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Ferroelastic and ferroelectric phase transition in a molecular crystal: tanane

1. Neutron and Brillouin scattering studies of the acoustic and pseudo-spin coupled modes

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Abstract. — Tanane exhibits at \( T_c = 287 \) K an order-disorder phase transition associated with an inversion motion of polar molecules. The coupling between the molecular ordering and the shear strain \( \tau_{xy} \) results in soft transverse acoustic modes \( (T_{xy}[010] \) and \( T_{xy}[100] \)) whose low frequency study is reported in the second part of this article.

In this first part, we report an investigation of the transverse and longitudinal acoustic modes by means of inelastic neutron scattering and Brillouin scattering. The transverse acoustic branch \( T_{xy}[100] \) thus observed, exhibits no softening over the frequency range \( 10 \text{ GHz} < \nu < 200 \text{ GHz} \), while a critical increase of the quasi-elastic (and elastic) neutron scattering is observed above \( T_c \).

The critical dynamical behaviour of tanane is analysed in terms of a pseudo-spin system linearly coupled to acoustic phonons. The pseudo-spins are characterized by an individual relaxation time \( \tau_0 \) which corresponds to the residence time of the molecular inversion far above \( T_c \). The estimate of \( \tau_0 \gg 10^{-10} \text{ s} \) from the results of Brillouin scattering experiments show that, for the proposed model, the calculated orders of magnitude of the quasi-elastic and inelastic intensities are consistent with the observed spectra.

1. Introduction. — In recent years, there have been many investigations of structural phase transitions in molecular crystals [1]. A number of those include a change in molecular dynamics, which results in a strong temperature dependence of the mechanical properties (thermal expansion coefficients, elastic constants, ...). A phase change in a pure molecular crystal may also induce dielectric anomalies if the molecule has a permanent dipole moment.

Tanane is a free-radical nitroxide \( (2,2,6,6,\text{tetramethyl-piperidine-1, oxyle}) \) which exhibits a phase change at \( T_c = 286.7 \) K. The high temperature phase
is characterized by the disorder of polar molecules switching up and down between two symmetrical positions [2]. Below \( T_c \) this motion is frozen out and single crystals divide into twinned ferroelectric domains as a result of the symmetry breakdown (point groups : \( 42m \rightarrow mm2 \) ) [3].

It has already been reported that dipole-dipole interactions cannot be responsible for the ferroelectric ordering of tanane which is essentially driven by Van der Waals intermolecular forces [4]. The molecule-molecule interaction energy responsible for the ordering can be described by an Ising Hamiltonian :

\[
\mathcal{H}_{ij} = -2 J_{ij} e_i e_j
\]

where the pseudo-spin variable \( e_i = \pm 1 \) specifies the orientation of each molecule.

Thus, the dimensionless order parameter, which is the variable of the free energy expansion is :

\[
\eta = \frac{\sum e_i}{\sum |e_i|} = \frac{N_+ - N_-}{N_+ + N_-} .
\]

In the prototype symmetry point group : \( 42m \), the order parameter \( \eta \) and the relevant strain component \( u_{xy} \), both transform according to the B2 representation. The phase change of tanane can thus be described by a *sharable Ising model* whose quadratic part of the free energy expansion \( F \) includes a *linear coupling term* \( D \eta u_{xy} \),

\[
F = A \left[ T - T_0 \right] \frac{\eta^2}{2} - D \eta u_{xy} + C_{66} u_{xy}^2 .
\]

In this expansion \( T_0 \) is the transition temperature for a clamped crystal, \( C_{66} \) is the \( u_{xy} \) elastic constant and the coefficient \( A \) can be estimated in the molecular field approximation as the ratio of the Boltzmann constant to the molecular volume [5].

It follows that the renormalized transition temperature is :

\[
T_0^* = T_0 + D^2/C_{66} \ A ,
\]

and that the renormalized elastic constant \( C_{66}^* \) in the high temperature phase is given by :

\[
\frac{1}{C_{66}^*} = \frac{1}{C_{66}} + \frac{D^2}{A C_{66}^2 \left( T - T_0^* \right)} .
\]

It must be remarked that the dielectric polarization component : \( P_z \) transforms also according to the B2 representation. However, linear coupling between \( \eta \) and \( P_z \) is not taken into account in this phenomenological model owing to the low value of the dipolar interaction energy [4].

This three components system recalls the descriptions of \( \text{KH}_2\text{PO}_4 \) which undergoes the same symmetry change with an order parameter \( \eta \) associated with the proton position [6]. However, the comparison points out a basic difference between tanane and \( \text{KH}_2\text{PO}_4 \). In tanane the most important coupling is between \( \eta \) and \( u_{xy} \) and *clamping* of \( P_z \) may only shift the transition temperature by 2 K [4], while in \( \text{KH}_2\text{PO}_4 \), the most important coupling is between \( \eta \) and \( P_z \) and *clamping* of \( u_{xy} \) may only shift the transition temperature by 4 K [7].

The above expression of the renormalized elastic compliance \( 1/C_{66}^* \), in the high temperature phase predicts a softening of the acoustic modes involving the shear strain component \( u_{xy} \). We report here an investigation of the acoustic modes over two different frequency ranges between 1 THz and 0.1 THz by means of inelastic neutron scattering (I.N.S.) and around 10 GHz by means of Brillouin scattering.

In order to reduce the incoherent scattering by the protons, the I.N.S. experiments were performed with deuterated tanane : \( \text{C}_9\text{D}_{18}\text{N}_0 \). Its transition temperature \( (T_c = 287.5 \text{ K}) \) does not differ significantly from that of normal tanane : \( \text{C}_9\text{H}_{18}\text{N}_0 \), as expected because there is no hydrogen bonding in this pure molecular crystal.

2. Inelastic neutron scattering experiments. — 2.1 Experimental. — Deuterated tanane has been synthesized by D. Bordeaux and R. Chiarelli in the Laboratoire de Chimie Organique Physique du Centre d'Etudes Nucléaires de Grenoble. Mass spectroscopy analysis has shown that the deuteration was higher than 85 %, and the mean molar weight thus obtained was \( M_D = 171.5 \text{ g} \).

Three single crystals of about 200 mm\(^3\) were grown by a vapour deposition method and mounted along different crystallographic axes inside tight aluminium cells to prohibit sublimation. Their mosaic width deduced from elastic neutron scattering measurements was smaller than 0.1°.

Two INS experiments have been performed at the high flux reactor of the Institut Laue Langéniev. The first one was done on the three-axis spectrometer IN2, with pyrolytic graphite as monochromator and analyser for the investigation of phonons propagating in the (001) plane. Longitudinal acoustic branches have been studied with an energy resolution better than 0.2 THz, using a constant incident wave vector : \( K_1 = 2.662 \text{ Å}^{-1} \), and a graphite filter to eliminate second order contamination. Transverse acoustic branches and quasi-elastic intensities have been studied with an energy resolution better than 0.04 THz [8] using a constant incident wave vector \( K_1 = 1.55 \text{ Å}^{-1} \) and a cold beryllium filter to eliminate second order contamination.

The second experiment, to investigate phonons propagating in the (010) tetragonal plane was performed on the three-axis spectrometer IN3, involving a curved analyser which increases the coherent signal from small samples and provides best resolution when the dispersion curve has a very small slope [9]. Transverse acoustic branches and quasi-elastic intensities
have been studied with an energy resolution better than 0.03 THz using a constant scattered wave vector $K_f = 1.55 \, \text{Å}^{-1}$ and a cold beryllium filter. Longitudinal acoustic branches have been studied with an energy resolution better than 0.2 THz using a constant scattered wave vector $K_f = 2.662 \, \text{Å}^{-1}$.

The inelastic and quasi-elastic neutron scattering has been only investigated in the disordered phase ($T > T_c$) because in the ordered phase the ferroelastic twinning splits most of the Bragg reflections. The samples were mounted in a thermostat whose temperature regulation was ensured by circulation of temperature controlled water. Temperature stability in the thermostat was better than 0.05 K over several hours.

2.2 Acoustic modes and high frequency elastic constants at room temperature. — According to the symmetry point group 42m the elastic stiffness tensor has the following form:

$$
\begin{array}{cccc}
C_{11} & C_{12} & C_{13} & 0 \\
C_{12} & C_{11} & C_{13} & 0 \\
C_{13} & C_{13} & C_{33} & 0 \\
0 & 0 & 0 & C_{44} \\
0 & 0 & 0 & 0 \\
0 & 0 & 0 & C_{66}
\end{array}
$$

The acoustic modes which have been studied in various points of the reciprocal lattice are listed in table I, together with the relations between sound velocities near the Brillouin zone centre and high frequency elastic constants [10].

Table I. — Acoustic modes studied by neutron and Brillouin scattering (the indices (i) indicate the equivalences between modes at the transition temperature).

<table>
<thead>
<tr>
<th>Notation</th>
<th>Wave vector direction</th>
<th>Polarization</th>
<th>Velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L[100] (1)$</td>
<td>[100]</td>
<td>[100]</td>
<td>$[C_{11}/\rho]^{1/2}$</td>
</tr>
<tr>
<td>$T[100] (2)$</td>
<td>[100]</td>
<td>[010]</td>
<td>$[C_{66}/\rho]^{1/2}$</td>
</tr>
<tr>
<td>$T[010]$</td>
<td>[010]</td>
<td>[001]</td>
<td>$[C_{44}/\rho]^{1/2}$</td>
</tr>
<tr>
<td>$L[001] (3)$</td>
<td>[001]</td>
<td>[010]</td>
<td>$[C_{11}/\rho]^{1/2}$</td>
</tr>
<tr>
<td>$L[110] (4)$</td>
<td>[110]</td>
<td>[110]</td>
<td>$[(C_{11} + C_{13} + 2 C_{66})/2 \rho]^{1/2}$</td>
</tr>
<tr>
<td>$T_{a1}[110]$</td>
<td>[110]</td>
<td>$[(C_{11} - C_{13})/2 \rho]^{1/2}$</td>
<td></td>
</tr>
<tr>
<td>$L[101]$</td>
<td>[101]</td>
<td>[101]</td>
<td>$\approx \left{ \frac{0.21 C_{11} + 0.79 C_{33} + C_{44} + \sqrt{[0.21(C_{11} - C_{44}) + 0.79(C_{44} - C_{33})]^2 + 0.66(C_{11} + C_{44})^2}}{2 \rho} \right}^{1/2}$</td>
</tr>
<tr>
<td>$L[310]$</td>
<td>[310]</td>
<td>[310]</td>
<td>$\approx \left{ \frac{(C_{11} + C_{44} + 0.64(C_{11} - C_{44})^2 + 0.36(C_{12} + C_{66})^2)}{2 \rho} \right}^{1/2}$</td>
</tr>
</tbody>
</table>

ORTHORHOMBIC LATTICE ($T < T_c$)

<table>
<thead>
<tr>
<th>Notation</th>
<th>Wave vector direction</th>
<th>Polarization</th>
<th>Velocity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L[110] (1)$</td>
<td>[110]</td>
<td>[110]</td>
<td>$[(C_{11} + C_{33} + 2 C_{66}/4 \rho)]^{1/2}$</td>
</tr>
<tr>
<td>$T_{a1}[110] (2)$</td>
<td>[110]</td>
<td>[110]</td>
<td>$[(C_{11} + C_{33} - 2 C_{12}/4 \rho)]^{1/2}$</td>
</tr>
<tr>
<td>$L[001] (2)$</td>
<td>[001]</td>
<td>[001]</td>
<td>$[C_{33}/\rho]^{1/2}$</td>
</tr>
<tr>
<td>$L[100] (4)$</td>
<td>[100]</td>
<td>[100]</td>
<td>$[C_{11}/\rho]^{1/2}$</td>
</tr>
<tr>
<td>$L[010] (4)$</td>
<td>[010]</td>
<td>[010]</td>
<td>$[C_{22}/\rho]^{1/2}$</td>
</tr>
</tbody>
</table>

Four different longitudinal or quasi-longitudinal acoustic branches investigated by means of constant wave vector scans are plotted in figure 1. All the experimental points are on the same dispersion curve regardless of wave vector direction. The sound velocity of the longitudinal waves derived from the initial slope is:

$$V_L = 2 \, 600 \pm 50 \, \text{m.s}^{-1}, \quad \text{at} \quad 294.7 \, \text{K}.$$  

Four different transverse or quasi-transverse acoustic branches are plotted on figure 2. Again, all the experimental points are on the same dispersion curve regardless of wave vector direction. The sound velocity of the transverse waves derived from the slope is:

$$V_T = 1 \, 400 \pm 50 \, \text{m.s}^{-1}, \quad \text{at} \quad 294.7 \, \text{K}.$$  

These results show that the symmetry of the high frequency elastic properties appears higher than the crystalline symmetry. Within the experimental uncertainty, (symbol $\approx$), the following relations between sound velocities are obtained (notations according to table I):

$$V_L[010] \approx V_L[001]$$

$$V_T[100] \approx V_T[100]$$

which are compatible with a fourfold axis along [100] and therefore with a cubic symmetry.
Fig. 1. — Dispersion curve of pure longitudinal and quasi-longitudinal acoustic phonons. Measurements deduced from constant q scans [0, 0, 4 + qz] [4 + qy, 0, 0] [3.3, 1.1, 0] [2.2, 0, 2.2] with an incident wave vector \( K_i = 2.622 \text{ Å}^{-1} \) (full circles : \( K_i = 1.55 \text{ Å}^{-1} \)). The Brillouin zone boundary lies at \( q = 0.40 \text{ Å}^{-1} \) along [100] and at \( q = 0.48 \text{ Å}^{-1} \) along [001]. The dispersion curve is obtained by a least square fit refinement using: \( v = V \sqrt{q/2} - wq^3 \).

Fig. 2. — Dispersion curve of pure transverse and quasi-transverse acoustic phonons near the centre of the Brillouin zone. Measurements deduced from constant q scans \([q_x, 4, 0], [4, q_y, 0], [1 + q_x, 3, 0], [6, 2 + q_y, 0], [1 + q_x, 0, 3] [4, 0, q_y] \) with an incident wave vector \( K_i = 1.55 \text{ Å}^{-1} \). The dispersion straight line is obtained by a least square fit refinement.

Table II. — Hypersonic elastic constants of tanane.

<table>
<thead>
<tr>
<th>Temperature ( K )</th>
<th>( \rho - T_e ) (kg m(^{-3}))</th>
<th>( C_{11} ) ((10^{10} \text{ N m}^{-2}))</th>
<th>( C_{33} ) ((10^{10} \text{ N m}^{-2}))</th>
<th>( C_{12} ) ((10^{10} \text{ N m}^{-2}))</th>
<th>( C_{13} ) ((10^{10} \text{ N m}^{-2}))</th>
<th>( C_{44} ) ((10^{10} \text{ N m}^{-2}))</th>
<th>( C_{66} ) ((10^{10} \text{ N m}^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A) Deuterated Tanane</strong> (I.N.S. experiments)</td>
<td>21.5</td>
<td>7.2</td>
<td>131</td>
<td>0.76 ± 0.03</td>
<td>0.76 ± 0.03</td>
<td>0.32 ± 0.04</td>
<td>0.32 ± 0.05</td>
</tr>
<tr>
<td>14.3</td>
<td>0.1</td>
<td>133</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.3</td>
<td>7.2</td>
<td>1029</td>
<td>0.72 ± 0.02</td>
<td>0.72 ± 0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13.5</td>
<td>0</td>
<td>1031</td>
<td>0.74 ± 0.02</td>
<td>0.74 ± 0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>B) Tanane</strong> (Brillouin scatt. experiments)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature ( K )</td>
<td>( \rho - T_e ) (kg m(^{-3}))</td>
<td>( C_{11} ) ((10^{10} \text{ N m}^{-2}))</td>
<td>( C_{22} ) ((10^{10} \text{ N m}^{-2}))</td>
<td>( C_{33} ) ((10^{10} \text{ N m}^{-2}))</td>
<td>( C_{12} ) ((10^{10} \text{ N m}^{-2}))</td>
<td>( C_{13} ) ((10^{10} \text{ N m}^{-2}))</td>
<td>( C_{44} ) ((10^{10} \text{ N m}^{-2}))</td>
</tr>
<tr>
<td>13.5</td>
<td>0</td>
<td>1031</td>
<td>0.74 ± 0.02</td>
<td>0.74 ± 0.02</td>
<td>0.74 ± 0.02</td>
<td>0.74 ± 0.02</td>
<td>0.74 ± 0.02</td>
</tr>
</tbody>
</table>

In addition, the following relations:

\[
\begin{align*}
V_{T_e[110]} & \approx V_{T_e[100]} \\
V_{[310]} & \approx V_{[010]} \\
V_{[101]} & \approx V_{[001]}
\end{align*}
\]

indicate that there is no significant cubic anisotropy particularly in the xy-plane where all the sound velocities appear rotationally symmetric. Accordingly there is quasi isotropic symmetry of the high frequency elastic properties (\( \nu > 10^{11} \text{ Hz} \)), which can be described by only two Lamé constants \( \lambda \) and \( \mu \) related to the components of the elastic stiffness tensor by the following expressions:

\[
\begin{align*}
\mu & = \rho V_t^2 = C_{44} \approx C_{66} \approx \frac{C_{11} - C_{12}}{2} \approx \frac{C_{33} - C_{13}}{2} \\
\lambda & + 2 \mu = \rho V_t^2 = C_{11} \approx C_{33} \approx \frac{C_{11} + C_{12} + 2C_{66}}{2} \approx \frac{C_{33} + C_{13} + 2C_{44}}{2}.
\end{align*}
\]

Hypersonic elastic constants, calculated from the above results at room temperature are listed on Table II.A.

2.3 Temperature Dependence of Inelastic and Central Intensities above \( T_e \). — When temperature was decreased from room temperature (21.5 °C) to \( T_e \) (14.2 °C) all the observed acoustic branches remained almost unchanged in position but some scattered inelastic intensities were slightly affected. Particular attention has been paid to transverse acoustic modes \( T_e[100] \) (and equivalent \( T_e[010] \)) supposed to be directly coupled to the transition mechanism from symmetry arguments and low frequency experiments [11]. Within the measured frequency range (0.07 THz < \( \nu < 0.2 \) THz) they do not exhibit any softening from \( T_e + 7.2 \text{ K} \) to \( T_e + 0.1 \text{ K} \) but a decrease of the inelastic intensity was observed: around -15% at the frequency \( \nu = 0.09 \text{ THz} \).
Fig. 3a). These results show that the coupling with the molecular inversion motion which drives the low frequency velocity \( V_T[100] \) to zero lies at a frequency lower than 0.07 THz, near the centre of the Brillouin zone. But this part of the dispersion curve could not be studied because the inelastic peaks were hidden by two intense phenomena:

- Part of the Bragg intensity was detected through the four dimensional resolution function of the instrument and it appeared a so-called Bragg-tail.

- Central peaks particularly intense along the reciprocal lines where the transverse acoustic phonons \( T_{x}[010] \) or \( T_{x}[100] \) have been observed ([4, \( q_x \), 0], \( [q_x, 4, 0], [1 + q_x, 3, 0] \) and \( [6, 2 + q_x, 0] \)).

Although we did not perform extensive studies of all the intensity contours versus temperature, we observed two types of central peaks with different wave vector dependences and different temperature dependences and we present in figure 3 two typical spectra recorded near two Bragg peaks having similar intensities.

In figure 3a one observes an inelastic peak corresponding to \( T_{x}[010] \) acoustic phonons and a central peak corresponding to the first type of anisotropic diffuse scattering around 10 times more intense along \( [4, q_x, 0] \) than along \( [4 + q_x, 0, 0] \) and \( [4, 0, q_x] \) at room temperature.

In figure 3b one observes an inelastic peak corresponding to \( T_{x}[100] \) acoustic phonons not directly coupled to the transition mechanism and a central peak corresponding to the second type of less diffuse scattering which appears just above \( T_c \).

A number of weak and broad inelastic intensities have also been observed at various points of the Brillouin zone between 0.1 THz and 1.5 THz. Preliminary investigations have shown that some of them slightly shift toward higher frequencies when the temperature is decreased toward \( T_c \). They can probably be attributed to optical modes or librations more or less affected by the order-disorder transition, but lengthy experiments would be needed to investigate all these modes. Considering that there are four molecules in the primitive cell. These observations however allow to give an interpretation of the anomalous width and behaviour of the inelastic intensity plotted in figure 3b. On account to other spectra recorded for different values of \( q_x \) we can mainly attribute this inelastic peak to \( T_{x}[100] \) acoustic phonons, but its width and its apparent shift when the temperature is decreased are attributed to other phonons or librations more or less coupled with it around 0.1 THz, and whose frequencies shift near the transition temperature.

As stated above, the molecular inversion motion responsible for the transition lies in the quasi-elastic frequency range. Thus it is supposed that the collective slowing down of this motion near \( T_c \) gives rise to critical quasi-elastic scattering near certain Bragg peaks. But it is clear that from experimental considerations we could not attribute the critical increase of the central peaks (with constant width) either to quasi-elastic scattering or to elastic scattering due to impurities, imperfections or internal stresses.

This situation already encountered in a number of phase transitions [12] has lead to considerable theoretical developments [13, 14, 15, 16...], and we will just here use some of them to give a qualitative interpretation of the above reported observations.

2.4 ACOUSTIC AND PSEUDO-SPIN COUPLED MODES GIVING RISE TO CRITICAL QUASI-ELASTIC SCATTERING IN THE DISORDERED PHASE.

The quasi-elastic and inelastic scattered intensities must be interpreted together taking into account the linear coupling between the molecular inversion and the acoustic \( T_{x}[100] \) and \( T_{x}[010] \) phonons. This type of linear dynamical coupling has been theoretically investigated by Y. Yamada et al. [15], R. A. Cowley [13], K. A. Michel and J. Naudts [16], using different formalisms which lead to similar results for the scattered intensities. In the disordered phase of tanane the mechanism of the molecular inversion motion is not yet completely elucidated (reorientation or interconversion ?) [2] but X-ray results show that the inversion motion is very fast compared to the residence time between two inversions.
The dynamical properties of such a disordered system, and particularly its response function can be described by an Ising model characterized by a relaxation time $\tau_0$ of the flipping motion of the individual pseudo-spin. Following Yamada et al., we emphasize that the pseudo-spin $e_i$ is essentially a stochastic variable whose time variation is only statistically determined. The individual relaxation time $\tau_w$ which thus corresponds to the mean residence time far above the transition temperature, can be written $\tau_0 = 1/\gamma k_B T$ where $\gamma$ is a transport coefficient [15]. Introduction of a linear coupling between the spin variable $e_i$ and the shear strain $u_{xy}$ gives rise to coupled modes which can be compared to those of an oscillator coupled to a purely dissipative system.

As we deal with coupled pseudo-spin and acoustic modes the coupled modes frequencies depend on the wave vector, and to interpret the spectra of figure 3 we will consider only the case of a pseudo-spin relaxation rate slow compared to the phonon frequency ($\nu = 0.09$ THz). Calculations of the structure factors of these coupled modes (Appendix A) show that there are three components for the scattered intensities:

- $S_{ee}$ which is the Fourier transform of the spin-spin correlation function;
- $S_{uu}$ which is the Fourier transform of the phonon-phonon correlation function;
- $S_{su}$ which is the Fourier transform of the spin-phonon correlation function.

It is also shown in Appendix A that $S_{ee}$ and $S_{uu}$ differ from zero only around Bragg peaks whose structure factor is affected by the order-disorder transition, while $S_{uu}$ and $S_{su}$ differ from zero only along reciprocal lines where components of the $T_{[010]}$ and $T_{[100]}$ acoustic phonons can be observed.

As the structure factors $F_0[103]$ and $F_0[103]$ respectively calculated in the ordered and disordered phases differ by

$$F_0[103] - F_0[103] = (1.5 - i 2.2).10^{-12} \text{ cm},$$

we see that the observed spectrum at the reciprocal lattice point [0.9, 0.3] can be attributed to $S_{uu}$ superimposed on the inelastic intensity from $T_{[100]}$ phonons (Fig. 3b).

According to Yamada et al. (Fig. 1a in Ref. [15]), the spectrum of $S_{uu}$ exhibits a quasi-elastic component whose integrated intensity critically increases as $(T - T_c)^{-1}$, and our results at three different temperatures are in qualitative agreement with this prediction.

As the calculated structure factor $F[400]$ does not change across $T_c$ from symmetry arguments

$$F_D[400] - F_0[400] = 0,$$

we see that the observed spectrum at the reciprocal lattice point [4 0.1 0] can be attributed to $S_{uu}$ which includes, according to Yamada et al. (Fig. 1B in Ref. [15]) a quasi-elastic component and two inelastic components ($T_{[010]}$ acoustic mode).

The following predictions of Yamada et al. are also in qualitative agreement with the observed behaviour when the temperature is decreased towards $T_c$ (Fig. 3a).

- The frequency $\omega_0/2 \pi$ of the inelastic peak does not shift appreciably if $\omega_0 \tau_0 > 5$. This result is consistent with the order of magnitude estimated from Brillouin scattering experiments : $\tau_0 \approx 10^{-10}$ s and with the frequency of the observed inelastic peak $\omega_0/2 \pi = 9 \times 10^{10}$ Hz.
- The intensity of the quasi-elastic peak critically increases while that of the inelastic peak is slightly reduced.

One must however remark that the observed spectra correspond to values of $T - T_c$ around 50 times lower than those considered by Yamada et al. So one would expect much more intense quasi-elastic scattering compared to the inelastic intensities, unless if the relaxation time $\tau_0$ is around 50 times longer than $10^{-9}$ s. From these results and this order of magnitude estimate we conclude that the contribution of critical quasi-elastic scattering as predicted by Yamada cannot be neglected in the observed central intensities.

Nevertheless the temperature behaviour of the first type of central peaks (Fig. 3a) indicates that, especially at room temperature, another mechanism is probably responsible for anisotropic diffuse scattering.

2.5 MECHANICAL IMPERFECTIONS RESPONSIBLE FOR TEMPERATURE DEPENDENT DIFFUSE SCATTERING AND EXTINCTION PHENOMENA. — We will here consider another mechanism associated with defects and mechanical imperfections which can also be responsible for central peaks of static origin. If the stress fields associated with mechanical imperfections include stress components coupled to the order parameter one can expect anisotropic long range strains which increase as the corresponding elastic constant softens in the vicinity of the critical temperature. Especially near ferroelastic phase transitions, we think that a number of central peaks could be attributed to such a mechanism due to the softening of an elastic constant. In tanane, the static elastic constant $C_{66}$ goes to zero at $T_c$.

So one can expect more or less intense diffuse scattering which can be described by a static correlation function $\langle u_{xy}, u_{xy} \rangle$ with the same symmetry as the dynamical correlation function $S_{uu}$ calculated from thermodynamical considerations, but with temperature and wave vector dependences which may be somewhat different. It thus appears that this type of anisotropic diffuse scattering directly
coupled to the transition mechanism can be responsible for a part of the central peaks along the \([4, q_y, 0]\) and equivalent reciprocal lines but not along the \([1 + q_x, 0, 3]\) reciprocal lines where \(\langle u_{xy}, u_{xy} \rangle \approx 0\). This interpretation also agrees with the fact that in two different samples the anisotropic diffuse scattering observed along \([4, q_y, 0]\) at room temperature differ from a factor 2 while the Bragg intensities were nearly identical below \(T_c\). It is however clear that additional and more quantitative investigations with higher resolution would be needed to confirm all the above qualitative interpretations because we did not consider all the possible higher order effects.

When temperature was decreased towards \(T_c\) we observed another effect which points out the role of mechanical imperfections just above the ferroelastic phase transition of tanane. We first observed that some of the Bragg intensities recorded at room temperature were very different from those calculated while better agreement was obtained near or below \(T_c\). So particular attention was paid to the integrated Bragg intensity \(S_0[400]\) which was supposed from symmetry arguments to exhibit no change across the order-disorder transition. On three different samples we observed a strong decrease of this integrated intensity just above \(T_c\). These decreases were 60 % in the first sample using a neutron wavelength of 2.36 \(\AA\), 80 % in the second sample using 4.04 \(\AA\) wavelength (Fig. 4), and only 50 % in the third sample using 4.04 \(\AA\) wavelength. We attribute these decreases to extinction phenomena due to sample dependent modifications of the mosaic texture above \(T_c\). The arguments already developed to explain similar observations in KH$_2$PO$_4$ [18] are the following:

- We estimate the extinction length \(t_0[400]\) and the dynamical integrated reflecting power \(K_{DYN}[400]\) for a 0.2 cm thick crystal using the two beams theory of Zachariasen [17] and the calculated value of the structure factor \(F_0[400] = 9.72 \times 10^{-12} \text{ cm}^{-1}\). For a neutron wavelength of 4.04 \(\AA\) we get

\[
t_0 \approx 20 \mu\text{m} \quad \text{and} \quad \frac{K_{DYN}[400]}{K_{KIN}[400]} \approx 0.01 ;
\]

For a neutron wavelength of 2.36 \(\AA\), we get

\[
t_0 \approx 35 \mu\text{m} \quad \text{and} \quad \frac{K_{DYN}[400]}{K_{KIN}[400]} \approx 0.02 .
\]

- According to previous optical observations [19] the width of the ferroelastic twins is around 5 \(\mu\text{m}\) just below \(T_c\). Thus the observed integrated intensities nearly constant below \(T_c\) (Fig. 4) can be accounted for by the structure factors calculated using the kinematical theory.

These observations also indicate that the mosaic texture above \(T_c\) related to the ferroelastic twins texture anneals when the temperature is increased. The fact that such an extinction effect was not observed another Bragg peaks such as \([004]\) and \([103]\) again points out the particular role of \(u_{xy}\) local strains due to mechanical imperfections on account to the softening if the static elastic constant \(C_{66}\).

3. Brillouin scattering experiments. — Measurements of hypersonic velocities in the high and low temperature phases of undeuterated tanane have been performed making use of a Brillouin set-up at the Centre National d’Etudes des Télécommunications [21].

3.1 EXPERIMENTAL. — The excitation was provided by a 100 mW He-Ne laser emitting in a single transverse mode at 632.8 nm. The incident light was focused on a single crystal and to prevent heating and melting of the sample, the incident power was reduced to 10 mW. The light scattered at \(90^\circ\), from an active volume of 150 \(\mu\text{m}\) width, was analysed with a pressure scanned plane Fabry-Pérot used in a three pass configuration (free spectral range : 1.45 cm$^{-1}$, finesse 80, contrast : \(2 \times 10^{6}\)), and photon-counting electronics. The spectra were scaled in frequency using the fringes of a Michelson interferometer one arm of which is connected to the Fabry-Pérot cell. Thus, Brillouin shifts were measured with an accuracy of about \(4 \times 10^{-3} \text{ cm}^{-1}\).

The crystal was mounted in a tight parallelepipedic silica cell inside a silver thermostat provided with four apertures. Temperature regulation was ensured by a flow of temperature controlled nitrogen and temperature stability of the sample was better than 0.1 K over several hours.

In order to determine the velocity of sound propagating along the \([100]\), \([001]\) and \([110]\) tetragonal axes...
we used two different prismatic crystals with square section 5 mm x 5 mm, cut and polished on four faces. Improvement of the index matching was obtained by filling with water the silica cell in which the crystal was mounted.

Sound velocities are deduced from Brillouin shifts $\Delta \nu$ using:

$$V = \frac{c}{\sqrt{n_i^2 + n_s^2}} \frac{\Delta \nu}{\nu_i}$$

where $\nu_i$ is the frequency of the incident light, $c$ is the light velocity in vacuum and $n_i$ and $n_s$ are respectively the refractive indices for the incident and scattered light.

It is shown in Appendix B that the values of the birefingences at 20 °C and 0 °C indicate a variation of the absolute indices of less than 1% between 20 °C and 0 °C. Thus, all the sound velocities are calculated using

$$V = \frac{c}{1.52} \frac{\Delta \nu}{\nu_i}.$$

3.2 Temperature dependence of the longitudinal sound velocities. — At room temperature, the Brillouin shifts due to longitudinal acoustic waves confirms the isotropic symmetry of the elastic properties observed at higher frequency by inelastic neutron scattering on deuterated tanane, but with a slightly higher value of the sound velocities:

$$V_L[001] \approx V_L[100] \approx V_L[110] = (2.650 \pm 30) \text{ m}. \text{s}^{-1}.$$

When temperature is decreased towards the critical temperature $T_c = 13.5$ °C, the sound velocities increase but the isotropic symmetry holds (Fig. 5). From the above equality one can deduce the following relations between the elastic constants in the whole high temperature phase

$$C_{33} \approx C_{11} \approx \frac{C_{11} + C_{12} + 2 C_{66}}{2}$$

or

$$C_{66} \approx \frac{C_{11} - C_{12}}{2} \approx \frac{C_{33} - C_{12}}{2}.$$

Thus, it appears that the elastic constant $C_{66}$ measured at 9 GHz exhibits no more softening above $T_c$ than that measured at 100 GHz by means of inelastic neutron scattering, in contrast with similar experiments in KD$_2$PO$_4$ [22] and KH$_2$PO$_4$ [23]. In the case of tanane the rate of the molecular motion responsible for the transition is too slow to be coupled with acoustic phonons at 9 GHz. This result confirms the estimate of the residence time of the molecular motion (cf. Sect. 2)

$$\tau_0 \approx 10^{-10} \text{ s}.$$

It can be observed that in the low temperature phase the symmetry of the elastic properties breaks down (Fig. 5). The longitudinal sound velocity along the [110] tetragonal axis takes two different values on opposite sides of a twinning plane, because the propagation is either along the [100] or the [010] inequivalent orthorhombic axes.

3.3 Weak photoelastic effects associated with transverse acoustic modes. — It is well known that the intensity of a Brillouin line is approximately proportional to the square of the corresponding photoelastic coefficient [24]. Previous measurements of the spontaneous shear strain $(\mu_{xy})_s$ below $T_c$ [19] provided an estimate of the static photoelastic coefficient $\rho_{66}$ renormalized by the coupling with the molecular ordering:

$$\rho_{66} = \frac{1}{n_s^2} \frac{(n_{s'} - n_s)}{(u_{xy})_s} = 1.4 \times 10^{-2} \text{ (see appendix B)}.$$

If one compares this value to typical ones in solids $\rho_{ij} \approx 10^{-1}$ [25], one may a priori expect a weak intensity of Brillouin lines corresponding to $T_c[100]$ phonons. However, at the high frequency of the Brillouin effect the photoelastic coefficient $\rho_{66}$ does not include the order parameter contribution and may thus have a different value. Actually, several attempts to resolve Brillouin lines corresponding to transverse acoustic modes propagating along the [001], [100] and [110] tetragonal axes were unsuccessful.

Only at low temperature and with maximum laser power was it possible to observe in the background...
a very weak Brillouin intensity (Fig. 6) which corresponds to a sound velocity

\[ V_{T_s[100]} = (1500 \pm 50) \text{ m.s}^{-1}. \]

If the intensity \( I_{T_s} \) scattered by this transverse mode is compared to the longitudinal intensity \( I_L \) recorded during the same scan, the ratio of the photelastic coefficients \( \rho_{66}/\rho_{12} \) can be evaluated. Following Vacher and Boyer [24] one obtains (indices referred to the tetragonal lattice):

\[ \frac{\rho_{66}}{\rho_{12}} = \left( \frac{C_{66}}{C_{11}} \frac{I_{T_s}}{I_L} \right)^{1/2} \approx 0.06. \]

In addition, failure to observe other transverse modes indicates that all the photelastic coefficients associated with shear strains are very weak in tanane. It must be noted that similar observations have yet been made in other organic solids [26].

3.4 Elastic constants. — Calculations of the elastic constants at various temperatures must take into account the temperature dependence of the specific gravity \( \rho \). Dilatometric measurements along the [001] axis [11] and X-ray measurements of the lattice parameters [2] give the temperature dependence of the specific gravity with a relative accuracy better than 0.5 % (values on table II).

Several elastic constants at room temperature, at \( T_c \) and 9.3 K below \( T_c \) are calculated from the above results using the relations of table I in the high and low temperature phases. The hypersonic elastic constants of normal tanane are listed in table II just below those deduced from neutron measurements on deuterated tanane.

As noted above, the elastic constant \( C_{66} \) exhibits near the transition temperature a strong dispersion due to the linear coupling between the \( u_{xy} \) strain and the order parameter. The other elastic constants have only been measured at high frequency, but we believe they will not exhibit strong dispersion because the transition is expected to induce at most second order effects on these constants.

Comparison with the elastic constants measured at various frequencies in other molecular crystals [26, 27] shows that the hypersonic elastic constants of tanane have standard values. However, isotropic symmetry of the elastic properties appears rather unusual even in close-packed structures. It would be attractive to attribute it to the disorder but comparison with other plastic crystals shows that such isotropic symmetry generally does not appear.

4. Conclusion. — The description of the phase transition of tanane within the pseudo-spin formalism (Ising model) accounts not only for the equilibrium properties [3, 4, 11] but also for the dynamical properties if one introduces an individual relaxation time of the pseudo-spin \( \tau_0 = 1/\gamma k_B T_c \) closely related to the residence time between two inversions far above the transition temperature.

A linear coupling between the pseudo-spin mode and the transverse acoustic \( T_s[010] \) and \( T_s[100] \) modes renormalizes the low frequency properties (cf. second part of this article) but is not relevant at frequencies much higher than the pseudo-spin relaxation rate. Since the acoustic phonons investigated by Brillouin scattering and neutron scattering are essentially unaffected by the transition we conclude that the pseudo-spin relaxation time \( \tau_0 \gg 10^{-10} \text{ s} \).

The critical behaviour of the observed central peaks can be qualitatively accounted for by the pseudo-spin phonon model of Yamada et al. [15], but it also appears when the temperature is lowered towards \( T_c \) an increase of the mosaicity which can be responsible for an intense anisotropic elastic diffuse scattering. So we conclude that further quasi-elastic experiments with higher resolution would be needed to provide a more quantitative analysis of the individual molecular motion responsible for the transition.

We report a number of physical properties of tanane and the physical constants which have been measured between \( 0 \) °C and \( 20 \) °C (Transition temperature, elastic constants, specific gravity, refractive indices, photelastic coefficients) show that tanane exhibits typical values encountered in molecular crystals except for those directly affected by the transition.

Finally, the determination of the high frequency elastic constant \( C_{66} \) allows reconsideration of the contribution of long range interactions to the transition mechanism, especially the elastic ones [4].

The order of magnitude of the relevant elastic energy per molecule is given by:

\[ W_{EI} = v_0 C_{66} \frac{\kappa^2_{xy}}{2} \]

where the molecular volume \( v_0 = 2.5 \times 10^{-28} \text{ m}^3 \), the elastic constant \( C_{66} = 2.2 \times 10^9 \text{ Nm}^{-2} \) and the spontaneous shear strain \( \kappa_{xy} = 7 \times 10^{-2} \) [3].
obtains $W_{\text{EI}} = 1.35 \times 10^{-21}$ J or $W_{\text{EI}}/k_B \simeq 100$ K. At the transition temperature $T_c$ the Ising hamiltonian including elastic interactions takes on a value of order $k_B T_c$. Since $W_{\text{EI}}$ is 35% as large as $k_B T_c$, the long range elastic interactions may strongly influence the nature of singularities near the critical temperature, in contrast with the dipolar long range interactions which represent only 1% of $k_B T_c$ in tanane [4].

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APENDIX A

Structure factors of the acoustic and pseudo-spin coupled modes. — The total structure factor at a reciprocal lattice point $Q$ includes both atomic displacements $e_j r_n$ associated with the inversion mode motion and molecular translations $u_j$ associated with the transverse acoustic mode $T_j(q_x)$ or $T_j(q_y)$:

$F(Q) = \sum_j \sum_n f_n e^{iQ(Q \cdot r_n + e_j u_n)}$.

Owing to the spin variable ($e_j = \pm 1$), $F(Q)$ appears as a linear function of the pseudo-spin $e_j$

$F(Q) = \sum_j e^{iQ(Q \cdot u_j)} \{ A(Q) + ie_j B(Q) \}$

with

$A(Q) = \sum_n f_n e^{iQ(Q \cdot r_n)}$ and $B(Q) = \sum_n f_n e^{iQ(Q \cdot r_n)}$.

Owing to the small amplitude of the molecular translations ($Q \cdot u_j \ll 1$) one can write the structure factor:

$F(Q) = \sum_j \{ A(Q) + ie_j B(Q) \} e^{iQ(Q \cdot u_j)}$

and the scattered intensity

$S(Q) = F(Q).F^*(Q)$.

In the high temperature phase, the scattered intensity near a reciprocal lattice node $Q_0$ ($Q = Q_0 + q, \mid q \mid \ll \mid Q_0 \mid$) contains essentially four terms:

1) $S_{\text{el}}(Q_0, 0) = A(Q_0) A^*(Q_0)$ which is the Bragg intensity,

2) $S_{\text{el}}(Q_0, q) = B(Q_0) B^*(Q_0) \langle \sigma(q) \sigma(-q) \rangle$ which is the Fourier transform of the spin-spin correlation function,

3) $S_{\text{el}}(Q_0, q) = A(Q_0) A^*(Q_0) \langle Q_0 u(q) Q_0 u(-q) \rangle$ which is the Fourier transform of the phonon-phonon correlation function,

4) $S_{\text{el}}(Q_0, q) = A(Q_0) B^*(Q_0) \langle \sigma(q) Q_0 u(q) \rangle + A^*(Q_0) B(Q_0) \langle \sigma(-q) Q_0 u(-q) \rangle$ which is the Fourier transform of the spin-phonon correlation function.

At reciprocal lattice points $[1 + q_x, 0, 3]$ where critical quasi-elastic scattering is observed ($Q_0 = [103], q = [q_x, 0, 0]$). The molecular translation $u_j$ associated with $T_j(q_x)$ phonons is perpendicular to $Q_0$. Thus

$Q_0 \cdot u = 0$; $S_{\text{el}}[1 + q_x, 0, 3] = 0$;

$S_{\text{el}}[1 + q_x, 0, 3] = 0$,

and the scattered intensity is only $S_{\text{el}}[1 + q_x, 0, 3]$. Calculations of the elastic structure factors in the ordered ($\langle e_j \rangle = 1$) and disordered ($\langle e_j \rangle = 0$) phases show that:

$F_{\langle e_j \rangle} = 0[103] = (8.5 - i 8.5).10^{-12}$ cm;

$F_{\langle e_j \rangle} = 1[103] = (10 - i 6.3).10^{-12}$ cm;

$F_{\langle e_j \rangle} = 0[400] = 9.7 \times 10^{-12}$ cm;

$F_{\langle e_j \rangle} = 1[400] = 9.7 \times 10^{-12}$ cm.

So we get $B[103] \neq 0$, while $B[400] = 0$.

At reciprocal lattice points $[4, q_y, 0]$ one obtains $S_{\text{el}}[4, q_y, 0] = 0$. $S_{\text{el}}[4, q_y, 0] = 0$ and the only non zero scattered intensity is $S_{\text{el}}[4, q_y, 0]$, which includes the inelastic intensity of $T_j(q_y)$ phonon acoustic phonons. However, in order to simplify the above expressions only one molecule per primitive cell was considered. Actually there are four molecules per primitive cell and the pseudo-spin system can therefore be described by four sub-lattices and four linear functions of the pseudo-spin variable:

$A_1(Q) + ie_j B_1(Q)$;

$A_2(Q) + ie_j B_2(Q)$;

$A_3(Q) + ie_j B_3(Q)$;

$A_4(Q) + ie_j B_4(Q)$.

Additional correlation functions appear and the scattered intensity includes additional terms. Nevertheless for the ferroelectric pseudo-spin mode one can still write $e_j B = e_j (B_1 + B_2 + B_3 + B_4)$. Coming back to the [400] structure factor, symmetry analysis shows that $B_1[400] = B_2[400] = 0$ while $B_4[400] = - B_3[400]$. It follows that around the reciprocal lattice point [400], no quasi-elastic intensity coming from the pseudo-spin ferroelectric mode can be observed, while non-critical pseudo-spin modes such
as the antiferroelectric mode ($\varepsilon_1 = 1, \varepsilon_2 = -1$) could give rise to quasi-elastic scattering but less intense than that from the critical mode near the critical temperature.

**APPENDIX B**

**Refractive indices.** — The principal refractive indices referred to the tetragonal axes are $n_x = n_y$ and $n_z$. The uniaxial birefringence measured at room temperature with a tilting compensator is:

$$n_z - n_x = 3.1 \times 10^{-3}.$$ 

In the low temperature phase, the orthorhombic axes [100] and [010] are approximately rotated by 45° with respect to the [100] and [010] tetragonal axes. If the corresponding refracted indices are written $n_{x'}$, $n_{y'}$, $n_{z'}$, the birefringences of biaxial tanane measured at 0°C are:

$$n_{x'} - n_{y'} = 2.3 \times 10^{-3}$$
$$n_{y'} - n_{x'} = 1.3 \times 10^{-3}$$
$$n_{z'} - n_{y'} = 3.6 \times 10^{-3}.$$

Absolute indices are more difficult to measure accurately because durable plane refractive surfaces are difficult to obtain, on account of the sublimation of tanane and its solubility in most of the index matching liquids. Our previously reported evaluation of the absolute index $n_x$ [4] appears to be wrong according to more accurate new measurements. Both the dihedral angle of a small prism and the minimum deviation angle by the prism are measured with a thin laser beam and give at room temperature:

$$n_x = n_y = 1.52 \pm 0.01.$$

No reliable dispersion was found between 632.8 nm and 592.5 nm making use of a tunable dye laser. On account of the above uncertainty and the weak temperature dependence of the birefringences, the sound velocities are deduced from the Brillouin shifts using:

$$n_x \approx n_y \approx 1.52$$

from room temperature to 0°C.

**References**


[2] The two equilibrium positions of each molecule are deduced from each other by a two-fold [010] (or [001]) axis, thus the inversion motion can either consist in a 180° reorientation or in a chair-chair interconversion. 


