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Raman spectra and reentrant phase diagram of malononitrile CH$_2$(CN)$_2$

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Résumé. — Les spectres Raman du malononitrile sous des pressions pouvant s'élever jusqu'à 8 kbar et à des températures allant de 77 K à 320 K ont été mesurés. Ils permettent de compléter le domaine des basses pressions du diagramme de phase qui contient une transition de phase réentrante dont on montre que le caractère réentrant provient d'un fort couplage anharmonique avec une déformation élastique de symétrie Ag. Dans le domaine des pressions plus élevées du diagramme de phases, on a découvert une nouvelle transition de phase, du premier ordre et également réentrante.

Abstract. — Raman spectra of malononitrile are investigated under pressure up to 8 kbar at temperatures extending from 77 K to 320 K. The low pressure part of the phase diagram, containing a second order reentrant phase transition is completed and it is shown that the origin of the reentrant character can be interpreted on the basis of a strong anharmonic coupling with an elastic deformation of Ag symmetry. A new first order phase transition, also reentrant, is discovered in the higher pressure part of the phase diagram.

1. Introduction.

The structure of malononitrile CH$_2$(CN)$_2$ has been shown to be rather unstable : four solid phases are known to exist at room pressure that we shall label according to reference [1]. If the very slow transformation into phase III (1) at 260 K is avoided by returning every day the crystal to the room temperature and pressure, one is left with an unusual reentrant system of three phases I, II, IV (Fig. 1), i.e. the structure of phase IV is identical to that of phase I, the two phase transitions at $T_1$ and $T_2$ being of second order. Previous investigations using Raman scattering [1, 2, 5], infrared absorption [2], calorimetry [9], nuclear quadrupole resonance [4, 8] and X-ray diffraction [3, 6, 7] agree generally with the space groups and $Z$, number of molecules per cell given in the caption of figure 1, with, however, a controversy on the structure of phase II. Nevertheless we think that our measurements confirm the last X-ray determination of Dove and Rae [3] by providing strong enough evidences to close the discussion (see section 4.1).

The aim of this paper is to report an investigation, by Raman scattering, of the pressure-temperature phase diagram in which, up to now, only the I-II transition line $T_1(P)$ was known [4]. The results turn out to be rather rich, allowing for:

- the discovery of a new phase (labelled V) lying inside the domain of existence of phase II. The set of phases exhibits a doubly reentrant character, i.e. it exists some values of the pressure for which, upon cooling, the phases are scanned in the order I, II, V, II, IV (≡ I);
- an interpretation, based on a Landau theory, of the reentrant character of the I-II-IV set of phases.

Furthermore, many of our experiments were based on the study of two internal modes, the frequencies of which were very sensitive to the phase transitions and we shall elaborate briefly on the origin of this effect.

This paper is organized as follows:

- The experimental procedure and results are described in sections 2 and 3. A discussion of the symmetry

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(1) Little is known about the structure of phase III, and this phase will not be dealt with any more in this paper.
of phase II, of the origin of the unusual splitting of these two internal modes in phases II and V, of the ferro-elastic character of the IV-II phase transition and of the structure of the new phase V is performed in section 4. Finally, section 5 is devoted to the discussion of a phenomenological model for the description of the successive phase transitions IV-II and II-I, and it is shown that this model agrees with the experimental data presently available.

2. Experimental procedure.

Commercial malononitrile (Fluka A.G.) has been dissolved in isopropanol, recrystallized by evaporating the solution and further purified by sublimation in vacuum. Crystallization in a helium or nitrogen atmosphere was obtained by the Bridgman method in which the cold part of the oven was set at $-12^\circ$C to avoid supercooling. Good single oriented crystals of approximately $3 \times 3 \times 5$ mm were cut for the atmospheric pressure experiments from 80 K to 300 K, where polarized spectra could be used to determine the symmetry of the modes in phases I and IV. Extra spectra were taken between 4 K and 80 K from clear and transparent polycrystals of about $6 \times 6 \times 7$ mm. These polycrystals were also used for the measurements under pressure. Those were performed in a helium fed pressure cell of maraging alloy with three sapphire windows. The pressure was scanned (at constant $T$ for convenience) from 0 to 8 kbar and measured by the resistance variation of a manganin coil located in a separate pressure cell kept at room temperature but connected in parallel with the sample cell. The temperature was varied from 78 K to 320 K and measured with a thermocouple at room pressure, located inside the tip of a narrow glove finger so that the thermocouple was at atmospheric pressure and close to the centre of the pressure cell. The latter was kept at constant temperature through two spiraled pipes carrying liquid nitrogen and further wrapped with resistive heaters, embedded in a copper flat cylinder and pressed on two opposite flat surfaces of the sample pressure cell.

The excitation of the Raman spectra was produced by an argon laser 5145 Å line, the power of which never exceeded 0.3 W.

As mentioned in the introduction, care was taken to prevent the transition to phase III by spending less than 10 hours at temperatures below 270 K. Otherwise, the spectral range from 50 to 180 cm$^{-1}$ is strongly and characteristically modified [1], and the sample shatters.

3. Experimental results.

3.1 Zero Pressure Measurements. — The corresponding spectra have been published by various authors [1, 2, 5]. In the next sections we shall therefore focus our attention only on the soft mode (Fig. 2), which is observed in phases II and IV, and on the behaviour of two internal modes near resp. 1 200 cm$^{-1}$ and 1 400 cm$^{-1}$ which are almost degenerated in phases I and IV, this degeneracy being lifted in phases II and V.

The rest of the spectra have been fully analysed [5]; let us simply recall that all the internal modes have been assigned and that all the twelve active external modes are observed at least at sufficiently low temperature.

3.2 The I-II and II-IV Transition Lines. — A transition point can frequently be determined in a Raman

![Fig. 2. — Room pressure frequency of the soft mode versus temperature. The open circles (O) are direct positioning of the spectral maximum of the peak while the crosses (x) are the frequencies of the maximum of a Lorentzian curve fitted to the spectra. The soft mode frequencies calculated from equation (15) (...) and from our model (-----) differ in phase II but coincide in phases I and IV (- - -).](image)

![Fig. 3. — Band profile of the internal mode near 1 400 cm$^{-1}$ at 320 K. a) In phase I : $P$ = 1.45 kbar; b) At the I-II transition, $P$ = 1.63 kbar. In phase II : c) $P$ = 1.73 kbar; d) $P$ = 1.83 kbar; e) $P$ = 2.01 kbar; f) $P$ = 3 kbar; g) $P$ = 4.01 kbar; h) $P$ = 6 kbar; i) $P$ = 7.9 kbar.](image)
scattering experiment by studying the $T$ or $P$ dependence of the frequency of a mode which is sensitive to the transition. A priori, the soft mode is a good candidate, but the sensitivity of the method is actually limited by the width of this mode (relatively broad near the II $\rightarrow$ I transition line [5], cf. Fig. 2) and by its intensity which is smaller than the adjacent Rayleigh line by several orders of magnitude. In the present case, we believe that this is the reason why the soft modes has not been observed in the narrow domain of existence of phase I.

We have found another way of studying the various transitions reported here, by observing two internal modes, one near 1400 cm$^{-1}$ (Fig. 3) and one near 1200 cm$^{-1}$. Figure 4 shows that, at 79 K, the splitting of the 1400 cm$^{-1}$ line, as a function of pressure, starts exactly at the IV $\rightarrow$ II transition while figure 5 illustrates the fact that, at 320 K, the apparent splittings of the 1200 and 1400 cm$^{-1}$ lines start at the same pressure, within experimental errors. On the other hand, at the same temperature, the width of the soft mode yields an unprecise determination of its frequency below $\sim 4$ kbar, i.e. $\sim 17$ cm$^{-1}$.

The pressure at which such splittings started was used to determine the I-II and the II-IV transition lines and checks were made, when possible, to ensure that this did not disagree with the extrapolation to zero of the soft mode frequency.

3.3 Existence of an additional phase (Phase V). — By increasing the pressure in phase II, several new features were observed:

- The frequency of the soft mode increased and jumped at a certain pressure $P \uparrow (T)$ to another value (Fig. 6).
- This phenomenon was accompanied by a similar jump in the splittings of the two internal test modes discussed in the preceding section (Fig. 6).
- The total number of lines did not change at $P \uparrow$ but the relative intensities of the external modes were strongly modified (Fig. 7).

Any one of the above features is a signature of a transition from phase II to a new phase that we shall label phase V.

When decreasing the pressure from phase V, the reverse facts were observed but the recovery of phase II occurred with an hysteresis effect, the transition pressure $P \downarrow$ being several hundred of bars below $P \uparrow$. In some cases, we even succeeded in getting the coexistence of phases II and V and observing the superposition of both characteristic spectra.

Figure 8 shows the phase diagram in the full explored domain (79 K $\leq T$ $\leq$ 320 K; 0 $\leq$ $P$ $\leq$ 8 kbar) where the II-V transition pressure is arbitrarily taken as:

$$P(T) = \frac{[P \uparrow(T) + P \downarrow(T)]}{2}.$$
Fig. 7. Low frequency Raman spectra at $T = 80$ K. 
a) In phase IV, at $P = 0.205$ kbar; b) In phase II at $P = 1.79$ kbar; c) In phase V at $P = 1.6$ kbar; d) In phase V at $P = 7.99$ kbar. Note that, owing to an hysteresis effect, pressure ranges of phases II and V overlap.

Fig. 8. The phase diagram of malononitrile. The crosses ($\times$) are transition points from phase II to phase I or IV determined by fits of our Raman data. The two straight lines $T_1(P) = 142 - 44P$ and $T_2(P) = 294 + 16P$, $P$ in kbar, $T$ in K are the transition lines calculated by our model. The vertical bars indicate the size of the pressure hysteresis of the II-V transition and the corresponding transition line is drawn arbitrarily in the middle of the bars.

Fig. 9. The soft mode frequencies $\omega_s$ at the II-V transition. (O) : Phase II value, obtained by decreasing the pressure; (●) : Phase II value, obtained by increasing the pressure; stars (∗) : Phase V value; in this last phase, the pressure dependence of $\omega_s$ is too small to produce a visible hysteresis effect at the scale of this figure. (All lines are guides for the eye.)

On figure 9 are plotted the soft mode frequencies at $P \uparrow$ and $P \downarrow$ in both phases.

The width of the soft mode increases markedly with temperature but is quite independent of pressure, except at the II $\rightarrow$ V transition where it is divided by a factor of about 2 (see Fig. 10 which shows the soft

Fig. 10. The soft mode profile at $T = 320$ K and $P = 7.855$ kbar where, due to hysteresis effects, the state of malononitrile may be selected among two phases; (---) : Phase II, obtained by increasing the pressure; (-----) : Phase V, obtained by decreasing the pressure. The intensity scales are different in order to get comparable heights.
mode profile in both phases at the same temperature and pressure). This change in line width was actually used as an additional test for drawing the phase diagram when the jumps of the soft mode and of the splittings were very small.

4. Discussion.

In this section, we shall concentrate simply on the problem of the structure of phase II. This will enable us to make precise the order parameter related to the IV-II phase transition (§ 4.1), then the origin of the splitting of the 1 200 and 1 400 cm$^{-1}$ modes in that phase (§ 4.2). Comparing this splitting with the low frequency results we shall conclude that the ferroelastic character of the IV-II phase transition is weak and can be ignored in the remaining of this paper (see section 5). Finally, we shall elaborate on the possible structure of phase V.

4.1 The structure of phase II. — The second order and displacive characters of the I-II and II-IV transitions have been early recognized from the calorimetric [9] and NQR [8] measurements. The structures of phase I [6, 7] and II [3] have been determined by X-ray diffraction to be P2$_1$/a(C$_2$n) and P1(C$_1$) respectively and the phases I and IV have been stated to be crystallographically identical by Dove and Rae [3] on the basis of the NQR data of [8]. However, the phase II space group given in [3] disagrees with the conclusions of several papers [6, 1, 5]. The observation of a soft mode in phases IV and II [15 and Fig. 2 in this paper] provides strong evidences for the correctness of a C$_1$ structure:

- This soft mode is unique and softens at the two transition temperatures. This confirms the displacive and second order characters of both the transitions and the identity of the space groups of phases I and IV. The unique relevant order parameter of the set of phases I-II-IV will be labelled $Q$.

- The soft mode is observed in phases IV and II. From the Raman selection rules, this means that the order parameter of the second order II-IV transition belongs to a Brillouin zone centre even (gerade) representation. Thus the number of molecules per unit cell is the same ($Z = 4$) in both phases and the inversion symmetry is retained in phase II. This confirms the results of Dove and Rae [3] which are summarized on figure 1 and assigns to $Q$ a representation B$_g$, i.e. symmetrical with respect to the inversion operation and antisymmetrical with respect to the screw binary axis and to the glide plane.

4.2 The splitting of two internal modes. — With our experimental set up, two internal modes (near 1 200 cm$^{-1}$ and 1 400 cm$^{-1}$) have been found to apparently no splitting in phase I (and IV); these lines also generally show splittings proportional to $\omega_s$, the soft mode frequency, in phase II (and phase V) (Figs. 3, 4 and 6). These effects can be understood through the following argument:

4.2.1. Let us first concentrate on the mode near 1 200 cm$^{-1}$. This mode has been assigned to the twist mode, $v_{14}$, of the two CH bonds of the free molecule [10] which is Raman active but infrared inactive. From the structure of malononitrile [3, 6, 7], it is found that the nearest neighbours of the H atoms are nitrogen atoms belonging to other molecules. The latter belong to nitrile groups which have a stretching frequency of $\sim 2 100$ cm$^{-1}$. This creates such a large mechanical shielding between two molecules that there is no dynamical coupling between the $v_{14}$ modes of the four different molecules which belong to the same unit cell.

This analysis leads to the following conclusions:

a) whatever is the pressure or the temperature, as long as the four molecules belong to the same family (which is the case in phases I and IV), only one frequency will be measured in the Raman scattering experiments and this agrees with our experimental findings;

b) on the contrary in phase II, the point group is C$_1$ and the four molecules split into two families which have different local environments; thus, two different Raman frequencies will be recorded. It is easily shown (see Appendix) that this splitting is proportional to $\langle Q \rangle$, the amplitude of the frozen soft mode in phase II (and V). The splitting between the two $v_{14}$ frequencies is thus an easy way of measuring a quantity proportional to $\langle Q \rangle$. In section 4.3, taking into account the weakness of the ferroelastic character of the IV-II and II-I transitions, we shall show that this results in a proportionality between $\omega_s$ and the $v_{14}$ splitting.

4.2.2. The situation is a priori more complex for the case of the $v_3$ mode (near 1 400 cm$^{-1}$). This mode has been assigned, in the free molecule [10], to the scissor mode of the same CH$_2$ group. The same argument for the mechanical shielding between the modes of the various molecules thus holds. Unfortunately this mode is infrared active in the free molecule so that there is an induced dipole interaction between the molecules, which cannot be a priori neglected. It results in a 6 cm$^{-1}$ splitting between the infrared A$_u$ and B$_u$ modes at 300 K [2] and a 5 cm$^{-1}$ splitting between the Raman A$_u$ and B$_u$ modes. The theory outlined in the appendix should thus take this effect into account, which can easily be done. This turns out to be unnecessary, due to two facts:

a) In phase IV, the induced dipole-induced dipole coupling leads to a splitting which is so small that it can be neglected and the same results as for $v_{14}$ directly used.

b) In phase I, this splitting is $\sim 5$ cm$^{-1}$. Nevertheless, it cannot be detected in a polycrystal (Figs. 3a and b) because of the linewidths and of the slit width
we had to use. Furthermore, the effect of the local environment is so large, that it immediately affects the band widths of the soft mode as soon as \( \langle Q \rangle \) is not zero (Figs. 3c and d). The study of this band profile as a function of pressure — assuming that close to the I-II transition the band widths are constant and equal to those measured in phase II (Fig. 3f) — leads to the « apparent splitting » reported on figure 5, which shows how sensitive this test for the detection of the phase transition.

### 4.3 Ferroelastic Aspect of the I-II and II-IV Transitions

As \( Q \) is in the \( B_g \) representation, it exists in the Landau free energy, a harmonic coupling between the order parameter and the two elastic strains \( e_4 \) and \( e_5 \) (if \( z \) is parallel to the screw axis) which are in the same representation. Near the transitions, this free energy reads

\[
F = \frac{1}{2} A Q^2 + \frac{1}{4} B Q^4 + D_4 Q e_4 + D_5 Q e_5 + \frac{1}{3} C_{44} e_4^2 + \frac{1}{3} C_{55} e_5^2 \quad (1)
\]

where we have chosen the directions \( x \) and \( y \) in such a way that they diagonalize the part of the elastic energy involving \( e_4 \) and \( e_5 \).

The large range of variation of the soft mode frequency (Fig. 2) shows that the transitions have an improper ferroelastic character, i.e. the transitions are driven by the \( T \) and \( P \) dependence of the coefficient \( A = A(T, P) \). Applying the Landau theory to the II-IV transition at constant \( T \) (in order to stay away from the I-II transitions), the coefficient \( A \) may be written:

\[
A = K(P - P_0)
\]

where \( K \) and \( P_0 \) are positive constants.

Minimizing (1) with respect to \( Q, e_4 \) and \( e_5 \) leads to a second order transition occurring with \( Q = 0 \) at a pressure \( P_0 \) given by:

\[
P_0 = P_c - \Delta P
\]

with

\[
\Delta P = \left( \frac{D_4^2}{C_{44}} + \frac{D_5^2}{C_{55}} \right) K \quad (2)
\]

in phase IV:

\[
\langle Q \rangle = 0 \quad \text{and} \quad \omega_s = K^{1/2}(P_0 + \Delta P - P)^{1/2}
\]

while in phase II:

\[
\langle Q \rangle \sim (P - P_0)^{1/2} \quad (3)
\]

and

\[
\omega_s = (2K)^{1/2} [P - (P_0 - \Delta P / 2)]^{1/2} \quad (4)
\]

An illustration of these results is given in figure 4. According to the conclusion of section 4.2 and to equation (3), the splitting \( \Delta \omega(P) \) of the internal mode vanishes at \( P = P_0 \). As the soft mode extrapolates to nearly zero at the same pressure, this shows that, within experimental errors, \( \Delta P = 0 \); in other words, the coupling constants \( D_4 \) and \( D_5 \) of equations (1) and (2), i.e. the ferroelastic character of the transition, can be neglected. Our experimental results are consistent with this approximation in the whole range of our measurements. They also agree with the very narrow temperature range (1.5 K) in which the II-I transition affects a sound velocity directly coupled to the elastic constants which go to zero in a ferroelastic transition [11].

### 4.4 Discussion of Phase V

— In spite of the lack of crystallographic data, our measurements provide many informations on phase V. The transition from phase II (space group \( P_{1}\equiv C_{1} : Z = 4 \)) to phase V has the following properties:

a) it has a first order character with a hysteresis reaching several hundreds of bars (see section 3.3);

b) it is a reentrant transition (Fig. 8): phase V exists only above 1.3 kbar; above 1.5 kbar, the hysteresis does not in principle prevent the successive occurrences of phases I, II, V, II, IV (\( \equiv I \)) when decreasing the temperature at constant pressure;

c) it involves an order parameter \( R \) which is different from \( Q \). This last point comes from the following facts: the twelve external modes (6 \( A_g \) + 6 \( B_g \)) are easily seen at low temperature (e.g. at 15 K in [5]) and broaden progressively when \( T \) increases. At 80 K it is still possible to detect all of them, both in phases IV and II owing to their different sensitivities to pressure which modifies their overlap. This is exemplified in figure 7 where these modes are numbered from 1 to 12. [For instance the mode number 12 coinciding with the mode number 11 at 0.2 kbar (Fig. 7a) increases strongly and continuously in frequency with pressure and starts to overlap with an internal mode at 1.79 kbar (Fig. 7b).] The driving mode of the transition is thus neither \( Q \) nor another Raman active mode of phase II.

In phase V, an inspection of the 80 K spectra at several pressures shows that new modes are very slowly increasing in intensity with increasing pressure (Figs. 7c and d). A careful numbering results in 25 modes in the 0-200 cm\(^{-1}\) spectral range (including a low frequency internal vibration \( v_6 \) [10] of the molecule) which are well separated from the next internal mode which lies above 330 cm\(^{-1}\). Admitting that \( v_6 \) is split into 4 active modes, one is left with 21 detected external Raman active modes. If the space group of phase V is assumed to be a subgroup of that of phase II, the preceding result can be interpreted either as a cell doubling without change in the symmetry or a lost of the inversion centre, with the size of the cell unchanged. In the absence of crystallographic data, we have no argument to discriminate between those possibilities. Taking the \( P_{2_1}/n \) space group as the parent phase, the various possible solutions are shown in table I.

One must nevertheless point out that such an analysis is dubious. Indeed the new modes are not seen at the II-V transition, and their intensities increase with pressure. This means that the order
Table I. — Possible symmetry of phase V.

<table>
<thead>
<tr>
<th>Representation</th>
<th>Order parameter R</th>
<th>Wave vector q</th>
<th>Space group</th>
<th>$N_R$ (*)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_u$</td>
<td>$q = 0$</td>
<td>$P1 \equiv C_1, Z = 4$</td>
<td>21</td>
<td>inversion center lost</td>
<td></td>
</tr>
<tr>
<td>even or odd</td>
<td>$q = \alpha \mathbf{a}^* + \beta \mathbf{b}^* + \gamma \mathbf{c}^* \neq 0$</td>
<td>$P \bar{1} \equiv C_p, Z = 8$</td>
<td>24</td>
<td>cell doubling</td>
<td></td>
</tr>
</tbody>
</table>

(* ) $N_R$: expected number of Raman active external modes.

Parameter $R$ is far from its maximum value, at the phase transition. When this is the case, and when one is dealing with a displacive transition, there is one mode (related directly to $R$) which must have an intensity practically pressure independent and thus should be detected already at the phase transition. Such a situation is not encountered when $R$ relates to an order disorder transition, in which case no new mode is expected to appear; nevertheless no disorder has been reported up to now in $\text{CH}_2(\text{CN})_2$. The meaning of $R$ and the microscopic nature of the transition is thus unknown, so that the group-subgroup relationship may be questionable.

d) The order parameter $R$ is anharmonically and strongly coupled to $Q$ in order to produce the large jumps of the soft mode frequency (Fig. 6) or in the splittings of the two internal modes [cf. Eq. (A.4)]. It is probable that the $T$ and $P$ dependence of $Q$ partially triggers the II-V transition and transmits the reentrant character.

e) We cannot predict whether the II-V first order and the II-IV second order transition lines are or are not crossing at a lower temperature, out of our measurement range. In the case of a crossing, interesting effects have been predicted theoretically [12] that could be observed on malononitrile.

5. A model for the reentrant I-II-IV transition.

As reentrant transitions are quite rare phenomena, we have tried to carefully study all the information which could be obtained from our experiments, and see whether a suitable model could emerge out of it. The one we are presenting below is, in fact, an extension of the recent work of Muralt et al. [13], and we shall see that such a model contains the basic physics necessary to explain our data.

5.1 THE FREE ENERGY MODEL. — In the Landau theory of second order displacive phase transitions, the relevant part of the free energy is usually expressed as:

$$F = \frac{1}{2} \omega^2(T) Q + \frac{1}{4} b Q^4$$

with

$$\omega^2(T) = \alpha(T - T_1) = \alpha T - \omega_0^2; \quad \alpha > 0.$$  (6)

From the classical paper by Bruce and Cowley [14] on the phase transition of cubic $\text{SrTiO}_3$, it is known that this linear dependence on temperature contains at least two types of contribution:

- an intrinsic dependence of the soft mode frequency on the temperature, related to the third and fourth order anharmonicities, computed at constant volume:

$$\left( \frac{\partial \omega^2}{\partial T} \right)_V = \alpha_1,$$  (7)

- an extrinsic contribution related to the change of volume of the lattice cell, the latter being, naturally, also due to the anharmonic processes:

$$\left( \frac{\partial \omega^2}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P = \alpha_2,$$  (8)

$$\alpha = \alpha_1 + \alpha_2 .$$

This means that equation (6) may be rewritten as:

$$\omega^2(T) = \alpha_1 T + \left( \frac{\partial \omega^2}{\partial V} \right)_T V \eta(T) - \omega_0^2,$$  (9)

where $\eta$ is the relative volume change which, in the cubic phase, can be expressed as

$$\eta(T) = 3 \lambda T ,$$  (10)

$\lambda$ being the thermal linear expansion coefficient.

The preceding analysis must, in the case of malononitrile, be generalized in three different ways:

a) Malononitrile being monoclinic, any phonon mode depends linearly not only on the volume change, but also on the anisotropic dilatation plus the shear deformation which maintain the monoclinic symmetry. The coefficient $\eta$ can thus be any linear combination of these four deformations which all belong to the identity representation of the $C_{2h}$ point group;

b) There is no reason to restrict the $\eta$ dependence to terms linear in $\eta$, and in the present case, we have found necessary to include an explicit dependence of $\omega^2$ on $\eta^2$;

c) Equation (10) represents only the deformation of the lattice in the high temperature phase; in order
to represent in an adequate manner the influence of any deformation on the properties of the crystal in all phases, it is necessary to include explicitly a variation of the elastic energy with temperature and pressure.

Our starting free energy thus reads

\[ F = \frac{1}{2} \omega^2 Q^2 + \frac{1}{4} bQ^4 + (\beta T + \lambda P) \eta + \frac{1}{2} d \eta^2 \]  

with

\[ \omega^2 = \alpha_1 T + g \eta + f \eta^2 - \omega_0^2. \]  

5.2 DISCUSSION OF THE PHASE TRANSITION AT ZERO PRESSURE. — Minimizing equation (11) with respect to \( \eta \) yields in phase I or IV:

\[ \omega^2 = \left( \alpha_1 - \frac{bg}{d} \right) T + \frac{bP^2}{d^2} T^2 - \omega_0^2 \]

\[ \equiv \alpha(T - T_1)(T - T_2) \]

which shows that, for properly chosen values of \( g \) and \( f \), a reentrant phase transition, with transitions temperatures \( T_1 \) and \( T_2 \), is an immediate consequence of the model.

Such a form for \( \omega^2 \) was in fact postulated by Zussman and Alexander [8] in order to explain their NQR data, and by Dove and Rae [3] as a heuristic description of the reentrant system.

Actually, as shown above, equation (13) gives directly the soft mode frequency in phase IV (and I) and this formula agrees rather well with our Raman data, close to \( T_2 \). It does not fit properly the very low temperature data, but this is largely related to the fact that the anharmonic effects (both direct and indirect) are not linear at low temperature.

It is more important to note that the direct \( \eta^2 Q^2 \) and \( \eta \theta Q^2 \) couplings which appear in equations (11) and (12) have an important consequence on the soft mode frequency in phase II. Following equation (13) one could have been tempted to write for any temperature, instead of equation (11), the expression:

\[ F = \frac{\alpha}{2} (T - T_1)(T - T_2) Q^2 + \frac{b}{4} Q^4, \]  

which gives the same soft mode frequency in phases IV and I but yields:

\[ \omega_s^2 = -2 \alpha(T - T_1)(T - T_2), \]  

in phase II. Equation (15) gives totally unacceptable results (see Fig. 2) in this phase because its maximum (which takes place at \( T = (T_1 + T_2)/2 \)) is very shallow in contradiction with the sharp variation of our data. On the other hand, it has already been recognized that a very steep variation of the soft mode frequency can be accounted for by a direct high order coupling between the soft mode normal coordinate and some elastic distortion; this mechanism has, for instance, been used by Errandonea [15] to explain the soft mode variation in the monoclinic phase of LaP\(_2\)O\(_4\). As is clear on figure 2, this high order term plays an important role in the agreement between the experimental data and our model.

5.3 DISCUSSION OF THE PHASE DIAGRAM. — The transition lines between phases IV, II and I are given by putting \( \omega^2 = 0 \) in equation (12), once equation (11) has been minimized at \( Q = 0 \) with respect to \( \eta \). This yields:

\[ \eta = - (\beta T + \lambda P)/d; \]

\[ \alpha_1 T - g(\beta T + \lambda P)/d + f(\beta T + \lambda P)^2/d^2 - \omega_0^2 = 0. \]

The transition lines appear then as parts of a parabola with an axis parallel to the line \( \lambda P + \beta T = 0 \). This means that the transition lines should display some curvature, which is not revealed by our data. This has forced us to an ad hoc modification of equation (12) which is finally written as:

\[ \omega^2 = \alpha T + \mu P + \nu P^2 + g \eta + f \eta^2 - \omega_0^2, \]

in which an explicit dependence of the soft mode frequency on pressure has been added.

Note that as \( \eta \) is an elastic deformation, the square of the soft mode frequency is always given by \( \omega_s^2 = \partial^2 F/\partial Q^2 \) computed at constant \( T \), \( P \). For \( \langle Q \rangle \neq 0 \), this always yields \( \omega_s \sim Q \), as was the case in section 4.3.

5.4 NUMERICAL RESULTS. — As the absolute value of \( Q \) and of the deformation \( \eta \) are unknown, if one writes \( t = T - T_2 \), one is left with seven parameters. Those have been adjusted to the value of \( T_1 \), the value of the soft mode frequency in phase IV at zero pressure, the phase transition lines IV-II and I-II, and the overall agreement of the soft mode frequencies in phase II.

The numerical values related to the free energy expansion:

\[ F = \frac{\omega^2}{2} Q^2 + \frac{b}{4} Q^4 + (\beta t + \lambda P) \eta + \frac{d}{2} \eta^2, \]

Table II. — Model parameters.

<table>
<thead>
<tr>
<th>( \alpha )</th>
<th>( \mu )</th>
<th>( \nu )</th>
<th>( g )</th>
<th>( f )</th>
<th>( b )</th>
<th>( \beta )</th>
<th>( \lambda )</th>
<th>( d )</th>
</tr>
</thead>
<tbody>
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<td>11.0</td>
<td>64.712</td>
<td>-4.850</td>
<td>5</td>
<td>330.94</td>
<td>4.225</td>
<td>4</td>
<td>34.624.7</td>
<td>0.071</td>
</tr>
</tbody>
</table>

Parameters of equations (19) and (20) where \( t \) is in K, \( P \) in kbar and \( \omega \) in cm\(^{-1}\).
6. Conclusion.

Raman scattering data on malononitrile have been investigated under pressure up to 8 kbar. They show that the mechanisms of the transitions can be well understood on the basis of a Landau-type theory:

- at low pressure, an order parameter $Q$ of $Bg$ symmetry is driving the transition from a monoclinic $P2_1/n$ (phase I and phase IV) to a triclinic $P1$ phase II with a negligible ferroelastic character;
- the strong anharmonic coupling of $Q$ with an elastic strain $\eta$ (dilatation or shear) of $Ag$ symmetry is responsible for the reentrance of phase II back to a phase IV crystallographically identical to phase I;
- a soft mode as well as the splittings of two special internal modes have been observed to accompany the order parameter $Q$;
- a new transition from phase II to a lower symmetry phase V has been discovered. Its order parameter $R$ is strongly coupled to $Q$ which results in a further reentrant character of this transition inside the phase II; we suggest that this phase is either $P1$ with $Z = 4$ or $P1$ with $Z = 8$, but the nature of the order parameter is, presently, very unclear.

It is hoped that new crystallographic determinations under pressure at low temperatures will help to characterize $Q$, $\eta$, and $R$.

Appendix.

In the $C_{2h}$ phase, when, for a given internal mode of a molecule, there is no coupling between the different molecules of the crystal, the corresponding harmonic free energy for the $q = 0$ phonon can be written as:

$$F = \frac{1}{2} \omega_i^2 \sum Q_i^2,$$

(A.1)

where $Q_i$ is the normal mode coordinate of molecule $i$ for this wave vector. Due to this degeneracy, using, instead of $Q_i$, the four linear combinations of $Q_i$ which transform as the four irreducible representations $A_g$, $B_g$, $A_u$, $B_u$ of the $C_{2h}$ group, one can rewrite (A.1) as:

$$F = \frac{1}{2} \omega_i^2 (Q_{A_g}^2 + Q_{B_g}^2 + Q_{A_u}^2 + Q_{B_u}^2).$$

(A.2)

let us concentrate on the two Raman active modes $A_g$ and $B_g$. These two modes can be anharmonically coupled, up to third order, by any phonon of $B_g$ symmetry. Physically, the phonon which drives the ferroelastic phase transition and thus distorts the local environment of a molecule, must give the strongest coupling; this phonon has, in fact the $B_g$ symmetry. We can thus restrict the free energy to:

$$F = \frac{1}{2} \omega_i^2 (Q_{A_g}^2 + Q_{B_g}^2 + VQ_{A_g}Q_{B_g}Q).$$

(A.3)

In any phase (II or V) in which $\langle Q \rangle$ is different from zero, this leads to:

$$\omega = \omega_a \pm V \langle Q \rangle/2 \omega_a,$$

(A.4)

and to a splitting proportional to $\langle Q \rangle$ which is a measure of the local environment distortion.

References


