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Ferroelastic and ferroelectric phase transition in a molecular crystal: tanane

3. — From ab initio computation of the intermolecular forces to statistical mechanics of the transition

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Résumé. — A partir de la structure de la phase quadratique désordonnée du tanane, nous avons calculé les énergies intermoléculaires de Van der Waals pour les 16 premières voisines d’une molécule donnée. Les énergies de paire, obtenues dans le cas du réseau quadratique « rigide », sont analysées à l’aide d’un formalisme de pseudo-spin qui montre que les principales interactions responsables de la mise en ordre définissent des chaînes linéaires de molécules le long de l’axe ferroélectrique Z. En l’absence de solution statistique exacte pour le modèle d’Ising à 3 dimensions, nous calculons simplement la température de transition $T_0$ dans l’approximation du champ moléculaire. Le résultat obtenu : $T_0 \approx 200 \text{ K}$ est en bon accord avec la température de transition, en réseau « rigide », déduite des études expérimentales : $T_0 = 235 \text{ K}$. Ensuite, nous considérons le couplage de type « piézo-électrique » entre la mise en ordre des molécules et le cisaillement $u_{xy}$ du réseau. A l’aide d’un traitement « à la Bragg-Williams » nous construisons, à partir de l’Hamiltonien d’Ising dépendant de la déformation, un développement de l’énergie libre qui prévoit des valeurs en bon accord avec l’expérience pour le module de cisaillement $C_{66}$, le coefficient de type « piézo-électrique » $D$ et la température de transition $T_c \approx 240 \text{ K}$ (à comparer à la valeur réelle $T_c = 287 \text{ K}$). Cette analyse révèle aussi un important couplage d’ordre supérieur, qui doit augmenter l’instabilité de la structure au voisinage de $T_c$.

Abstract. — On the basis of structural data of the disordered tetragonal phase of tanane, the Van der Waals intermolecular forces are computed for the 16 nearest neighbours of a given molecule. Considering first the molecular ordering in a « rigid » tetragonal lattice, the pair energies between neighbouring molecules are analysed within a pseudo-spin formalism which shows that the main ordering interactions define linear chains of molecules along the ferroelectric Z-axis. As there is no exact procedure for a statistical treatment of the 3-d Ising Hamiltonian, we just calculate the transition temperature $T_0$ in the mean-field approximation. The predicted result : $T_0 \approx 200 \text{ K}$ is in good agreement with the ordering temperature in the « rigid » lattice deduced from experimental investigations : $T_0 = 235 \text{ K}$. In a second step, we consider the « piezo-electric-like » coupling between the molecular ordering and the $u_{xy}$ shear of the lattice. Using a « Bragg-Williams-like » treatment of the strain-dependent Ising Hamiltonian, we build a free energy expansion whose bilinear terms agree well with those determined from experiments (shear modulus $C_{66}$ and « piezo-electric-like » coefficient $D$), and which yields for the predicted transition temperature : $T_c \approx 240 \text{ K}$ (actual value : $T_c = 287 \text{ K}$). This analysis also reveals an important biquadratic coupling term which is supposed to enhance the instability of the structure in the vicinity of $T_c$.

1. Introduction. — The nitroxyde 2,2,6,6 tetramethyl-piperidine-1 oxyle (tanane) is a molecular crystal which undergoes a structural phase transition at $T_c = 287 \text{ K}$, from a piezo-electric high temperature phase (point group 42 m) to ferroelastic and ferroelectric low temperature phase (point group mm2) [1]. In the high temperature phase the molecules are disordered between two equilibrium positions, while in the ordered phase the molecular flipping motion is frozen out. Such a system can be described by an
Ising model but actually the ordering mechanism involves three different kinds of interactions:

- "Ising-like" interactions between the nearest neighbour molecules,
- long range elastic interactions via the "piezo-electric-like" coupling between the molecular ordering and the \( u_{xy} \) shear of the lattice,
- and long range dipolar interactions between the permanent dipole moments of the molecules (free radical nitroxyde).

We have shown previously that the dipolar interaction energy represents less than 1% of the total ordering energy [2, 3]; so we just consider here the van der Waals interaction energy which is computed from structural data using semi-empirical potential parameters [4, 5]. The results obtained for various pseudo-spin configurations and various strains of the lattice, thus are analysed with a Hamiltonian including in addition to the Ising term, a "piezo-electric" coupling term and an elastic interaction term. Due to these relevant terms, the fluctuation regime is dominated by the critical slowing down of the acoustic velocity at \( T_c \) and the classical Landau approach is appropriate [6]. So we build, from the computed Hamiltonian, a free energy expansion whose coefficients calculated using the Bragg-Williams approximation can be compared to those determined from experiments [11].

2. Intermolecular interaction energies. — 2.1 "Rigid" TETRAGONAL LATTICE. — Considering the tetragonal structure of tanane [7], the coordinates of the atoms can be written using an Ising pseudo-spin variable \( \varepsilon_i = \pm 1 \) which describes the two equilibrium positions of each molecule. For example, in figure 1, the coordinates of the atoms (n) of the "central" molecule (i) can be written:

\[
X_i + x_n, \quad Y_i + \varepsilon_i y_n, \quad Z_i + \varepsilon_i z_n,
\]

with \( X_p, Y_p, Z_p \) the coordinates of the molecular centre of mass positioned on a [100] twofold axis.

The pair interaction energy of the molecules (i) and (j) thus can be written as:

\[
E_{ij}(\varepsilon_i, \varepsilon_j) = 2(A_{ij} + \varepsilon_i B_{ij} + \varepsilon_j B_{ji} + \varepsilon_i \varepsilon_j J_{ij}),
\]

with \( \varepsilon_i = \pm 1 \) and \( \varepsilon_j = \pm 1 \) the pseudo-spin states of the molecules.

Without special symmetry (especially for no centre of symmetry), the pair energy \( E_{ij} \) takes four different values for the four pseudo-spin configurations illustrated in figure 2. The coefficients \( A_{ij}, B_{ij}, B_{ji} \) and \( J_{ij} \) therefore can be deduced from the differences between these energies.

The pair energies have been computed for the 16 nearest neighbours of a given molecule (i) (see Fig. 1), using the program P.A.C.K.R.B. [8] and two alter-
Table I. — Calculated half-pair-energies (in kcal. mole\(^{-1}\)) for the 16 nearest neighbours of the molecule \(i\), analysed according to expression (1) (the values calculated using K.M. parameters are at the top left, those calculated using E.G. parameters are at the lower right of each box). According to the symmetry operator of a given group of neighbours, identical values appear twice or four times in the table.

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Fig. 2. - Schematic diagram showing the four different interactions between two molecules with two possible orientations corresponding to each other by a twofold axis and described the pseudo-spin variable: $g_i = \pm 1$ and $j = \pm 1$.

$E_{ij} = 2 \left[ A_{ij} + B_{ij} + B_{ji} + J_{ij} \right]$

$E_{ij} = 2 \left[ A_{ij} - B_{ij} - B_{ji} - J_{ij} \right]$

$E_{ij} = 2 \left[ A_{ij} - B_{ij} + B_{ji} + J_{ij} \right]$

$E_{ij} = 2 \left[ A_{ij} + B_{ij} - B_{ji} - J_{ij} \right]$

The native sets of atom-atom potential parameters: those determined by E. Giglio [9] (noted E.G. in the following) and those determined by K. Mirsky [5] (noted K.M. in the following). It must also be noted here that the two procedures are not exactly the same: following E.G., the methyl groups are considered as a whole, while following K.M., the coordinates of all the hydrogen atoms are needed.

The results listed in table I show a rather good consistency between the two sets of values, and the small discrepancies which can be observed illustrate the limited accuracy of such a differential analysis. The results also confirm that beyond the 14th neighbour, the interaction energies and a fortiori their differences become negligible.

The coefficients $A_{ij}$ represent the interactions between « mean molecules », which are the only interactions in the disordered phase ($A_{ij} = A_{ji}$). The coefficient $B_{ij}$ represents the interaction between the « mean molecule » (i) and the « pseudo-spin-state » $g_i$. It is different from the interaction ($B_{ji}$) between the « mean molecule » (i) and the « pseudo-spin-state » $g_j$ (see Fig. 2). Finally, the coefficients $J_{ij}$ represent the interactions between the « pseudo-spin-states » responsible for the order-disorder phase transition ($J_{ij} = J_{ji}$). Some are positive and favour an « antiferroelectric » ordering; the others, the main ones, are negative and are responsible for the « ferroelectric » ordering. From both sets of values, it appears that the main ordering interactions ($J_{15}$, $J_{16}$, $J_{111}$ and $J_{112}$) define linear chains of strongly interacting molecules along the [001] axis (Fig. 1B), with much weaker transverse interactions between chains. From the results of table I, these transverse interactions appear within the uncertainty range, but it can be shown that even ten times weaker than the longitudinal interactions, they would be merely sufficient to suppress any unidimensional character for the phase transition.

The Hamiltonian representing the total interaction energy of $N$ molecules is:

$$\mathcal{H} = \frac{1}{2} \sum_{i=1}^{N} \sum_{j=1}^{16} E_{ij}$$

$$\mathcal{H} = \sum_{i} \sum_{j} \left( A_{ij} + \varepsilon_i B_{ij} + \varepsilon_j B_{ji} + \varepsilon_i \varepsilon_j J_{ij} \right).$$

(2)

It can also be transformed to the form:

$$\mathcal{H} = \sum_{i=1}^{N} \mathcal{H}_i,$$

if attention is focused on all the interactions of a « central » molecule (i) which are represented by:

$$\mathcal{H}_i = \sum_{j} A_{ij} + 2 \varepsilon_i \sum_{j} B_{ij} + \varepsilon_j \sum_{j} \varepsilon_j J_{ij}.$$  

(3)

The sums performed in table I show that, in the « rigid » tetragonal lattice:

$$\sum_{j} B_{ij} = 0$$ (in agreement with the symmetry).

Thus, the Hamiltonian $\mathcal{H}_i$ separates into a pure « lattice » part: $\sum_{j} A_{ij}$, which represents the van der Waals cohesion energy, per molecule, in the disordered phase [14]; and an Ising part: $\varepsilon_i \sum_{j} \varepsilon_j J_{ij}$, for which there is no exact solution in case of 3-d Ising model. Thus we simply use the « mean-field » approximation which yields for the ordering temperature of the pseudo-spin system:

$$T_0 = \frac{2 J_0}{k_B} \text{ with } J_0 = -\sum_{j} J_{ij}.$$  

In our opinion, better approximation methods (for instance: « Cluster » or « Bethe ») are not needed insofar as more accurate values of the differential energies $J_{ij}$ are not available.

From the results of table I we get:

$$J_0 = 0.16 \text{ kcal/mole}$$  

and

$$T_0 = 160 \text{ K}, \text{ with K.M. parameters}$$
Especially this last prediction appears to be in remarkable agreement with the transition temperature of the «damped» crystal deduced from the (mean-field) analysis of the experimental results [11]:

\[ T_0 = 235 \text{ K} \]

However, the ordering temperature given by the «mean-field» approximation should be higher than the actual transition temperature, because this approximation does not take into account the effects of the fluctuations [10].

Also the calculated interaction energies appear rather sensitive to slight changes in the intramolecular distances [20]. Thus, following the usual procedure [18], we use standard interatomic distances for the C-H bonds (1.08 Å) instead of those determined with poor accuracy from neutron diffraction [14].

Nevertheless, the above results show that such an analysis from structural data predicts the right order of magnitude for the temperature of an order-disorder phase transition and reveals which are the main intermolecular interactions responsible for the transition.

2.2 SHEAR STRAIN OF THE TETRAGONAL LATTICE. — Following K.M. [18], the simulation of a pure \( u_{xy} \) shear of the lattice is obtained by an appropriate change of the parameters \( a_1 \) and \( a_2 \). The intermolecular interaction energies thus computed for several values of the shear strain are analysed with an expression of the Hamiltonian similar to (3), but with coefficients that now depend on the shear strain \( u_{xy} \) (noted \( u \) for convenience):

\[
\mathcal{H}_s(u) = \sum_j A_{ij}(u) + 2 \varepsilon_i \sum_j B_{ij}(u) + \varepsilon_i \sum_j \varepsilon_j J_{ij}(u).
\]

(4)

Since in the prototype symmetry group \( \overline{42} \text{m} \), the shear strain \( u \) transforms according to the same representation \( (B_2) \) as the pseudo-spin variable \( \varepsilon_i \), the symmetry invariance of the Hamiltonian implies that \( B_{ij}(u) \) must be odd functions of the variable \( u \) while \( A_{ij}(u) \) and \( J_{ij}(u) \) must be even functions of the variable \( u \). For small values of the shear strain \( u \), the coefficients of the Hamiltonian therefore can be expanded as:

\[
\begin{align*}
\sum_j A_{ij}(u) &= A_0 + A_2 \frac{u^2}{2} \\
2 \sum_j B_{ij}(u) &= -B_1 u \\
\sum_j \varepsilon_j J_{ij}(u) &= -\langle \varepsilon_j \rangle \left( J_0 + J_2 \frac{u^2}{2} \right)
\end{align*}
\]

(5)

considering the last term within the «mean-field» approximation.

The Hamiltonian we must consider includes two coupled variables and in such a case, the Landau approach is probably one of the most convenient methods to minimize the free energy of the system. From the above Hamiltonian, a free energy density can be built using a «Bragg-Williams-like» method which is equivalent to the «mean-field» approximation: the partition function is calculated using a subdivision of the total volume into semi-microscopic cells in each of which the order parameter \( \eta \) is fixed:

\[
\eta = \frac{1}{\sum_i |\varepsilon_i|}.
\]

So we get the following expansion of the free energy density:

\[
F = A(T - T_0) \frac{\eta^2}{2} + B \frac{\eta^4}{4} + C\frac{u^2}{2} - Du\eta - G\frac{u^2 \eta^2}{2},
\]

(6)

including two «entropic» terms

\[
AT \frac{\eta^2}{v_0} = \frac{k_B T \eta^2}{2}
\]

and

\[
B \frac{\eta^4}{4} = \frac{k_B T \eta^4}{3 v_0}
\]

with \( v_0 \) the molecular volume and \( T \) the absolute temperature; and four competitive «energetic» terms whose coefficients are related as follows to those of the Hamiltonian:

- \( T_0 = \frac{2J_0}{k_B} \) is the transition temperature of the pseudo-spin system in a «rigid» lattice;
- \( C = \frac{A_2}{v_0} = \frac{1}{v_0} \frac{\partial^2}{\partial u^2} \left( \sum_i A_{ij} \right) \) is the elastic modulus \( C_{66} \) associated with the \( u_{xy} \) shear, but defined at constant \( \eta \) [11];
- \( D = \frac{B_1}{v_0} = -\frac{1}{v_0} \frac{\partial}{\partial u} \left( 2 \sum_i B_{ij} \right) \) is the «piezoelectric-like» coupling coefficient;
- \( G = \frac{J_2}{v_0} = -\frac{1}{v_0} \frac{\partial^2}{\partial u^2} \left( \sum_i J_{ij} \right) \) is a higher order coupling coefficient introduced to account for the sum \( \sum_i J_{ij} \) which exhibits from our calculations an unexpected but strong variation with the lattice shear strain \( u \) (see Fig. 3).

All these coefficients can be deduced from the intermolecular interaction energies calculated for several positive and negative values of the lattice shear strain \( u \), and for two «mean-field» configurations of the pseudo-spin order (represented in figure 1A):

\[
\{ \varepsilon_i = +1; \langle \varepsilon_j \rangle = +1 \}
\]

\[
\{ \varepsilon_i = -1; \langle \varepsilon_j \rangle = +1 \}
\]
The results are plotted in figure 3A and are analysed in terms of even or odd functions of the variable $u$ in figure 3B, for the two alternative sets of atom-atom potential parameters. It appears that the expansions (5) of the Hamiltonian coefficients are valid for the values of the shear strain $u$ limited to the range:

$$-5 \times 10^{-2} < u < 5 \times 10^{-2}$$

In which the coefficients $C$, $D$ and $G$ listed in table II are thus calculated.

In addition, the order of magnitude estimates of the two other coefficients, given by the « Bragg-Williams » approximation, are:

$$A \approx \frac{k_B}{v_0} = 5.4 \times 10^8 \text{ J m}^{-3} \text{ K}^{-1},$$

and at room temperature ($T = 300$ K)

$$B \approx \frac{k_B}{3v_0} T = 5.4 \times 10^6 \text{ J m}^{-3}.$$

In the high temperature phase, the free energy expansion (6) can be limited to bilinear terms and its minimization yields for the coupled system, a renormalized transition temperature at:

$$T_c = T_0 + \frac{D^2}{AC}$$

and an anomaly of the coupled elastic modulus $C^*_{66}$ which can be described by the Curie-Weiss law:

$$\frac{1}{C^*_{66}} = \frac{1}{C_{66}} \frac{T_c - T_0}{T - T_c}.$$

So we obtain from the analysis of figure 3B

$$C^*_{66} = 2.0 \times 10^9 \text{ N m}^{-2}$$

and $T_c - T_0 = 18$ K with K.M. parameters or alternatively

$$C^*_{66} = 2.8 \times 10^9 \text{ N m}^{-2}$$

and $T_c - T_0 = 58$ K with E.G. parameters

in rather good agreement with the results of experimental investigations above $T_c : C^*_{66} = 2.1 \times 10^9 \text{ N m}^{-2}$ from inelastic neutron scattering experiments in a high frequency range where the pseudo-spin variable is « clamped » [3]; and $T_c - T_0 = 50$ K from a low frequency investigation of the elastic anomaly (acoustic resonance technique) [11].

According to the Landau approach, the higher order terms in the free energy expansion (6) only appear in the properties of the low temperature phase.

Due to the biquadratic coupling term $-G \frac{u^2 \eta^2}{2}$, the relation between the order parameter and the...
spontaneous shear strain is predicted to be non-linear below $T_c$:

$$u = \frac{D}{C - G \eta^2} \eta,$$

unless in the near vicinity of $T_c$ where we get ($|\eta| \ll 1$):

$$\frac{u}{\eta} = \frac{D}{C} = 2.2 \times 10^{-2} \text{ with K.M. parameters},$$

or

$$\frac{u}{\eta} = \frac{D}{C} = 3.4 \times 10^{-2} \text{ with E.G. parameters}.$$

At lower temperature, as $\eta$ increases, the ratio $u/\eta$ is also expected to increase and we get for the completely ordered system ($|\eta| = 1$):

$$u_{\text{sat}} = 22 \times 10^{-2} \text{ with K.M. parameters},$$

or

$$u_{\text{sat}} = 15 \times 10^{-2} \text{ with E.G. parameters}.$$

These last values appear to be much overestimated in comparison with the spontaneous shear strain measured at low temperature [1]:

$$u_{\text{sat}} = 7 \times 10^{-2};$$

but, since we find: $C \approx G$, this discrepancy can be attributed to the large relative uncertainty in the difference $(C - G)$ (note added in proof).

Another effect of this biquadratic coupling term is to renormalize the coefficient $B$ of the free energy expansion (6). With $B^* = B - 2\frac{D^2 G}{C^2}$, it can now be written as a function of a single variable:

$$F = A(T - T_c) \frac{\eta^2}{2} + B^* \frac{\eta^4}{4}.$$ 

Thus, a positive value of $G$ gives the same effect as the « electrostrictive » coupling with the compression strains at the lattice [12]. If such a coupling is strong, it can transform a second order phase transition in a rigid lattice ($B > 0$) into a first order phase transition in a compressible lattice ($B^* < 0$) [19]. From a number of experiments performed on tanane, the transition appears as a second order one, and the birefringence measurements performed close to $T_c$ yield [2]:

$$B^* = 1.9 \times 10^5 \text{ J m}^{-3}.$$

This is a rather low value compared with the « Bragg-Williams » estimate of $B$ ($54 \times 10^5 \text{ J m}^{-3}$, see above) and this result suggests that, in case of tanane, the quadratic coupling terms with the lattice strains strongly renormalize the transition towards a tricritical point. The role of the « electrostrictive » couplings with the compression strains $u_{xz}$ and $(u_{xx} + u_{yy})$ already has been analysed from dilatometric measurements [12]. It was found that these couplings only contribute to the reduction of the coefficient $B$ by the amount: $-5 \times 10^5 \text{ J m}^{-3}$.

In contrast, the influence of the biquadratic coupling with the shear strain $u_{xy}$ appears much more important on the renormalization of the coefficient $B$, since we get from the results of table II:

$$-2 \frac{D^2 G}{C^2} = -18 \times 10^5 \text{ J m}^{-3} \quad \text{(K.M.)}$$

$$-2 \frac{D^2 G}{C^2} = -48 \times 10^5 \text{ J m}^{-3} \quad \text{(E.G.)}.$$ 

Thus the quadratic increase of the ordering interactions $\left(-\sum J_{ij}\right)$ with the shear strain $u$ has the effect of a strong enhancement of the instability of the structure in the vicinity of $T_c$.

Two other consequences of experimental interest appear when considering the Landau free energy expansion (6) in which $G \approx C$. First, the coupled shear modulus $C_{66}^*$ would be drastically reduced as $\eta$ increases and this could be checked by further experiments in the low temperature phase [11]. Secondly, such a result makes rather questionable the assumption that the spontaneous shear strain and birefrin-

Table II. — Calculated results compared with available experimental results on tanane.

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Calculated values (K.M.)</th>
<th>Calculated values (E.G.)</th>
<th>Experimental values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Van der Waals energy of the tetragonal phase: $A_0$</td>
<td>57 kJ mole$^{-1}$</td>
<td>61 kJ mole$^{-1}$</td>
<td>—</td>
</tr>
<tr>
<td>Shear modulus: $C_{66}^*$</td>
<td>$2.0 \times 10^9$ N m$^{-2}$</td>
<td>$2.8 \times 10^9$ N m$^{-2}$</td>
<td>$2.1 \times 10^9$ N m$^{-2}$ [3]</td>
</tr>
<tr>
<td>« Piezo-electric » coupling coefficient: $D$</td>
<td>$4.4 \times 10^7$ N m$^{-2}$</td>
<td>$9.4 \times 10^7$ N m$^{-2}$</td>
<td>$7.4 \times 10^7$ N m$^{-2}$ [11]</td>
</tr>
<tr>
<td>« Quadratic » coupling coefficient: $G$</td>
<td>$1.8 \times 10^9$ N m$^{-2}$</td>
<td>$2.2 \times 10^9$ N m$^{-2}$</td>
<td>$1 \times 10^9$ N m$^{-2}$ (note added in proof)</td>
</tr>
<tr>
<td>Transition temperature: $T_0$ (« rigid » lattice)</td>
<td>160 K</td>
<td>240 K</td>
<td>235 K [11]</td>
</tr>
<tr>
<td>Transition temperature: $T_c$ (free of strain lattice)</td>
<td>178 K</td>
<td>298 K</td>
<td>287 K [2]</td>
</tr>
</tbody>
</table>
gence remain proportional to the order parameter far below $T_c$ [2].

If we now consider the permanent dipole moments $\mu$ of the molecules oriented along the N-O bond and estimated to be : $\mu = 3.14$ Debyes from measurements in solutions [13], and $\mu = 2.95$ Debyes from calculations of the electronic density [14], the spontaneous polarization $P_z$ of the completely ordered crystal can be estimated from structural data to be :

$$(P_z)_{\text{sat}} = \frac{\mu_z}{\nu_0} = 5 \times 10^{-3} \text{ C m}^{-2} [14].$$

In addition, the piezo-electric response coefficient

$$d_{36} = \left. \frac{\partial P_z}{\partial \sigma_{xy}} \right|_{E=0} = \left. \frac{\partial u_{xy}}{\partial E_z} \right|_{E=0}$$

can also be written from the free energy expansion (6) (in which the couplings with the high frequency polarization components [11] are neglected) :

$$d_{36} = \frac{\delta}{T - T_c}$$

with a Curie-Weiss constant

$$\delta = \frac{\mu_z}{\nu_0} \frac{D}{AC}.$$

From the calculated values of $D$ and $C$ we get :

$$\delta = 2 \times 10^{-9} \text{ mV}^{-1} \text{ K}^{-1} \text{ (K.M.)}$$

or

$$\delta = 3 \times 10^{-9} \text{ mV}^{-1} \text{ K}^{-1} \text{ (E.G.).}$$

If these results are compared with those of experimental investigations

$$(P_z)_{\text{sat}} = 3.0 \times 10^{-3} \text{ C m}^{-2} [5]$$

and

$$\delta = 0.98 \times 10^{-9} \text{ mV}^{-1} \text{ K}^{-1} [11],$$

it appears that the above predictions only yield a good order of magnitude agreement. However we did not take into account in the present model the couplings with the electronic and infra-red polarizabilities which have the effect of reducing the « effective » value of the dipolar momentum $\mu_z$ [11].

From the whole comparison between the calculated values and the experimental results (see table II), it appears that better agreement is obtained using the data given by E. Giglio ; but we must recall that using the data given by K. Mirsky we have in fact taken calculated, instead of experimental, hydrogen coordinates. So we conclude that without accurate determination of the actual hydrogens positions, the approximation proposed by E. Giglio may yield better results than the detailed analysis proposed by K. Mirsky. In addition, it is confirmed [14] that the simulation of a strained lattice performed by just changing the lattice parameters remains valid for strains lower than $5 \times 10^{-2}$ (especially for the calculation of the elastic moduli) although in such a simulation both the intermolecular distances (van der Waals interactions) and the intramolecular distances (covalent bonds) are changed in a similar way.

3. Conclusion. — We have shown in this paper how in a pure molecular crystal, the semi-empirical energies calculated from structural data can be analysed using simple thermodynamical results to predict :

- the elastic moduli
- the heat of sublimation (see also [14])
- an order-disorder transition temperature
- and other phase transition features,

in very good agreement with the experimental results without using any adjustable parameter.

The use of two different sets of atom-atom potential parameters shows that some of the close agreements between calculated and experimental results may be partly fortuitous, but it confirms that the method gives at least the good order of magnitude agreement with experimental data.

Several papers have already shown the interest of such energy calculations for the investigation of lattice dynamics [17], of plastic phase transitions [18] and of order-disorder transitions in solid solutions [16]. So we suggest that similar analyses could be successfully developed in a number of other molecular crystals with available structural data, in order to predict several physical properties and even to predict the possible structural phase transitions they may undergo.

Note added in proof. — The experimental evidence of a discrepancy between the value $u/\eta = D/C = 3.5 \times 10^{-2}$ deduced from measurements above $T_c$ and the saturated value of the spontaneous shear $u_{\text{sat}} = 7 \times 10^{-2}$ at very low temperature ($\eta \approx 1$), can be explained by a biquadratic coupling coefficient $G \approx 1 \times 10^9 \text{ N m}^{-2}$.

References


