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Orientalational disorder in plastic neopentane

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Résumé. — Des expériences de diffraction de neutrons ont été effectuées à plusieurs températures dans la phase à désordre d'orientation (ou plastique) du néopentane deutéré ($C(D_3)_4$). L'analyse du facteur de structure expérimental en utilisant des fonctions adaptées à la symétrie du cristal et de la molécule fournit les premiers coefficients du développement de la densité de probabilité d'orientation moléculaire. On obtient ainsi des maximums de probabilité lorsque l'un des axes de symétrie $\bar{4}$ de la molécule tétraédrique est parallèle à l'un des axes d'ordre 4 du réseau cubique, tandis que les deux autres axes $\bar{4}$ sont parallèles à des axes binaires du cube. Six orientations physiquement distinctes, appelées D_{2d} , sont ainsi accessibles. L'influence de la température est essentiellement une rapide croissance du facteur de Debye-Waller. L'effet du couplage rotation-translation est aussi abordé.

Abstract. — Single crystal neutron elastic scattering data have been collected at several temperatures for deuterated neopentane $C(D_3)_4$ in the orientationally disordered (or plastic) phase. The analysis of the observed structure factor, using symmetry adapted functions, gives the first coefficients of the expansion of the orientational probability density function (o.p.d.f.). The molecules have preferentially a D_{2d} orientation giving 6 physically distinct orientations. The influence of temperature is mainly a strikingly rapid increase of the Debye Waller factor. Rotation-translation coupling is also discussed.

1. Introduction.

An elastic scattering experiment performed on a plastic crystal gives Bragg reflexions as well as a conventional ordered crystal does since the molecular centers of mass form a regular lattice. However the molecules perform frequent large angle rotations so that a large orientational disorder occurs [1].

Thus, no acceptable result can be expected from a classical structure analysis in which one assumes that the atoms perform only small amplitude oscillations around an equilibrium position: the motion of the atoms which are not located on the molecular center of mass is too large during molecular reorientations to be accounted for by the usual Debye Waller factor. Conversely, the orientational disorder may be conveniently described through the orientational probability density function (o.p.d.f.), $P(\Omega)$, which is the probability that the molecular coordinate system can be deduced from the crystal one by a rotation Ω . The o.p.d.f. may be attained through the static structure factor which is precisely the result of a diffraction experiment.

This experiment has been performed by neutron scattering on deuterated neopentane (or 2,2 dimethylpropane- d_{12} $C(D_3)_4$) which displays between the ordered solid and the liquid phases a plastic phase (140 K-256.5 K). The molecular centres of mass of these globular molecules with T_d symmetry form a f.c.c. lattice ($a = 8.78 \text{ \AA}$; $z = 4$) [2], while the orientational disorder is suggested by a strong entropy change at the solid-plastic transition ($16.4 \text{ JK}^{-1} \text{ mol}^{-1}$ vs. $12.7 \text{ JK}^{-1} \text{ mol}^{-1}$ at the melting point) [3].

Part 2 points out some experimental details; part 3 outlines how the Bragg intensities were converted into an o.p.d.f. and part 4 gives a physical interpretation of our results.

2. Experimental procedure.

The experiments were performed on the 5C-2 four circle diffractometer (Laboratoire Léon Brillouin (¹), C.E.N. Saclay) at 150 K, 173 K, 187 K, 225 K and 253 K (incident beam wavelength: $0.832 \text{ \AA}$).

Because of the high neutron incoherent scattering length of hydrogen, deuterated neopentane was

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used (purity 0.98). The single crystals were grown from the vapour as described in [4], but the glass cells were replaced by smaller ($\varnothing$ 8 mm, length $\approx$ 15 mm, sample volume approx. 0.1 cm^3) silica cells. This has two unavoidable drawbacks: the melting point of silica is much higher than the decomposition temperature of neopentane, which makes the sealing of these cells delicate; the growth process is more difficult to control in a smaller cell because the self diffusion of the neopentane vapour does not slow down the transfer of matter as well.

The cells were placed in aluminium sample holders and carried to the site of the experiment in a Dewar bottle cooled at -78°C , because of the low melting point and of the high vapour pressure of neopentane. For the same reason, the cryostat which was used during the experiment was cooled before setting in the sample, and therefore had to be modified beforehand so that opening it while cold could be possible and not cause icing. By construction of the cryostat, the sample could be kept in a temperature gradient which prevented sublimation to take place.

The orientation of the samples was performed on the diffractometer itself since neopentane single crystals display no natural faces and are optically isotropic, and since X-ray orientation is also impossible because of the silica cell.

The data collection itself was fairly classical. Bragg intensities were measured through the usual ω -scan technique⁽²⁾ in order to eliminate the aluminium and silica contributions. The main difference, however, with a conventional diffraction experiment is that, because of the high degree of disorder, the intensities of the Bragg reflexions become rapidly very weak as h , k , l increase. The data collection is consequently long. 32 independent reflexions could be measured at 150 K, 31 at 173 K, 13⁽³⁾ at 187 K, 27 at 225 K and 21 at 253 K, which is not unusual in a plastic crystal [5]. As many equivalent reflexions as compatible with the angle limits imposed on the Euler mount by the size of the cryostat were collected which amounted to a total of 150 reflexions.

3. Results.

Following [6], $P(\Omega)$ can be expanded on a complete orthonormal set of symmetry adapted functions which involve both the molecular and the crystalline symmetries. For a tetrahedral molecule (T_d) on a

cubic site (O_h) these functions $R_{\lambda\lambda'}^l(\Omega)$ are often called cubic rotators⁽⁴⁾:

$$P(\Omega) = \sum_{l,\lambda,\lambda'} \frac{2l+1}{8\pi^2} A_{\lambda\lambda'}^l R_{\lambda\lambda'}^l(\Omega) \quad (1)$$

where $A_{\lambda\lambda'}^l$ is a coefficient which *a priori* depends on temperature. Index l is the same as in the spherical harmonics $Y_m^l(\theta, \phi)$ and is thus related to the number of nodes of $R_{\lambda\lambda'}^l(\Omega)$. The index λ , which takes $2l+1$ values, labels the irreducible representations of the site symmetry point group, and λ' the irreducible representations of the molecular symmetry point group.

Because of the symmetry properties of $P(\Omega)$, λ and λ' must correspond to the identity representation of their point group so that most $A_{\lambda\lambda'}^l$ coefficients vanish [7]; the first non zero ones (i.e. those related to the smoothest $R_{\lambda\lambda'}^l(\Omega)$) are $A_{11}^0 = 1$, A_{11}^4 , A_{11}^6 , A_{11}^8 and A_{11}^{10} .

Treating the molecule as a rigid body [8], one can describe the molecule by three shells of equivalent atoms; the central carbon atom forms the first shell, the four carbon atoms belonging to the methyl groups the second shell and the twelve hydrogen atoms the third one. Then, neglecting correlations between translations and rotations, the diffraction factor [6] is given by

$$F(\mathbf{Q}) = e^{-\frac{1}{2}Q^2\langle u^2 \rangle} F^{\text{rot}}(\mathbf{Q})$$

with

$$F^{\text{rot}}(\mathbf{Q}) = 4\pi \sum_{p=1}^3 n_p f_p \sum_{l,\lambda} i^l J_l(Qr_p) K_{\lambda}^l(\theta_Q, \phi_Q) \sum_{\lambda'} A_{\lambda\lambda'}^l b_{\lambda'}^l \quad (2)$$

where

p labels the different shells of equivalent atoms, f_p is the coherent scattering length of an atom on the p^{th} shell,

$J_l(Qr_p)$ is the l order Bessel function,

r_p is the radius of the p^{th} shell,

K_{λ}^l is the l , λ cubic harmonic,

θ_Q, ϕ_Q are the polar angles of the scattering vector in the crystal axes,

and $b_{\lambda'}^l$ is the l , λ' coefficient of the orientational density of the atoms of the p^{th} shell in the molecular reference frame.

⁽²⁾ For each reflection, the detector remains at a constant scattering angle, while the sample rotates around an axis which is perpendicular to both the incident and scattered beams.

⁽³⁾ The experiment at 187 K was, in fact, a quick check while heating the sample.

⁽⁴⁾ In reference [7], the o.p.d.f. was written as: $P(\Omega) = \sum_{l,\lambda,\lambda'} A_{\lambda\lambda'}^l R_{\lambda\lambda'}^l(\Omega)$. There is thus a $\frac{2l+1}{8\pi^2}$ difference in the definition of $A_{\lambda\lambda'}^l$. The definition given in the present work has been chosen in order to agree with the majority of papers written on the subject.

A least square fit of this structure factor to the experimental intensities (Table I) was performed at each temperature. These results are summarized in table II, where the corresponding results for carbon-tetrabromide [5] are given for comparison. In this table, F_{norm} is proportional to the volume of the sample and the large difference between experiments simply points out that different samples were used for different temperatures.

In the final refinement, the radius of the first shell $r_1 = r_{\text{C-C}}$ (Fig. 1) was fixed at 1.58 Å, and that of the second $r_2 = r_{\text{C-D}}$ at 2.17 Å, so that the results at the five temperatures could be compared. These values are rather close to those measured in the liquid ($r_1 = 1.546$ Å [9]) and in the vapour phases ($r_1 = 1.534$ Å, $r_2 = 2.2$ Å [10]). They were chosen as a compromise which would give a good reliability factor to all five sets of Bragg reflexions simultaneously. Nevertheless, no emphasis should be given to these values because we have found that they were very sensitive to the value of the lattice parameter ($a = 8.56 \pm 0.13$ Å at 150 K, 8.66 ± 0.2 Å at 173 K, 8.76 ± 0.02 Å at 225 K and 8.80 ± 0.01 Å at 253 K) which is not known with a

Fig. 1. — Definition of the neopentane molecule. The T_d symmetry operations applied to this frame result in the whole molecule.

Table I. — Observed and calculated structure factors at 150 K.

hkl	F_{obs}	F_{calc}	hkl	F_{obs}	F_{calc}	hkl	F_{obs}	F_{calc}
111	12.04	12.95	200	6.32	6.32	220	3.54	3.27
311	3.69	3.66	222	5.70	5.42	400	0	0.28
331	3.54	3.41	420	4.12	4.12	422	2.10	2.15
511	2.53	2.77	333	1.28	1.02	440	4.18	3.93
531	1.73	1.62	600	2.19	2.30	442	1.54	1.64
620	0.71	0.89	533	0.84	1.10	622	0	0.09
444	2.24	2.56	711	1.30	1.27	551	0	0.56
640	0	0.72	642	0	0.33	553	1.58	1.50
731	0	0.30	800	1.79	1.46	733	0.77	0.83
644	1.38	1.29	820	0.95	0.91	822	0.92	0.77
660	0	0.15	751	0	0.41			

Table II. — Parameters for the calculated structure factors. The meaning of each parameter is given in the text. The second number in each column is the estimated standard deviation. The Debye Waller factor refers to the motion of the molecular centre of mass and is given in Å².

T	150 K	173 K	187 K	225 K	253 K	CBr_4
F_{norm}	4.97 (0.12)	2.74 (0.07)	4.45 (0.08)	5.65 (0.15)	5.37 (0.16)	20.7
$\langle u_z^2 \rangle$	0.103 (0.004)	0.101 (0.007)	0.112 (0.01)	0.172 (0.005)	0.212 (0.006)	0.167 (0.003)
A^4	-0.046 (0.018)	-0.043 (0.020)	-0.087 (0.043)	-0.0842 (0.017)	-0.10 (0.02)	-0.039 (0.013)
A^6	-0.419 (0.019)	-0.347 (0.024)	-0.328 (0.045)	-0.315 (0.017)	-0.28 (0.02)	-0.362 (0.018)
A^8	0.142 (0.018)	0.114 (0.038)	0.113 (0.080)	0.0834 (0.031)	0.09 (0.04)	0.17 (0.11)
A^{10}	0.21 (0.15)	0.37 (0.30)	-0.02 (0.45)	0.39 (0.20)	-0.05 (0.46)	
r_1	1.58					
r_2	2.17					
RW	6.8 %	7.3 %	3.3 %	6.4 %	6.1 %	7.8 %

good accuracy because all the necessary equivalent reflexions could not be measured due to the bulk of the cryostat. It was however checked that the final values of the parameters in the fit were not affected by the choice of a . The fit is also rather insensitive to the value chosen for θ_D (see Fig. 1).

4. Discussion.

4.1 ORIENTATIONAL SYMMETRY.

4.1.1 Introduction. — In a plastic crystal, one usually expects the molecules to favour orientations for which as many as possible molecular symmetry elements coincide with those of the crystal.

For a tetrahedral molecule (T_d) residing on a site with cubic symmetry (O_h), there are four such sets of particular orientations for which two or more crystal and molecule symmetry elements coincide [11]. These are called T_d , D_{2d} , C_{3v} and C_{2v} , the name of which labels the symmetry subgroup which

is common to the molecule and to the site when the molecule has such an orientation. One typical orientation of each set is shown in figure 2, and each set may be described briefly in the following way :

T_d : each 3-fold cubic axis is parallel to a threefold tetrahedral axis. Two distinguishable orientations of the molecule are possible.

D_{2d} : one $\bar{4}$ tetrahedral axis is common with a fourfold lattice axis and the other two are parallel to cubic twofold axes. Six possible orientations exist.

C_{3v} : a threefold axis of the cube and a 3-fold axis of the tetrahedron are common as well as 3 σ_v planes. Eight orientations are possible.

C_{2v} : a twofold cubic axis coincide with a $\bar{4}$ tetrahedral symmetry axis and two σ_v planes containing this axis are common to the crystal and the molecule. This provides 12 orientations.

These will be further referred to as « ideal » situations or orientations.

Fig. 2. — One orientation for each one of the four sets in which two or more symmetry elements are common to the cube and tetrahedron. As it is not the unit cell which is displayed, the neighbour molecules are positioned at the mid edge points of a larger cube.

When a plastic crystal is such that the molecules have orientations close to one of those described above, the corresponding $P(\Omega)$ has maxima for those orientations. This is for instance the case for adamantane in which $P(\Omega)$ is maximum for T_d orientations [12], and for CBr_4 where the D_{2d} distribution is favoured [5].

4.1.2 Comparison with the ideal case. — i) A first step in the understanding of our results is to compare the experimental values of $A_{\lambda\lambda'}^l$ with the theoretical values obtained for the situation in which the molecules have exactly the T_d , D_{2d} , C_{3v} or C_{2v} orientations (Table III). As our experimental results give a very weak A_{11}^4 , a markedly negative A_{11}^6 and positive A_{11}^8 and A_{11}^{10} , this suggests a D_{2d} situation although correspondence with the ideal case is far from being perfect.

ii) Before proceeding to a more precise comparison with the ideal case it is worth pointing out that the development of $P(\Omega)$ following equation (1) is based on the assumption that the coefficients $A_{\lambda\lambda'}^l$ decrease rapidly with increasing l . This is obviously incorrect for the ideal case (cf table III for a T_d orientation for instance), a situation analogous to that found in the expansion of a δ function in Fourier series. In the actual case, as $P(\Omega)$ is a smooth function (and not a sum of distributions), one expects, as in a usual Fourier expansion, the $A_{\lambda\lambda'}^l$ to become small when the variations of the rotator functions become rapid i.e. when l increases. However, there is no way to predict if the coefficients which could not be measured in a given experiment were small enough to be neglected. It is thus

Table III. — Rotator coefficients $A_{\lambda\lambda'}^l$ for the four ideal orientations.

T_d		D_{2d}	
l	$A_{\lambda\lambda'}^l$	l	$A_{\lambda\lambda'}^l$
0	1	0	1
4	1	4	0.166667
6	1	6	- 0.75
8	1	8	0.708335
10	1	10	0.312512
C_{3v}		C_{2v}	
l	$A_{\lambda\lambda'}^l$	l	$A_{\lambda\lambda'}^l$
0	1	0	1
4	- 0.481483	4	- 0.458333
6	0.423870	6	0.343750
8	0.231829	8	0.252609
10	0.251121	10	- 0.353492

important, when comparing an experimental result with an ideal situation, to use for such comparisons probability functions with the same number of rotator functions. This is why we have constructed $P_{\text{trunc}}(\Omega)$ obtained by truncating the expansion of the o.p.d.f. of an ideal case above the $l = 10$ term.

We have compared these $P_{\text{trunc}}(\Omega)$ with our experimental $P(\Omega)$ in table IV. The four first lines give the values of $P_{\text{trunc}}(\Omega)$ for respectively the T_d , D_{2d} , C_{3v} and C_{2v} orientations.

Table IV. — o.p.d.f. in the four sets of high symmetry orientations. The first lines show $P_{\text{trunc}}(\Omega)$ calculated in T_d , D_{2d} , C_{3v} , C_{2v} orientations, for a molecule in each one of these orientations; the last five lines give $P(\Omega)$ calculated with the experimental data.

	$P(T_d)$	$P(D_{2d})$	$P(C_{3v})$	$P(C_{2v})$
T_d	0.773	0.144	- 0.033	- 0.026
D_{2d}	0.144	0.243	- 0.021	- 0.029
C_{3v}	0.144	0.007	0.039	0.051
C_{2v}	- 0.023	- 0.029	0.079	0.103
$T = 150$ K	0.025	0.103	- 0.011	- 0.021
$T = 173$ K	0.074	0.103	- 0.021	- 0.033
$T = 187$ K	- 0.032	0.067	0.01	0.007
$T = 225$ K	0.073	0.095	- 0.020	- 0.033
$T = 253$ K	- 0.039	0.055	0.013	0.012

The fact that these values differ from 0 or 1 show the influence of the truncation of these functions. The last five lines correspond to the experimental o.p.d.f. at the five used temperatures. Comparison with the first four lines confirms that the measured $P(\Omega)$ is not far from a D_{2d} situation.

This tendency towards a D_{2d} orientation is in line with two previous results :

— an inelastic incoherent neutron scattering experiment performed on a powder sample [13] concluded that the most probable reorientations corresponded to jumps from one D_{2d} orientation to another through 90° rotations around the fourfold axis which is common to the molecule and the crystal.

— a molecular dynamics simulation [14] in which the methyl groups were represented by a single fictitious atom also concluded to a D_{2d} most probable orientation.

4.1.2 Stereographic projection. — The previous analysis takes into account only the four ideal orientations, while $P(\Omega)$ may be expected to contain more information. Nevertheless, as Ω is a function of three angular variables, it is not easy to give a representation of the o.p.d.f. One way to circumvent this difficulty is to draw a stereographic projection of $P(\theta, \phi)$ which is the probability of finding a C-C

bond (i.e. a molecular threefold axis) in the direction θ, ϕ . $P(\theta, \phi)$ is easily obtained from the $A_{\lambda\lambda}^l$ coefficients :

$$P(\theta, \phi) = \sum_{l, \lambda, \lambda'} K_{\lambda}^{l*}(\theta_0, \phi_0) A_{\lambda\lambda}^l K_{\lambda}^l(\theta, \phi) \quad (3)$$

where the direction θ_0, ϕ_0 points in the direction of a C-C bond in the molecular frame.

Figure 3 shows the stereographic projection of $P(\theta, \phi)$ for the experiment performed at 150 K. Maxima of $P(\theta, \phi)$ are observed in the $[110]$ directions showing that the C-C bonds are preferentially parallel to these directions, while minima occur in the $[111]$ and $[100]$ directions which are conse-

Fig. 3. — Stereographic projection of $P(\theta, \phi)$ at 150 K.

Fig. 4. — Stereographic projection of $P_{\text{trunc}}(\theta, \phi)$ for a crystal in which the molecules have exactly D_{2d} orientations.

quently forbidden. Of course it is not possible for the 4 threefold axes of the tetrahedron to be, at the same time, parallel to four $[110]$ crystal directions, as the angles between the twofold axes of the cube are 60° , 90° and 120° instead of the 109° of the tetrahedron. However, such a projection is in agreement with a D_{2d} situation, as can be seen through figure 4 which represents the stereographic projection of $P_{\text{trunc}}(\theta, \phi)$ obtained from the ideal case by truncating it above $K_1^{10}(\theta, \phi)$. Both figures have the same directions for their maxima and minima, even if the relative heights of these extrema are not the same. We must, nevertheless, notice that :

— on both figures, $P(\theta, \phi)$ is maximum for the direction where $K_1^6(\theta, \phi)$ is maximum. This is related to the strong negative value of A_{11}^6 (Eq. (3)) which is found both for our experimental results and the ideal D_{2d} orientation (Tables II and III). Inclusion of more coefficients in the development could thus slightly modify the directions of these maxima.

Nevertheless the comparison between figures 3 and 4 shows that the maxima are less important in the real case than in the ideal situation. It means that a non-negligible proportion of molecules are not in their ideal orientations, which may be explained by one or several of the following reasons among which a diffraction experiment performed at one temperature cannot discriminate.

— The actual most probable orientations are not exactly D_{2d} but slightly tilted because of steric hindrance.

— the molecules librate with a non-negligible amplitude around their equilibrium positions.

— the molecules perform non instantaneous reorientations between their six equilibrium positions.

4.1.4 Cuts of the $P(\Omega)$ surface. — A third way of presenting our results and of comparing them with different models consist in plotting $P(\Omega)$ along a given trajectory of the Ω space. We have chosen these trajectories to be possible reorientations around a crystal axis which brings a molecule with D_{2d} orientation into another D_{2d} orientation. As above, a plot of the experimental $P(\Omega)$ along such a trajectory has no meaning in itself and must be compared with the same plot for $P_{\text{trunc}}(\Omega)$ relative to the D_{2d} ideal cases.

Four such plots are given in figure 5a-d. They correspond to reorientations along : a) the four fold axis common to the crystal and the molecule, b) a crystal twofold axis which is parallel to a tetrahedron $\bar{4}$ axis, c) a crystal threefold axis and d) a crystal fourfold axis perpendicular to the one which is common. In figure 5b, the maximum after a 90° rotation corresponds also to a D_{2d} situation, although it is a rotation performed along a twofold axis, because of the molecular $\bar{4}$ axis.

Fig. 5. — Variations of $P(\Omega)$ throughout rotations around high symmetry axes, starting from and ending at D_{2d} orientations. *a.* 90° rotation around the fourfold axis which is common to the crystal and the molecule. The mid-point, after a 45° rotation is a T_d orientation. *b.* 180° rotation around a twofold axis of the cube which is perpendicular to the fourfold axis common to the cube and the tetrahedron, and parallel to another molecular fourfold axis. Because of this molecular $\bar{4}$ axis, the mid point, after a 90° rotation is also a D_{2d} orientation. *c.* 120° rotation around a crystal threefold axis. *d.* 90° rotation around a crystal fourfold axis which is perpendicular to the common fourfold axis. The full line correspond to an ideal D_{2d} set of coefficients, while the broken and dotted curves result from the experiments at 150 K and 173 K respectively.

The maxima of the o.p.d.f. are lower than those in the ideal D_{2d} situations, showing, as with the stereographic projection of $P(\theta, \phi)$, that a large proportion of molecules are not in the most probable orientations. However, the minima of the o.p.d.f. are not higher than those of $P_{\text{trunc}}(\Omega)$ in the forbidden orientations ⁽⁵⁾.

⁽⁵⁾ Except for the [111] rotation, but the latter case can be considered as an artefact related to the important oscillations of $P_{\text{trunc}}(\Omega)$ along this trajectory while $P(\Omega)$ is a much smoother function.

It appears therefore that no simple reorientational trajectory can be inferred from the present analysis. At this point, two different lines of thinking may be followed.

i) from a dynamic point of view one could propose that the tetrahedral molecules reorient with a complex motion, which could not be identified in reference [13], and was not observed in the present analysis because the wrong trajectories were chosen. This, however, seems difficult to prove.

ii) from a static point of view, it could be argued that only a finite proportion of molecules remain in

one of the six possible D_{2d} orientations while the others are isotropically distributed. This is however not very realistic as the series of $A_{\lambda\lambda}^l$ coefficients do not follow the ideal D_{2d} sequence, even if one multiplies the ideal coefficients by a population factor, for instance 0.5.

It is also possible that this inability to extract more information about the molecules which are not in the ideal orientation is related to the very use of the rotator functions. These convenient mathematical tools may be rather impractical for our problem. With the limitation to a small number of reliable parameters (inherent to the weak intensity of the Bragg peaks) one cannot represent with accuracy rather localized orientations and/or even smoother o.p.d.f. with lines of maxima along symmetry planes: The artefacts introduced by the unavoidable truncation (artificial secondary maxima, negative values of $P(\Omega)$) mask the physical interpretation one is looking for.

4.2 THERMAL EVOLUTION. — Although the orientational structure is not basically altered, the $A_{\lambda\lambda}^l$ coefficients vary (Fig. 6) with temperature: the absolute value of A_{11}^4 increases as temperature increases while $|A_{11}^6|$ and $|A_{11}^8|$ decrease. The variations with temperature are linear within the accuracy of the experiment. The probability of the D_{2d} orientation decreases when T increases. It is clear however that the structural evolution is not simply an increase of an isotropic contribution as this would result in a decrease of all coefficients (except $A_{11}^0 = 1$) by the same factor.

The thermal evolution of the Debye Waller factor is shown in figure 7, along with

$$\langle u_x^2 \rangle_{\text{Debye}} = \frac{1}{4\pi} \sqrt{\frac{3}{\pi}} \frac{a^2}{mv^2} RT$$

which results from a Debye model in which:

$R = 8.32 \text{ JK}^{-1} \text{ mol}^{-1}$,
 a is the cell parameter,
 m is the molar mass of neopentane, and
 v is an average sound velocity along these axis resulting from inelastic neutron scattering experiments [17].

It can be pointed out that

- i) $\langle u_x^2 \rangle$ is larger than $\langle u_x^2 \rangle_{\text{Debye}}$ and
- ii) $\langle u_x^2 \rangle$ increases with temperature faster than $\langle u_x^2 \rangle_{\text{Debye}}$.

It is thus clear that the Debye Waller factor does not result from a simple harmonic translational phonon contribution.

It is expected in plastic crystals, and has been observed [18] and computed [19] in alkali cyanides, that the steric hindrance leads to an important

Fig. 6. — Thermal evolution of the $A_{\lambda\lambda}^l$ coefficients of the expansion of the o.p.d.f. on a basis of symmetry adapted functions. Boxes correspond to A_{11}^4 ; circles to A_{11}^6 and triangles to A_{11}^8 . A_{11}^{10} is not shown because of its lack of precision. The dashed lines are fitted linear functions.

Fig. 7. — Thermal evolution of the Debye Waller factor (crosses). Vertical bars are estimated standard deviations, not error bars. The dashed line is a fitted second degree polynomial serving as a guide for the eye. The boxes show the calculated Debye Waller factor in a Debye model for translation phonons.

coupling between the orientations of a molecule and the centre of mass positions of neighbouring molecules ⁽⁶⁾ which completely masks the temperature dependent translation phonon contribution to the Debye Waller factor. This would account for the large value of $\langle u_x^2 \rangle$ at 150 K. However this translational disorder is usually expected to be constant or almost constant as temperature changes so that even if one adds the Debye contribution to it, its thermal variation is too slow, at least in the high temperature

⁽⁶⁾ And not its own centre of mass position as in the following section.

Table V. — *Parameters for the calculated structure factor including rotation-translation coupling.*

<i>T</i>	150 K	173 K	225 K	253 K
F_{norm}	4.83 (0.07)	2.69 (0.07)	5.5 (0.1)	5.28 (0.13)
$\langle u_x^2 \rangle$	0.098 (0.002)	0.098 (0.007)	0.169 (0.004)	0.209 (0.005)
A^4	0.054 (0.029)	0.051 (0.089)	0.032 (0.048)	− 0.104 (0.095)
A^6	− 0.396 (0.014)	− 0.366 (0.030)	− 0.357 (0.018)	− 0.290 (0.029)
A^8	0.185 (0.018)	0.131 (0.061)	0.153 (0.043)	0.022 (0.11)
A^{10}	0.353 (0.114)	0.19 (0.40)	0.27 (0.20)	− 0.23 (0.37)
$\tilde{C}_{31}$	0.031 (0.006)	0.024 (0.018)	0.020 (0.006)	0.004 (0.0095)
$\tilde{C}_{71}$	0.003 (0.002)	0.004 (0.007)	0.006 (0.003)	− 0.002 (0.0045)
$\tilde{C}_{72}$	0.030 (0.010)	− 0.014 (0.037)	− 0.020 (0.013)	0.012 (0.022)
r_1	1.58			
r_2	2.17			
RW	4 %	6.4 %	4.1 %	4.2 %

region. The thermal evolution of the orientational disorder is visible only with difficulty through the o.p.d.f. as the main effect shown by $P(\Omega)$ is the residence in or close to the D_{2d} orientations ; it follows that the number of molecules which are in the process of reorientation is small compared to that of the molecules residing in their most probable orientations. This rules out long reorientation times, but does not mean that the number of reorientation processes per time unit is small. Indeed, Raman scattering experiments [20] have shown rotational effects to increase rapidly with temperature. So, although the increase with temperature of the orientational disorder is not striking, we suggest that the rapid thermal increase of the translational disorder, as observed through the Debye Waller factor behaviour, is linked to the rotational motion by the steric hindrance process described above, which, unlike the case of alkali cyanides (¹), is thus not constant as temperature changes.

4.3 ORIENTATION-TRANSLATION COUPLING. — Our experimental data have been finally reanalysed using a model which takes into account the correlations between the orientation of a molecule and its centre of mass position, at the lowest order in the displacement variables. The role of this coupling has been studied in [16], and we have followed without modification the technique exposed in that paper, using the same notations.

We find, as shown in table V, that two coefficients, $\tilde{C}_{31}$ and $\tilde{C}_{72}$, which describe the coupling between the orientation and the centre of mass position, are non-zero, so that some coupling exists but those are weaker than in CBr_4 . Nevertheless, an important result is that the $A_{\lambda\lambda}^l$ coefficients and the Debye

Waller factor remain practically unaffected. No thermal effect is visible.

No increase of the Debye Waller factor is obtained when the rotation translation coupling was included, contrary to a peculiar feature observed in CBr_4 and the effect of the coupling on the purely rotational parameters is much weaker, which is satisfactory. It means that the quadratic terms in the orientation translation coupling can be safely neglected, so that the computed o.p.d.f. would not be affected by such effects.

5. Conclusion.

Compared to an ordered crystal, a plastic crystal provides little data in a diffraction experiment, precisely because of its orientational disorder which is its most interesting feature. Moreover, the use of the symmetry adapted functions in the analysis of the data provides only a series of coefficients which do not lend themselves to an easy interpretation, hence the long section devoted to the discussion of the results.

However, the information thus obtained ends up in a rather clear situation :

— the most frequent molecular orientation is D_{2d} ;

— an important proportion of molecules do not reside in the most probable orientations, even if no precise information about these molecules could be obtained ;

— there exists a small linear orientation translation coupling in neopentane. This effect is much weaker than that reported in CBr_4 ;

— the proportion of molecules not residing in the most probable orientation increases as temperature increases but it is not simply the increase of an isotropic contribution. The rapid increase of the Debye Waller factor with temperature cannot be accounted for by a simple harmonic translational

(¹) Which are ionic crystals and not Van der Waals crystals as neopentane.

phonon model. We suggest that it is caused by the coupling between the orientation of one molecule and the displacement of the centres of mass of the neighbouring molecules.

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