A new theoretical model for the re-entrant phase transitions in malononitrile

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Abstract. Malononitrile undergoes a series of 're-entrant' phase transitions from a low-temperature monoclinic phase to an intermediate triclinic phase and, finally, to a high-temperature monoclinic phase whose structure is nearly identical to that of the low-temperature phase. A model is suggested for this system which is based on the interaction between the order parameter associated with the transitions and strains in the unit cell caused by thermal expansion. The energy is calculated as a function of temperature on the basis of this model, using atom–atom '6–exp' potentials along with long-range dipole–dipole forces. The model produces values of the coupling coefficients that agree satisfactorily with values derived from the experimental data and predicts re-entrant behaviour quite similar to that observed experimentally.

1. Introduction

The molecular crystal malononitrile—$CH_2(CN)_2$—has a monoclinic unit cell of space-group $P2_1/n$ at temperatures above 294.7 K (Nakamura *et al* 1971, Obatake and Tanisaki 1973). At this temperature the substance undergoes a second-order phase transition to a triclinic structure (the β phase) with spacegroup $P\bar{1}$; there are no major changes in the unit cell parameters at the transition, which is accomplished by rotating symmetrically related molecules in opposite directions about axes parallel to the b axis of the unit cell and translating both molecules a small distance parallel to the a axis (Dove and Rae 1980). On further cooling to 141 K‡, a second phase transition occurs that restores the monoclinic symmetry and, indeed, the crystal structures of the low-temperature (α) phase and the high-temperature (γ) phase are no more different than would have been expected to result from thermal expansion if no intermediate phase had existed (Dove and Rae 1983). Such a sequence of phase transitions is often described as 're-entrant' (e.g. Pershan and Prost 1979).

The present paper describes a model, based on an interaction between the order parameter associated with the transition and strains associated with the thermal expansion of the crystal, that explains a number of features of this unusual sequence of phase

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‡ Below about 260 K, the stable form of malononitrile is yet another phase (Zussman and Alexander 1968). However the structure of this is unknown and, as the α and β phases are long-lived metastable forms below 260 K, this feature is not discussed further in this paper.

transitions. Confirmation of the importance of such interactions is obtained from cal-
culations of the crystal lattice energy. The next section briefly reviews the relevant
experimental data along with previous theoretical work and subsequent sections describe
the new theory and associated calculations.

2. Previous results

The crystal structure of the α and γ phases (Obatake and Tanisaki 1973, Dove and Rae
1983) are shown in projection down the c axis of the unit cell in figure 1(a), while figure

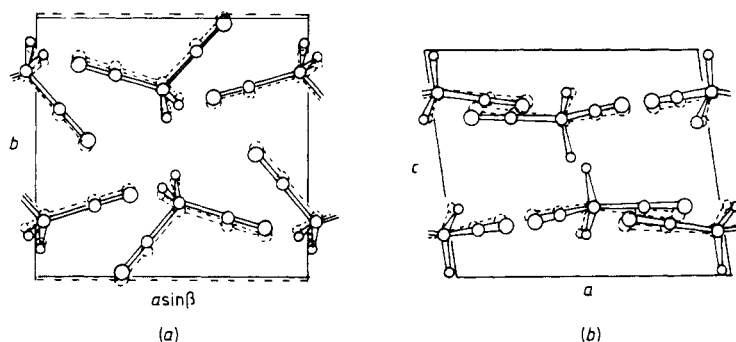**Figure 1.** (a) shows the structures of the α (full lines) and γ (broken lines) phases of
malononitrile in projection down the c axis of the unit cell and (b) shows the β (full lines) and
γ (broken lines) structures in projection down b. The large, medium and small circles
represent nitrogen, carbon and hydrogen atoms respectively.

1(b) shows the γ and β phases in projection down the b axis (Dove and Rae 1980). It is
clear from the latter figure that the order parameter associated with the transition
consists of opposite rotations of the two molecules, related by a screw axis in the
monoclinic phase, combined with a translation of the molecular centre of gravity in the
x direction. The temperature dependence of the order parameter in the β phase can be
derived from measurements of the splittings of nuclear quadrupole resonance frequen-
cies (Zussman and Alexander 1968): four of these frequencies have been measured as
functions of temperature and if the average of these splittings is taken to be proportional
to the order parameter and if this is scaled to the measured magnitude of the rotation
angle which is $3.5°$ at 273 K (Dove and Rae 1980) the temperature dependence of the
rotation angle is as in figure 2(a). Assuming that the relatively small translations
(0.007 nm at 273 K) of the molecular centres are always proportional to this angle, the
total order parameter can be taken to be a rotation about an axis parallel to b and
displaced by 0.11 nm in the z direction from the molecular centre of mass. Such a
distortion corresponds to a zone-centre optical phonon of symmetry B_g. The tempera-
ture dependence of the soft mode associated with this distortion has been measured by
Raman scattering in the α and β phases, but not the γ phase (Le Calv̇e *et al* 1980) and the
results of this are shown in figure 2(b).

   All the experimental evidence is consistent with both phase transitions being con-
tinuous and obeying mean-field theory: in particular, a classical value for the relevant
critical exponent was obtained from accurate measurements of the nuclear quadrupole

splittings close to the upper transition (Zussman and Alexander 1968) and no divergence of the heat capacity has been observed at either transition (Girdhar *et al* 1968, Dove *et al* 1983). In which case, the transitions should be capable of analysis by Landau theory, and Dove and Rae (1980) have shown that a re-entrant sequence of continuous phase
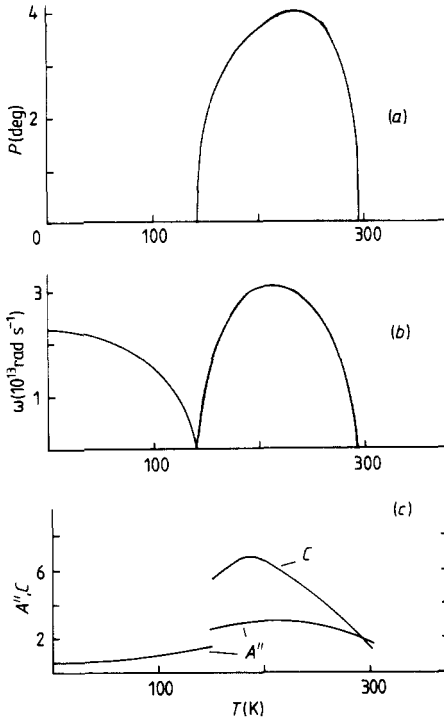

Figure 2. (*a*) shows the order parameter (*P*) and (*b*) shows the soft-mode frequency ω as functions of temperature. The temperature dependence of A'' (units: $J\ mol^{-1}\ deg^{-2}\ K^{-2}$) and C (units: $J\ mol^{-1}\ deg^{-4}$) are shown in (*c*).

transitions would result from a minimisation of the free-energy functional

$$F = AP^2 + CP^4 \tag{1}$$

with

$$A = A''(T - T_1)(T - T_2) \tag{2}$$

where P is the order parameter, T_1 and T_2 are the transition temperatures and A'' and C are constants or slowly varying functions of temperature. This model leads directly to expressions for the equilibrium value of the order parameter (P_0) and for the soft-mode frequency (ω):

$$P_0 = \begin{cases} (-A/2C)^{1/2} & T_1 < T < T_2 \\ 0 & T < T_1 \text{ or } T > T_2 \end{cases} \tag{3}$$

$$I\omega^2 = \frac{\partial^2 F}{\partial P^2} = \begin{cases} -4A & T_1 < T < T_2 \\ 2A & T < T_1 \text{ or } T > T_2 \end{cases} \tag{4}$$

where I is the molecular moment of inertia about the rotation axis (0.243×10^{-20} kg m^2). Equations (2), (3) and (4) were used along with the data in figures 2(a) and 2(b) to calculate the temperature dependence of the 'constants' A'' and C and the results of this are shown in figure 2(c). Two main points should be noted about this figure:

(i) The quantity A'' does not vary much over the intermediate-temperature phase and is also reasonably constant throughout the low-temperature phase. However, there is a significant difference between the values of A'' appropriate to the α and β phases, which is reflected in the discontinuity at the lower transition temperature; moreover, a similar discontinuity might well occur at the upper transition, but this has not been observed because no measurements of the γ-phase Raman frequencies were possible (Le Calvé *et al* 1980). These discontinuities are believed to be evidence of an interaction between the order parameter and the lattice strain and this is discussed in more detail in the next section.

(ii) The quantity C is more strongly dependent on temperature than is A'' in the intermediate-temperature phase, although it is still acceptably 'constant' considering the large temperature range involved. The fact that C goes through a maximum may indicate that a significant higher-order term, proportional to P^6, should be added to (1), but such a correction could not explain the asymmetry of the $C(T)$ curve which must therefore imply some intrinsic temperature dependence of this quantity.

3. Strain-induced phase transitions

The theory outlined in the previous section is phenomenological in that the temperature dependence of A (equation (2)) which gives rise to the re-entrant phase transitions has been assumed without justification. Moreover, the theory has failed to explain the different values of A'' above and below the lower (and also, presumably, the upper) phase transition. In this section it will be shown that the latter point can be accounted for by considering interactions between the order parameter and the lattice strain (Cowley 1980) and it will also be seen that these interactions provide a basis of a microscopic model underlying the phase transitions themselves. The free-energy functional is now written as

$$F = AP^2 + CP^4 + DP^2e + E(e - e_0)^2 \tag{5}$$

where A is now assumed to be independent of temperature and, for the sake of clarity, only one strain component, e, is considered at this stage†. The quantity e_0 represents the equilibrium strain in the absence of interaction with the order parameter, and is temperature dependent as a result of thermal expansion. Minimising with respect to e we get

$$e = e_0 - DP^2/2E \tag{6}$$

and, substituting in (5),

$$F = \tilde{A}P^2 + \tilde{C}P^4 \tag{7}$$

† The strain component e in equation (5) clearly does not belong to the same irreducible representation as P or a term of the form eP would also have to be included, and, as a result, the transition would be preceded by one characterised by an elastic instability (Miller and Axe 1967). In malononitrile the only strains of this type are those associated with changes in the α and γ angles of the triclinic cell of the β phase. However Dove and Rae (1980) have shown that these angles are very close to 90° in the β phase, and Brillouin scattering measurements in the vicinity of T_2 (Higashigaki and Wang 1979) indicate that the temperature range of the elastic instability is very narrow, so such interactions have been neglected in the present work.

where

$$\bar{A} = A + De_0 \quad \text{and} \quad \tilde{C} = C - D^2/4E. \tag{8}$$

At equilibrium we have

$$P = \begin{cases} 0 & \text{if } \bar{A} > 0 \\ P_0 = (-\bar{A}/2\tilde{C})^{1/2} & \text{if } \bar{A} < 0. \end{cases} \tag{9}$$

The Raman frequencies are given by the second differential of (5) with respect to P at *constant strain*, because the strain cannot follow this high-frequency motion (Cowley 1980). Hence

$$I\omega^2 = (\partial^2 F/\partial P^2)_e = 2A + 12CP^2 + 2De$$

$$= \begin{cases} 2\bar{A} & \text{if } P = 0 \\ -4\bar{A}C/\tilde{C} & \text{if } P = P_0. \end{cases} \tag{10}$$

The factor $(C/\tilde{C})$ in the second of equations (10) clearly accounts for the discrepancy in the observed values of A'' above and below the transition. From figure 2(c), we have $\tilde{C} = 0.054 \, \text{J deg}^{-4}$ and $C/\tilde{C} = 1.8$ at $T = T_1$, from which, using (8), we get $D^2/4E = 0.043 \, \text{J deg}^{-4}$. This quantity will be seen to be in good agreement with the results of lattice energy calculations later in this paper.

We also see from equations (9) and (10) that the lower phase transition itself can result from the interaction with strain, without needing to assume that the quantity A is temperature dependent if the quantity De_0 is negative and increases with temperature due to thermal expansion. In such circumstances, a phase transition from a low-temperature high-symmetry phase to a high-temperature low-symmetry phase is quite possible. Such a change, which corresponds to the lower transition is malononitrile, is very unusual and difficult to explain using more conventional models. Figure 3 shows the temperature variation of various external and internal strain components in malononitrile which were obtained by drawing smooth lines through the experimental data of Dove and Rae (1983), strain components not shown being insignificantly different from zero. Of considerable interest is the component e_1 which measures the thermal expansion of the a axis of the unit cell; this reduces at low temperature, goes through a minimum and increases at higher temperature. It is clear that, if the coupling constant D has the appropriate magnitude and sign, the quantity $\bar{A}$ will aquire a temperature dependence at least qualitatively similar to that given in equation (2) and a re-entrant sequence of phase transitions will result. The validity of this model has been investigated by carrying out lattice-energy calculations and this is discussed in the rest of this paper.

4. Lattice-energy calculations

The intermolecular potential of many molecular crystals has been successfully modelled by summing 'atom–atom' potentials of the '6–exp' form, in which the interaction energy w_{ij} between two atoms i and j is given by

$$w_{ij} = -Ar_{ij}^{-6} + B \exp(-Cr_{ij}) \tag{11}$$

where r_{ij} is the distance between the atoms and A, B and C are constants whose magnitudes depend on the atom types. Values of these constants in the case of carbon
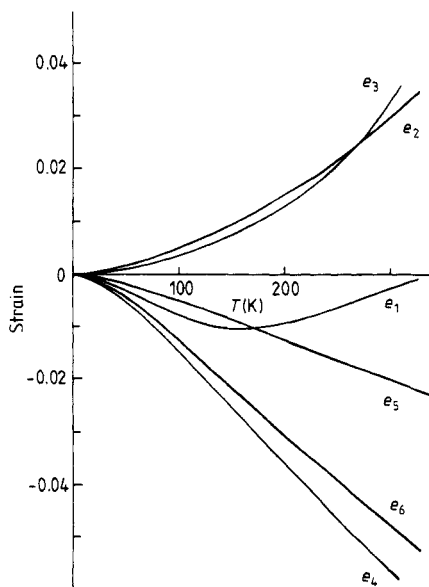
Figure 3. The temperature dependence of various external and internal strain components. These are defined as: $e_1 = \delta a/a$; $e_2 = \delta b/b$; $e_3 = \delta c/c$; $e_4 = \delta\beta$; $e_5 = \delta Y$; $e_6 = \delta\theta_y$ where Y is the fractional y coordinate of the molecular centre of mass and θ_y represents a molecular rotation about the y axis.

and hydrogen have been derived by fitting the results of calculations based on (11) to the experimental structures of a number of hydrocarbon crystals (Williams 1966, 1967) and these results have been extended to crystals containing nitrogen by Govers (1975). The resulting parameter set is given in table 1.

A 6–exp potential is a plausible representation of the short-range dispersive and repulsive interactions between molecules, but it ignores long-range electrostatic forces. The latter would be expected to be particularly important in the case of a molecule such as malononitrile which has a large dipole moment (1.19×10^{-21} C m $\equiv 3.57$ D—van Harverbeke and Harman (1975). In addition, the size of the malononitrile molecule is

Table 1. Atom–atom potential parameters and atomic dipole moments.

Atoms	A (10^9 kJ mol^{-1} nm^6)	B (kJ mol^{-1})	C (nm^{-5})	Atom	Dipole moment[†] (10^{-21} C m)
C–C	2.378	350075	0.360	C(cyano)	0.429
C–N	1.566	47469	0.360	C(central)	0.226
C–H	0.523	36694	0.367	N	0.268
N–N	3.190	442040	0.360	H	0.168
N–H	0.523	18423	0.367		
H–H	0.114	11110	0.374		
N–H (revised)	0.675	20250	0.373		

† The dipole moment of the central carbon points along the symmetry axis of the molecule; all other atomic dipoles are directed along the chemical bond to a neighbouring atom. The positive direction is from the nitrogen end of the molecule towards the hydrogens in each case.

comparable with the distance between neighbouring molecules, so a single dipole is unlikely to be a sufficiently accurate model of the molecular charge distribution. A similar problem was encountered in the calculation of the lattice energy of HCN (Rae 1969) and in this case the molecular dipole moment was divided into a number of local dipoles placed at or near the atomic centres from a consideration of the calculated electron density of the molecule. Electronic wavefunctions for malononitrile are not currently available, but local dipole moments for the nitrogens, the hydrogens and the cyano carbons can reasonably be assumed to be the same as in the HCN case. The remaining moment on the central carbon is then chosen to ensure that the total molecular dipole moment agrees with experiment. The results of this procedure are given in table 1 and the fact that the central carbon moment is of a reasonable size provides some confirmation of its validity.

The intermolecular potential was summed over the crystal by considering all the interactions between a reference molecule (or pair of molecules in the case of the β phase where the asymmetric unit contains two crystallographically distinct molecules) and the rest of the crystal using the standard Ewald procedure to ensure convergence of both the electrostatic and dispersive sums (Williams 1971). The program used also calculated the first and second derivations of the potential energy with respect to the unit cell parameters and the position and orientation of the molecule, and used these quantities to determine the configuration corresponding to the potential minimum. The results of this procedure as applied to the monoclinic (α or γ) phase are shown in table 2 along with experimental values of these parameters obtained by extrapolating the

Table 2. Lattice energy and structural parameters derived from the experimental data compared with those obtained by minimising the potential energy.

Parameter	Experiment‡	Minimisation of original potential	Minimisation of adjusted potential
W (kJ mol^{-1})	-84	-80 (-105, 60, -34)‡	-88 (-123, 72, -37)‡
a (nm)	0.788	0.737	0.726
b (nm)	0.744	0.694	0.687
c (nm)	0.601	0.582	0.579
β	99.5°	98.2°	97.1°
X§	0.438	0.441	0.442
Y§	0.163	0.154	0.155
Z§	0.720	0.720	0.719
θ_x¶	0°	$-1.8°$	$-4.0°$
θ_y¶	3.5°	1.6°	2.2°
θ_z¶	0°	0.1°	0.4°

‡ The experimental value of the lattice energy is obtained from the latent heat of sublimation at room temperature (80 kJ mol^{-1}—Boyd *et al* 1967) corrected for thermal effects by adding $2RT$ (Rae and Mason 1968). The experimental unit cell and structural parameters were obtained by extrapolating the results of Dove and Rae (1983) to absolute zero, taking into account the fact that the first derivatives with respect to temperature must vanish at zero temperature.
‡ The three figures in brackets are respectively the dispersive, repulsive and electrostatic contributions to the lattice energy.
§ X, Y, and Z are the coordinates of the centre of mass of the molecule expressed as fractions of the corresponding unit cell axis.
¶ θ_x, θ_y and θ_z represent rotations about orthogonal axes x, y and z where x is parallel to a, y is parallel to b and z is perpendicular to the ab plane. The reference orientation corresponds to the room-temperature γ-phase structure.

measured values as a function of temperature (Dove and Rae 1983) to absolute zero. There is generally good agreement, although the calculated linear cell dimensions are all a few per cent lower than their experimental values. This is not unexpected as the short-range potential parameters were obtained by fitting to experimental crystal structures without including electrostatic forces, the inclusion of which generally increases the overall attraction and hence reduces the unit cell size. It would be possible to modify the model to improve the agreement with experiment—for example, the potential parameters could be transformed in such a way as to increase the length scale without affecting any other quantities—but it was considered that the present model was adequate as a starting point for the investigation of the phase-transition mechanism.

5. Results and discussion

As a first step in the investigation of the phase transitions, the lattice energy was calculated with the monoclinic symmetry broken by rotating the molecules by $\pm 3°$ about axes parallel to b and passing through the molecular centres of mass. The resulting calculated lattice energy was 45 J mol^{-1} higher than in the monoclinic case, indicating that the monoclinic phase is stable with respect to the triclinic phase at 0 K in agreement with experiment, and this conclusion was confirmed by minimising the energy with respect to all the parameters of the triclinic structure when the monoclinic configuration was reproduced. If, however, the molecular rotations were fixed at $\pm 3°$ and the other parameters minimised, the only significant change was a translation of the molecular centres by 0.005 nm in the x direction. This is in good agreement with the displacement of 0.007 nm associated with a rotation of 3.5° which was observed experimentally at 273 K—see § 2 above.

To test the validity of a model of the type described in § 3, the quantity $\bar{A}$ in equation (7) was evaluated from the difference in lattice energy resulting when the structure was distorted into the β phase configuration by rotating the molecules through small angles ($\pm 1°$) about the appropriate rotation axes (see § 2). This procedure was repeated for a number of temperatures with the unit cell and structural parameters all strained from the minimum-energy configuration by amounts corresponding to the experimental strains associated with the thermal expansion (figure 3). The resulting temperature dependence of $\bar{A}$ is shown in figure 4 along with the corresponding experimental quantity derived from the Raman measurements using equation (10) and assuming $C/\bar{C} = 1.8$ throughout the β phase. Over the whole temperature range, the calculated value of $\bar{A}$ is considerably larger than that measured and there is no point where $\bar{A}$ is negative as would be expected if a phase transition is to occur. Nevertheless, the calculated $\bar{A}$ does show a pronounced minimum and the shape of this curve would be quite acceptable if its overall magnitude were lower. The possibility that this might be achieved by a relatively small adjustment of the intermolecular potential was therefore investigated.

The contributions to $\bar{A}$ from the dispersive, repulsive and electrostatic interactions were calculated separately as 8.4, -10.0 and 9.3 J mol^{-1} deg^{-2} respectively. This indicated that an increase in the repulsive energy could result in a decrease of $\bar{A}$ and this term was further divided into the contributions from the various atom–atom interactions when it was found that the largest negative contribution was from the N---H repulsions. This interaction was accordingly increased by 20%, the potential was reminimised and $\bar{A}$ was recalculated. However, the result was an increase in $\bar{A}$ rather than a decrease as a result of changes in the unit cell and structure parameters on reminimisation. To

overcome this, all three N----H parameters were increased in such a way as to leave the position of the N----H potential minimum unaltered, and the lattice energy was again minimised with respect to the monoclinic structural parameters, after which $\bar{A}$ was recalculated. A decrease in $\bar{A}$ resulted and the procedure was repeated with the N---H parameters increased by different amounts until a parameter set which best reproduced the experimental behaviour was obtained. This is given in table 1 while the corresponding monoclinic structural parameters are given in table 2, and are seen to be close to those previously determined. The resulting $\bar{A}$ as a function of temperature is included in figure 4 from which it is seen that a re-entrant sequence of phase transitions is predicted with transition temperatures $T_1 = 70$ K and $T_2 = 185$ K and a minimum value of $\bar{A}$ of -1.3 J deg^{-2}. This behaviour is remarkably similar to that observed experimentally except that the predicted transition temperatures are about 90 K too low. The constant $\bar{C}$ was also calculated using this lattice-energy model and was found to be approximately constant with temperature and equal to 0.007 J mol^{-1} deg^{-4} which is in quite good agreement with the average experimental value of about 0.005 J mol^{-1} deg^{-4} (figure 2(c)). Considering the approximations involved in the calculations, particularly the neglect of any vibrational contribution to the free energy, the agreement with experiment is very encouraging and is a strong indication that the mechanism underlying the phase transition has been correctly identified.

In order to relate the above calculation more directly to the theory set out in § 3, the contributions to $\bar{A}$ from the variation of each strain component separately were calculated. The results of this are shown in figure 5. The first point to be noted is that each contribution is, at least approximately, proportional to the corresponding strain component shown in figure 3 and that the total $\bar{A}$ is nearly equal to the linear superposition of the individual contributions. It follows therefore that equation (5), suitably generalised to more than one strain component, can reasonably be applied without the addition of terms higher order in the strain. A further point which follows from a comparison of figures 4 and 5 is confirmation of the importance of the strain e_1 in determining the re-entrant properties of the phase transition. However, although $\bar{A}$ is very strongly dependent on this component, the re-entrant behaviour would not occur if it were not for fortuitous cancellations of the contributions from the other strains.

To make a more quantitative comparison with the results of § 3, we first consider the contribution from the strain e_1 only. Comparison of the results given in figures 4 and 5 shows that the constant D in equation (5) has the value 450 J mol^{-1} deg^{-2} while E can be calculated from the second derivative of the potential with respect to e_1 which procedure leads to $E = 9.5 \times 10^5$ J mol^{-1}. These results lead immediately to $D^2/4E = 0.053$ J deg^{-4} in reasonably good agreement with the value of 0.043 J deg^{-4} obtained from the arguments set out in § 3. These results can also be used to predict the variation in the strain itself that would be expected to result from its coupling with the order parameter: substituting into equation (6) we get $e_1 = e_{10} - 0.00024P^2$ where P is measured in degrees. The maximum value of $e_1 - e_{10}$ is therefore -0.0038, while a similar calculation using the calculated E along with the experimental value of $D^2/2E$ yields a value of -0.0031 for this quantity. These values are quite significant when compared with the experimental values of the total strain (maximum $e_1 = -0.01$) and it is perhaps surprising that this feature was not apparent in the experimental measurements of e_1. However, the reasons for this are clear from figure 6 which shows the experimental data along with both the smooth curve assumed for the purposes of the calculations described earlier and another in which an extra strain equal to $-0.0002P^2$ is added to a smooth curve. It is clear that the present experimental data are not good enough to distinguish

between these two models, but it should be noted that accurate measurements of the lattice constants, particularly in the vicinity of the phase transitions, would provide valuable confirmation of the theoretical model.

A modification of the temperature dependence of e_1 in the manner just described would result in a change in the calculated temperature dependence of $\tilde{A}_1$ as it is clear
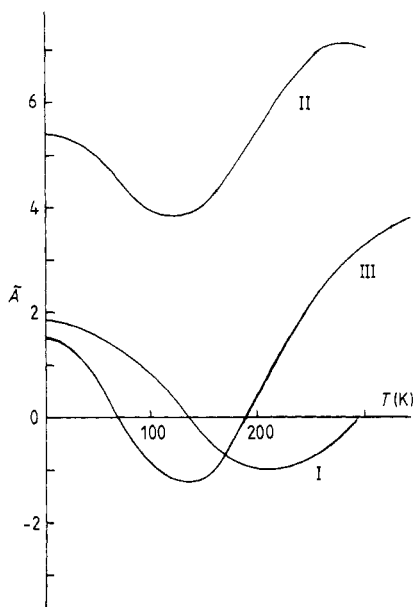

Figure 4. The temperature dependence of the soft-mode force constant $\tilde{A}$ (units: J mol^{-1} deg^{-2}) as measured experimentally (curve I) and as calculated using the original (curve II) and adjusted (curve III) intermolecular potential.
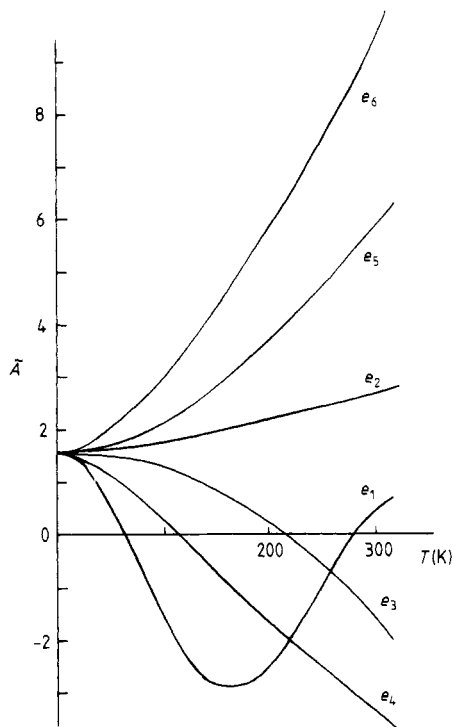
Figure 5. The contributions to the calculated soft-mode constant $\tilde{A}$ (units: J mol^{-1} deg^{-2}) resulting from the temperature variation of the individual strain components, defined in the legend to figure 3.

from equation (8) that the corrected strain e_{10} rather than the total experimental strain e_1 should have been used in the calculation. Comparison of figures 4, 5 and 6 shows that this would have led to a significant increase of $\tilde{A}$ over most of the temperature range and a further adjustment of the N---H potential would be required to restore the re-entrant behaviour.

The model for the phase transition depends crucially on the anomalous thermal contraction of the cell dimension a, represented by strain component e_1, in the monoclinic α phase. This behaviour can be qualitatively understood by reference to figure 1(*b*): thermal expansion of the c axis increases the space between parallel molecules, so permitting neighbouring molecules to close in along the x direction therefore reducing a; at higher temperatures this effect is overcome by the normal thermal expansion of a. Some theoretical support for this idea was obtained by minimising the lattice energy with respect to a with all the other parameters held at values corresponding to 150 K. A

contraction of a resulted although its magnitude ($e_1 = -0.003$) was considerably less than that observed.

The discussion in the last three paragraphs has neglected the variation of strain components other than e_1, whereas a complete treatment should consider all the strain components and the interactions between them. However, it turns out that the other calculated coupling constants are all considerably smaller than that associated with e_1, while the values of E are of the same order. If follows that, although these strains make significant (although largely mutually cancelling) contributions to $\bar{A}$, the corresponding
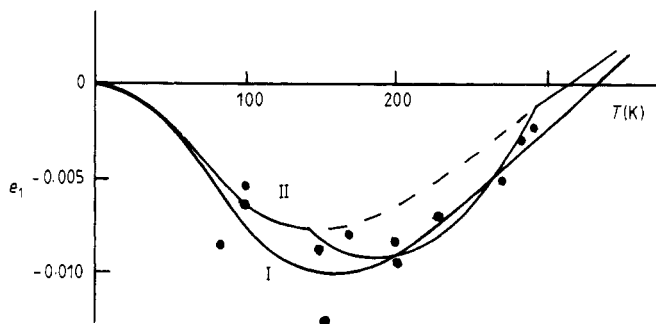

Figure 6. The temperature dependence of the strain e_1 ($= \delta a/a$). The full circles represent experimental measurements (Dove and Rae 1983), curve I is the smooth curve used in the calculations and curve II is a fit to the data, taking into account the contribution to e_1, associated with the phase transitions.

contributions to the quantity $D^2/2E$ are quite small as are the expected additional contributions to the strains themselves.

The lattice-energy calculations have produced a model for the re-entrant phase transition that is in good agreement with much of the experimental data, particularly the magnitude of the Raman frequencies and the order parameter and the size of the temperature range of the β phase. However, the transition temperatures are both considerably lower than those observed experimentally. This is quite probably due to the neglect of the vibrational contribution to the free energy except in so far as it gives rise to the thermal expansion of the monoclinic structure. A further consequence of the vibrational free energy is likely to be a temperature dependence of the soft-mode frequency, additional to that resulting from thermal expansion. If this new contribution were to cause a hardening of the soft mode with increasing temperature it would result in the movement of the calculated minimum in $\bar{A}$ towards the experimental value.

Finally, it is interesting to contrast the effect of the coupling between order parameter and strain in malononitrile with that operating in the case of the phase transition in s-triazine (Rae 1982). In the latter, the interaction is also between a strain component, e_1 and the amplitude of a zone-centre mode, P, although the latter now has the symmetry E_g and belongs to the same irreducible representation as the strain. As in malononitrile, a coupling term of the type P^2e, along with a higher-order term P^2e^2, plays an important role. In the case of triazine, however, the effect of these couplings is to cause only a slight softening of the optic mode, while giving rise to a large change in the elastic constant which becomes unstable at the transition temperature where an elastic phase transition occurs.

6. Conclusions

Results of calculations of the lattice energy of malononitrile are consistent with the re-entrant phase transitions resulting from a coupling between the order parameter associated with the transition (which consists of opposite rotations of the two molecules related by a screw axis in the high-temperature phase) and the lattice strain. Of particular importance is the component of strain corresponding to a change in the length of the *a* axis of the unit cell; this initially decreases as the temperature is raised from absolute zero, goes through a minimum and increases at higher temperature. The soft-mode force constant has been found to be approximately proportional to this strain and becomes negative, corresponding to a transition to a low-symmetry phase, over an intermediate temperature range, above and below which the high-symmetry structure is stable. Further evidence of the importance of the coupling between order parameter and strain has been obtained from a study of the relative values of the force constant above and below the lower transition temperature; results obtained from the analysis of the experimental data on this point have been found to be in good agreement with those derived from the lattice-energy calculations.

References

Boyd R H, Guha K R and Wuthrick R 1967 *J. Phys. Chem.* **71** 2187
Cowley R A 1980 *Adv. Phys.* **29** 1–110
Dove M T, Farrelly G F, Rae A I M and Wright L M 1983 *J. Phys. C: Solid State Phys.* **16** L195–8
Dove M T and Rae A I M 1980 *Faraday Discuss. Chem. Soc.* **69** 98–106
—— 1983 to be published
Girdhar H L, Westrum E F Jr and Wulff C A 1968 *J. Chem. Eng. Data* **13** 239
Govers H A J 1975 *Acta Crystallogr.* A **31** 380
van Haverbeke L and Herman M A 1975 *Bull. Soc. Chem. Belg.* **84** 439–51
Higashigaki Y and Wang C H 1979 *J. Chem. Phys.* **71** 3813–23
Le Calvé N, Pasquier B and Novak A 1980 *J. Chem. Phys.* **72** 6409–13
Miller P B and Axe J D 1967 *Phys. Rev.* **163** 924–6
Nakamura N, Tanisaki S and Obatake K 1971 *Phys. Lett.* **34A** 372
Obatake K and Tanisaki S 1973 *Phys. Lett.* **44A** 341
Pershan P S and Prost J 1979 *J. Physique* **40** L27–30
Rae A I M 1969 *Mol. Phys.* **16** 257–73
—— 1982 *J. Phys. C: Solid State Phys.* **15** 1883–96
Rae A I M and Mason R 1968 *Proc. R. Soc.* A **304** 479–87
Williams D E 1966 *J. Chem. Phys.* **45** 3770
—— 1967 *J. Chem. Phys.* **45** 4680
—— 1971 *Acta Crystallogr.* A **27** 452–5
Zussman A and Alexander S 1968 *J. Chem. Phys.* **49** 3792