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Dynamical Properties of a Disordered Crystal: Adamantane—$C_{10}D_{16}$

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Inelastic neutron scattering measurements on $C_{10}D_{16}$ show the existence of underdamped collective librational modes with temperature-independent frequency widths.

A preliminary dynamical model, with no adjustable parameters, shows that the observed widths are consistent with the existing quasi-static disorder.

Direct measurements of the orientational pair correlation function by means of elastic neutron scattering agree with the prediction of a simple Ising model.

Intensity measurements between room-temperature and the ordering temperature (T_c = 208.6K) indicate that the orientational correlations develop very slowly as $T \to T_c$.

Dynamical studies of plastic crystals are of great interest in the sense that they provide us with a microscopic understanding of the mechanisms which lead to the existence of both orientationally-disordered phases and cooperative order-disorder transitions.

Adamantane is an example of a simple and therefore attractive system on which such a study can be usefully carried out.

I THE MOLECULE AND THE CRYSTAL

Adamantane is a large, almost spherical molecule of formula $C_{10}D_{16}$. Since the 4 C-H groups occupy tetrahedral positions, the symmetry of the isolated molecule is $\bar{4}3m$.

It has long been recognized[1] that adamantane can exist under 2 different crystalline forms:

i) below $T_c = 208.6$ K the crystal has an ordered structure with symmetry group P$\bar{4}2_1$c.

ii) above T_c the crystal is disordered with a time-averaged f.c.c. symmetry[2,3] and one molecule per primitive unit cell (F m3m). At room-temperature the cubic lattice parameter is 9.445 Å.

The exact crystal structure in the f.c.c. phase is still somewhat controversial and it has been the object of a recent reinvestigation.[4]

In the ordered phase one of the cubic axes becomes the tetragonal c-axis. The amount of tetragonal strain is considerable even just below T_c. In addition a staggered rotation of the molecules of 9° about the c-axis sets in.

II THE NATURE OF THE DISORDER

X-ray diffraction data[2] as well as quasi-elastic incoherent scattering results on powders[6,7] indicate that:

i) each molecular site is occupied by a molecule having one of two rather well-defined and distinguishable orientations (say "+" and "−").

ii) several orientational jump mechanisms can in principle coexist, through which a molecule may change its orientation from + to − or − to +. Although the most probable one consists of 90° jumps around the 4-fold cubic axes, a recent quasi-elastic neutron scattering investigation on a single-crystal does not exclude the possibility of 180°-jumps around the 2-fold axes.[8]

Values for the residence time τ in each of the 2 orientations have been obtained using various techniques:

NMR Neutron Incoherent Scattering	293 K	Ref. 9 Ref. 6, 7	$\tau \simeq 2 \times 10^{-11}$ s.
Brillouin Scattering	~296 K	Ref. 10	$\tau \simeq 10^{-10}$ s.
NMR	T variable	Ref. 11	$\tau_{208} \simeq 10^{-8}$ s $\rightarrow \tau_{293} \simeq 1.5 \times 10^{-10}$ s.

As we shall see later, measured phonon frequencies are typically of the order of 1 THz in adamantane (as in analogous non-plastic molecular crystals, such as hexamine $C_6H_{12}N_4$[12]). For the majority of phonon frequencies ω_{ph} in the Brillouin zone, we then have:

$$\omega_{ph}\tau \gg 1$$

Thus from the point of view of lattice vibrations the disorder can be essentially treated as static.

This fact has guided us in setting up a dynamical model for the disordered crystal. In order to do this one first needs to derive an expression for the intermolecular interactions themselves.

III INTERMOLECULAR INTERACTIONS IN THE CRYSTAL

Interactions between neighboring molecules have been calculated by summing the atom–atom interactions (—C···C—, —C···H—, —H···H—) on the pair of interacting molecules. For the expression of the atom–atom pair interactions Buckingham potentials have been used:

$$\psi(r) = -Ar^{-6} + B\exp(-\alpha r)$$

with values for A, B and α as given by Ref. 13.

Each molecule consists of an essentially spherical carbon framework on which 16 protruding hydrogen atoms are attached. Since each molecule is surrounded by 12 near-neighbors one readily sees that:

i) interactions between near-neighbor molecules will be dominant

ii) furthermore these interactions will depend essentially upon the relative configuration of the atomic groups directly facing each other on pairs of near-neighbor molecules.

In practice we have neglected all atom–atom interactions other than those involving C and H atoms belonging to atomic groups directly facing each other on near-neighbor molecules. We have estimated the error on the calculated phonon frequencies due to this (greatly simplifying) approximation to be of the order of 10% at most.

Figure 1 shows the 2 possible relative configurations for a pair of near-neighbor molecules:

i) if the 2 molecules have like orientations (+ + or − − pairs), the 3 protruding H on each of the 2 molecules form parallel triangles.

ii) if the 2 molecules have opposite orientations (+ − pairs), the H-triangles are anti-parallel. In this configuration the 2 molecules can be thought of as enmeshed.

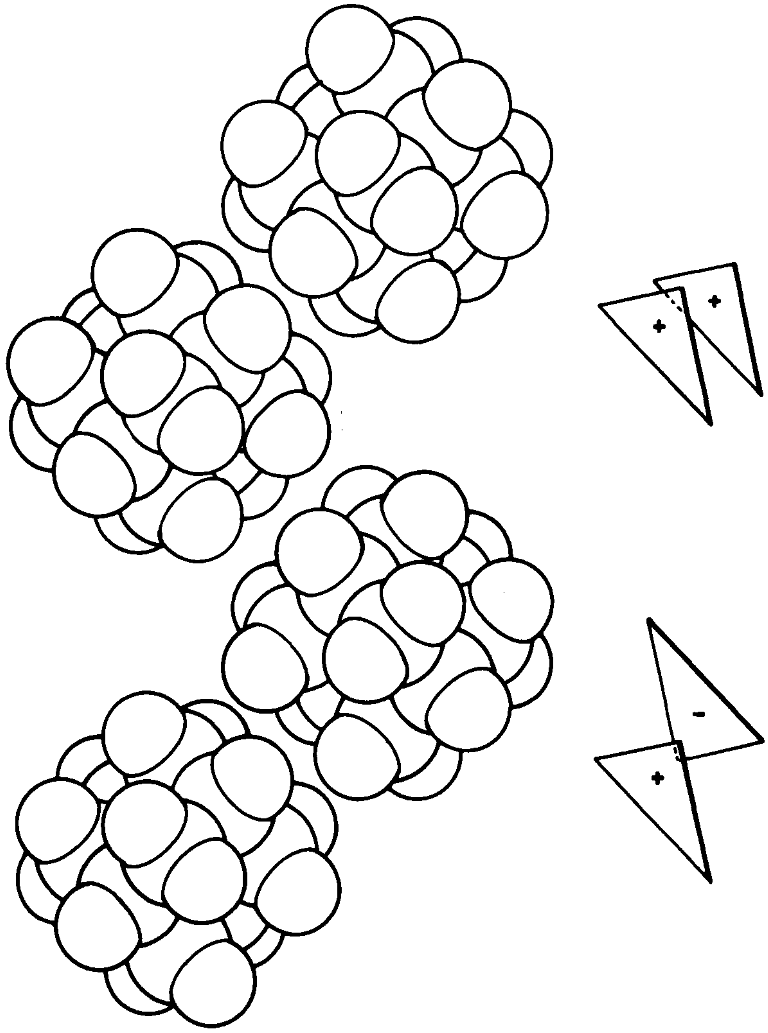

FIGURE 1 First neighbours—positions of the facing atomic groups for the two orientations.

Quantitatively, configuration i) corresponds to a distance of closest —H···H— approach of 2.42 Å (against 2.80 Å for case ii)) and is found to be unstable. Configuration ii) is found to be stable and corresponds in fact (except for the 9° tilt previously mentioned) to the low-temperature phase.

It is of some interest to point out the similarity between the above situation and that of the ammonium halides: in both cases the disordered molecular groups jump between *two* discrete orientations. One may also remark that the ammonium halides and as we shall see, adamantane are the only orientationally disordered systems in which reasonably well-defined librations have been observed.[14]

In other crystals such as CH_4 (where some molecules have random orientations), CBr_4, succinonitrile or KCN (where the disordered molecules or molecular groups can occupy a large number of different orientations in the crystal), neutron scattering studies have essentially failed to find collective modes other than long-wavelength acoustic phonons.

IV PHONON MEASUREMENTS

Coherent inelastic neutron scattering measurements have been carried out on the three-axis spectrometers H4 at Saclay and IN2 at ILL. The necessary dynamical structure factors have been precalculated using a model of random orientational disorder (see Figure 2). The 2 fully-deuterated samples used were grown in our laboratory by a vapor-growth method (sample sizes: 2.5 and 5.2 cc).

One main result of this study is the first determination of the optically-inactive zone-center librational frequency:

$$\nu_0 = 1.40 \text{ THz } (47 \text{ cm}^{-1})$$

The above value agrees well with what might have been expected on the basis of the hexamine results.[12]

Furthermore we are able to follow most of the branches predicted by group theory all the way to the zone boundary (see Figure 3). Branches for which the measurements fail or are inconclusive are indicated by broken lines on Figure 3. No attempt was made to measure the pure libration about the 3-fold axis (Λ_2 mode), since its observation requires a very special geometry.

Another significant feature of the results is the considerable measured frequency width of the librations at all wavelengths: FWHM's are generally found to be of the order of 1 THz while the instrumental broadening is of 0.15 THz at most. Nevertheless we feel the measured lineshapes remain sufficiently underdamped and exhibit enough dispersion across the Brillouin zone to allow us to speak of collective excitations.

Measurements at various temperatures[15] down to $T_c = 208.6$K showed small variations in the frequencies but essentially no change in the widths of the librational modes.

Comparing our results to the NMR results we conclude that the observed libron widths are not directly related to the time of residence of the molecule in a given orientation.

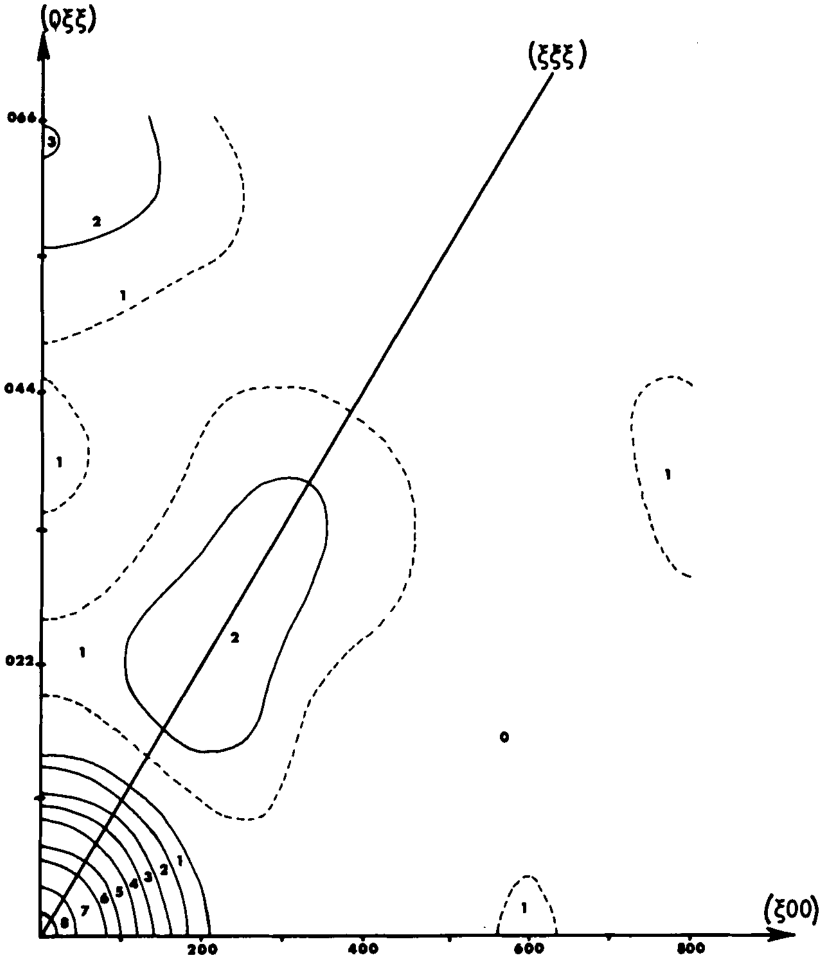

FIGURE 2 Average dynamical structure factor: $\frac{1}{2}[F_+(\mathbf{K}) + F_-(\mathbf{K})]$.

V THE DYNAMICAL MODEL

On the contrary, we believe the large libron widths to be a direct consequence of the existing (quasi-static) disorder. Phonon intensity and width anomalies in the ammonium halides have been accounted for by Sokoloff and Loveluck,[16] within a static disorder framework. Starting from the orientational pair correlation function, these authors show how the dynamical properties of the crystal may be derived, including both the elastic and inelastic neutron cross-sections.

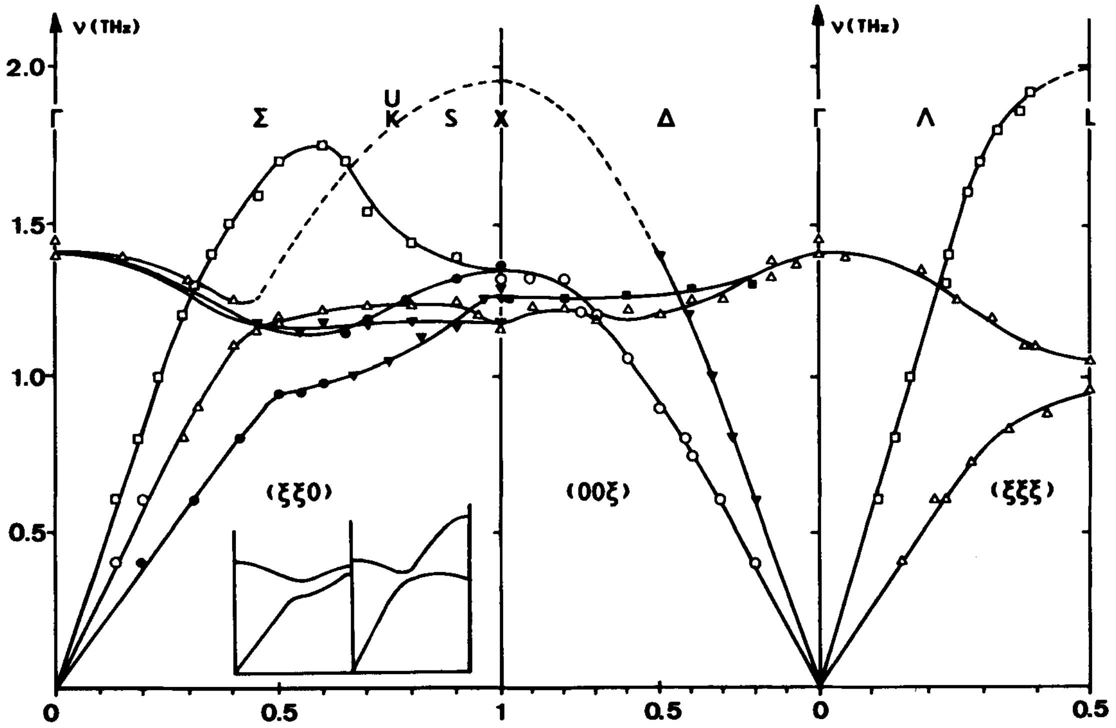

FIGURE 3 Dispersion curves for frequencies in $C_{10}D_{16}$. $\overset{\circ}{\bullet}$ neutron groups with a transverse character; $\overset{\square}{\blacksquare}$ longitudinal; $\overset{\vartriangle}{\blacktriangledown}$ mixt. Lines are guides for the eye.

However, one major assumption in these authors' analysis is the hypothesis that the cohesive forces and hence the elastic restoring forces depend only weakly on the degree of orientational order. This assumption unfortunately is much more questionable in the case of adamantane than in the ammonium halide case.

Hence in what follows, we have adopted a simpler and cruder approach based on the idea that phonon frequencies are essentially controlled by near-neighbor configurations: one then replaces the distribution of near-neighbor environments by the most probable one, which may be characterized by the number n of "parallel" neighbors (or the number 12-n of "anti-parallel" neighbors) surrounding a given molecule. One may then calculate the dynamical matrix and the phonon spectrum for this average (ordered) crystal, as a function of n, the most probable value for n being obtained by comparison with the experiment.

In practice, in order to obtain a dynamical matrix having the correct symmetry, the calculation has to be symmetrized and a given environment will be characterized by the following sum over near-neighbor configurations:

$$n[+-] + n[-+] + (6\text{-}n)[++] + (6\text{-}n)[--]$$

where now $n \leq 6$.

For example the case:

$n = 0$ corresponds to all molecules having the same orientation and is unstable

$n = 3$ corresponds to the randomly disordered crystal (no correla-) tions)

$n = 6$ corresponds essentially to the low-temperature phase.

The results of the calculations are shown in Figure 4:

i) librations are defined for all wavevectors only when $n > 3$. When this condition is not fulfilled, the corresponding eigenvalues ω^2 become negative, first at the zone-center and then progressively almost everywhere except near the zone boundaries.

ii) librational as well as translational frequencies are most sensitive to the value of n when the wavevector is close to a zone boundary. In general it must be pointed out that the above model (which has no adjustable parameters) has been quite successful in correlating the regions for which the neutron measurements have turned out to be difficult (low intensity, broad neutron groups) with regions of large dispersion with respect to n.

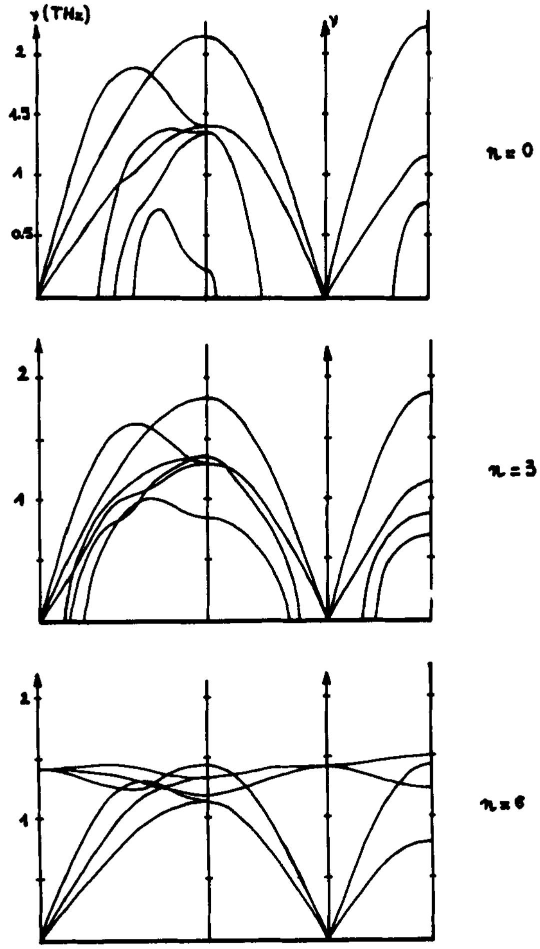

FIGURE 4 Evolution of phonon frequencies with n.

Hence we conclude that the large observed widths are indeed an effect of the quasi-static disorder. In order to proceed further, one must, as suggested by Ref. 16 calculate and measure the orientational pair correlation function.

VI THE PAIR CORRELATION FUNCTION

On the basis of the effective intermolecular interactions of Section 3, a simple Ising model (with near-neighbor interactions only) can be set up, from which the mean-field[17] orientational pair correlation function is obtained.

This quantity, or rather its Fourier transform $g(\mathbf{k})$, can also be measured directly by neutron scattering as it gives rise to the diffuse part of the coherent "elastic" cross-section (critical scattering). The word elastic is used here in an instrumental sense: strictly speaking the critical scattering cross-section has a finite wavevector- and temperature-dependent frequency width around zero-frequency.[20] This width originates from the fact that the orientational disorder is not frozen but fluctuates slowly with time. As long as this frequency width is small on the scale of the instrumental resolution, as is the case here, one may still talk about elastic diffuse scattering, as opposed to truly inelastic scattering: i.e. phonon scattering.

Quantitatively, the elastic diffuse intensity is obtained as the product of $g(\mathbf{k})$ by the "difference structure factor":[18]

$$|\Delta F(\mathbf{K})|^2 = |F_+(\mathbf{K}) - F_-(\mathbf{K})|^2$$

where the + and − signs refer to the 2 molecular orientations.

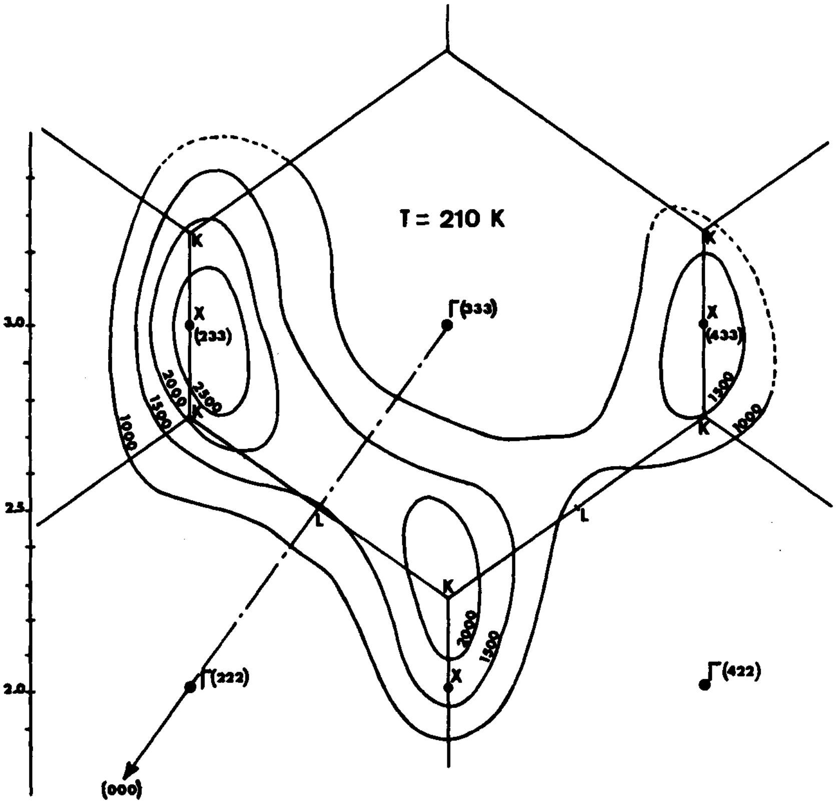

FIGURE 5 Experimental elastic diffuse scattering in the Γ (333) brillouin zone.

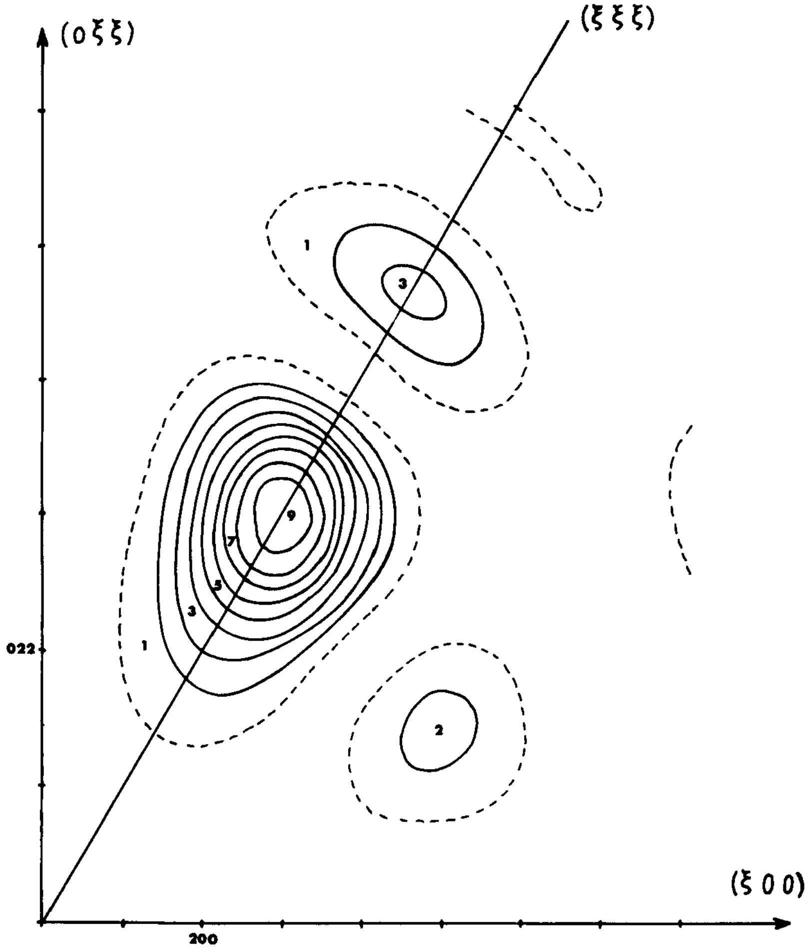

FIGURE 6 "Difference structure factor": $\frac{1}{2}[F_+(\mathbf{K}) - F_-(\mathbf{K})]$.

Figure 6 shows a map of the difference structure factor in the $(1\bar{1}0)$ zone while Figures 8 and 9 show the corresponding diffuse intensity maps (i.e.: $g(\mathbf{k}) \times |\Delta F(\mathbf{K})|^2$) in the $(1\bar{1}0)$ and $(1\bar{1}2)$ zones, respectively. Calculations have also been performed for a family of planes having a [110] direction in common: they show that the diffuse intensity is large in the $(1\bar{1}0)$ and $1\bar{1}2)$ zones and essentially zero in the $(1\bar{1}1)$ and (001) zones.

Figure 8 is to be compared to the measured $(1\bar{1}0)$ intensity contours shown in Figure 5 for $T = 210$ K ($T_c + 1.4$ K): the agreement is very satisfactory and confirms the correctness of the calculated $g(\mathbf{k})$.

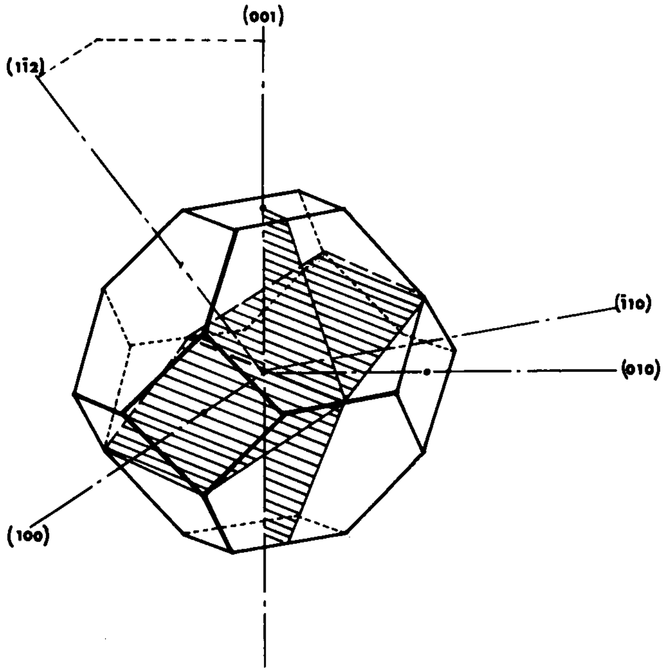

FIGURE 7 The brillouin zone for disordered adamantane.

Between room-temperature and T_c, the diffuse intensity concentrates progressively around the X-points (the low-temperature phase superlattice reflexions), but the overall change between room-temperature and T_c is not dramatic: the transition to the ordered phase is strongly discontinuous i.e. it occurs while the orientational correlations are still rather short-range.

VII CONCLUSION

Having obtained a reliable approximation for the pair correlation function one may now turn back towards the problem of calculating the collective excitation spectrum. However the method proposed by Sokoloff and Loveluck[16] is not applicable as such to the case of adamantane (where the dominant interactions are strongly order-dependent) and will have to be modified.

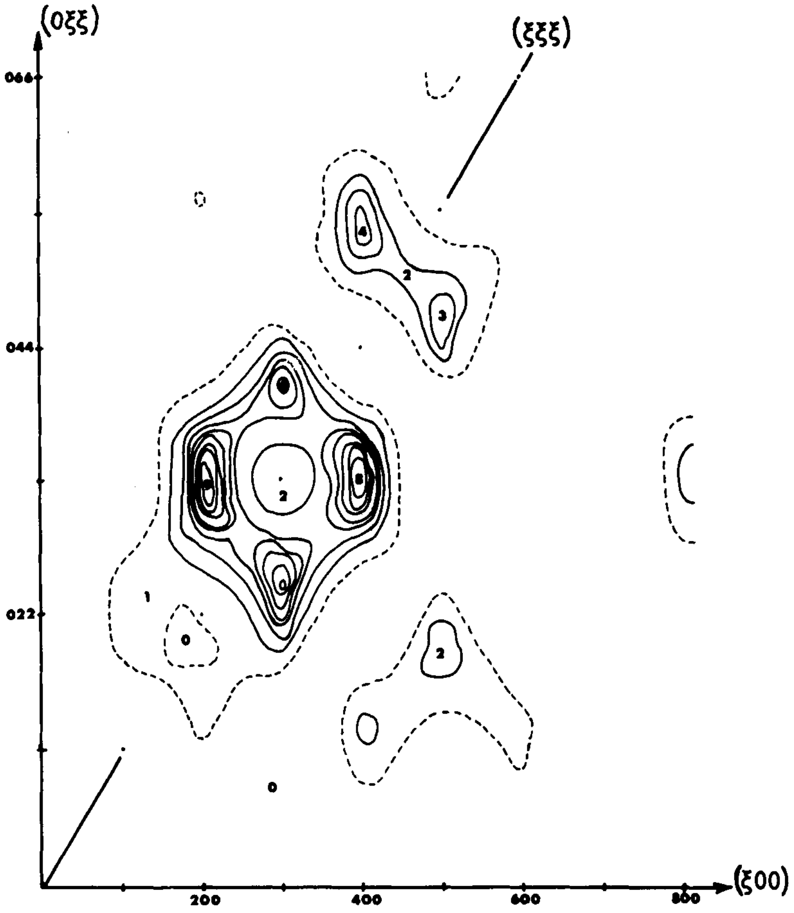

FIGURE 8 Calculated elastic diffuse scattering in the $(0\bar{1}1)$ plane.

On the experimental side it is clear that a static and dynamical study of the low-temperature phase would provide a useful element of comparison for our data in the plastic phase. It is our intention to undertake such a study in the near future.

A more complete account of this work is available upon request[5] and will be published shortly.[19]

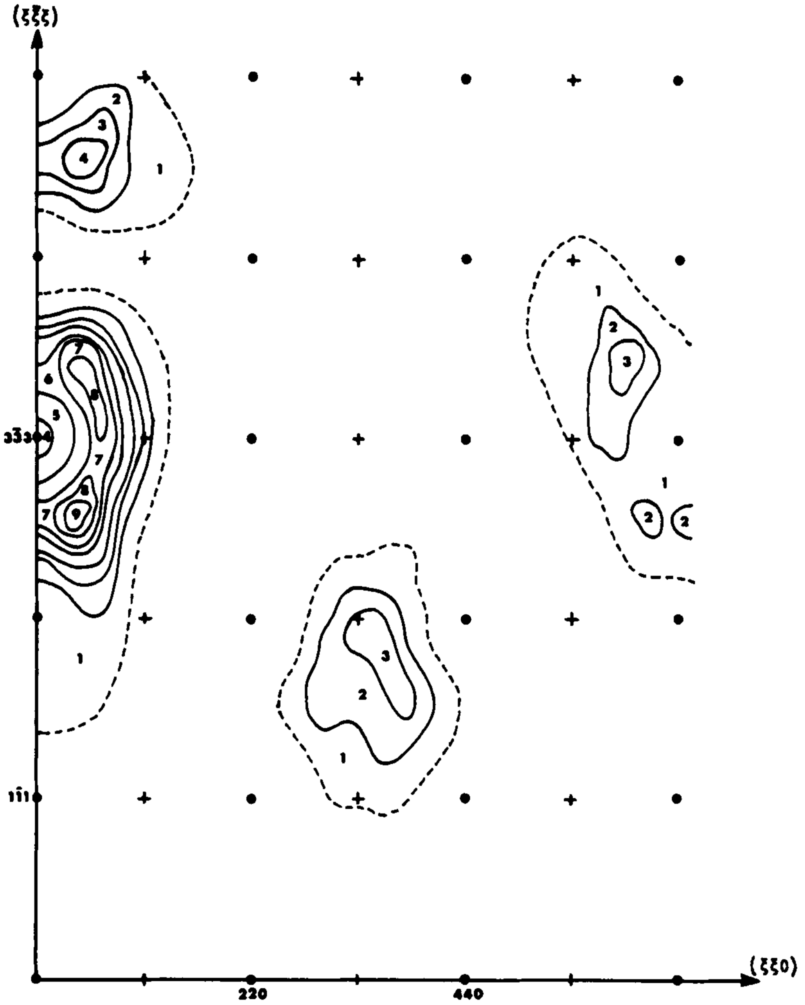

FIGURE 9 Calculated elastic diffuse scattering in the (1̄12) plane.

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