω_0 and the ω_j to simplify the mathematical expressions. These relations are only approximate because the Q_i are not actually normal coordinates for the system. The frequency Ω_0 is the mean field frequency in an effective anharmonic well (Lovesey 1980)

$$\Omega_0^2 \simeq \omega_0^2 + (4c/\omega_0^2)T \tag{7}$$

where $\omega_0^2 = a$, which is now treated as being temperature-independent.

The effective elastic constant in the high-temperature phase is readily calculated from equation (5) by

$$c_{44} = \frac{\partial^2 F}{\partial e_5^2}. \tag{8}$$

In the high-temperature limit $T > \omega_0$, equations (5) and (8) yield, neglecting cubic anharmonic terms dependent on γ,

$$c_{44} = c_{44}^0 - A^2/\omega_0^2 + [(\delta_1 + \delta_2)/\Omega_0^2]T \tag{9}$$

where Ω_0 is the mean field frequency (7). If one inserts the expressions for δ_1 and δ_2 above, one obtains

$$c_{44} = c_{44}^0 - A^2/\omega_0^2 + 4cA^2T/\omega_0^6 - 16c^2A^2T^2/\omega_0^{10} + \ldots . \tag{10}$$

This expression for c_{44} contains the bilinear coupling constant A and the second- and fourth-order orientational parameters a and c, but not the higher-order coupling parameters C, E and H of equation (1). It is worthwhile to note that the same expansion for c_{44} is also obtained from the Landau mean field expression (Raich and Bernstein 1980)

$$c_{44} = c_{44}^0 - A^2/(a_0(T - T_0)) \tag{11}$$

if one identifies $\Omega_0^2 = a_0(T - T_0)$. Again the approaches of Rae (1982) and Raich and Bernstein (1980) yield identical results.

Instead of the approach outlined above, Rae (1982) uses expressions of the form (6) to fit the strain dependence of the four E_g optical phonon frequencies observed by Raman scattering. The four different optical phonon coordinates contain varying contributions from molecular rotations and translations but the general form for the corresponding frequencies is assumed to be the same as equation (6). The strain dependences of the optical phonon frequencies in the low-temperature phase are then fitted employing equation (6) with $b = c = 0$, but treating γ, δ_1 and δ_2 as adjustable parameters. This approach, however, encounters some difficulties associated with the (slight) first-order nature of the phase transition; there are no data for the small, non-zero values of the strain e_5. Hence a fit based on equation (6) omits terms proportional to e_5^n with $n > 2$, which must also contribute to ω_f^2 at large values of the shear strain. These terms do not, however, contribute to c_{44} in the high-symmetry phase. Indeed, some of the parameters fitted by Rae appear to be rather large.

From this brief comparison of the calculation of c_{44} for the high-temperature phase we conclude that the quasiharmonic approach yields a result equivalent to the high-temperature result, equation (9). A possible difference might be the origin of the anharmonic coupling terms δ_1 and δ_2. It should also be pointed out that the quasiharmonic approximation as outlined by Rae (1982) represents an expansion about a potential energy maximum, rather than a minimum, as the zeroth-order elastic constant is negative. This problem with the quasiharmonic approximation is, however, not unique (Blink and Zecs 1974).

An alternative Landau approach to that taken by Raich and Bernstein with the assumption $a = a_0(T - T_0)$ is to employ an explicit temperature dependence for a 'soft' elastic constant of the form $c_{44} = c_{44}^0(T - T_0)$. The corresponding Landau mean field model will allow one to predict the temperature dependence of the optical phonon modes. Whether the first or second Landau-type descriptions are used usually depends on experimental observations: in particular, evidence for a 'soft' optical mode (Pinczuk *et al* 1977, Wada *et al* 1979, Benyuan *et al* 1981). In the case of s-triazine both phenomenological approaches seem to have some validity. The microscopic details of how the various parts of the anisotropic intermolecular potential contribute to anharmonic terms in the free energy expansion in the neighbourhood of the ferroelastic transition remain to be elucidated.

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