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A MOLECULAR DYNAMICS CALCULATION OF THE PLASTIC PHASE OF NaCN

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I - Introduction

A) A large number of molecular crystals are actually known to present a high temperature disordered phase named "plastic" which is an intermediate phase between the solid and the liquid states. In this plastic phase, the molecular centers of mass still form a regular lattice while the molecular orientations display some degree of disorder. A large amount of experimental work ([1,2]) has been devoted to the study of the static and dynamical aspects of this orientational disorder. The orientational probability density function (pdf) shows more or less sharp maxima: they correspond to the existence of preferred molecular orientations, the rotational dynamics includes large amplitude reorientations as well as rotational oscillations (called librations) around these preferred orientations. Besides, the steric hindrance in the crystal implies that the local orientational pattern is related to a local distortion of the center of mass lattice from the high symmetry average structure. Thus, molecular orientations should not occur as thermally activated jumps over a fixed potential barrier but they would rather be correlated to the fluctuations of the local distortion of the lattice. Reorientations processes appear thus to be strongly coupled to the phonon lattice modes, which give them a more or less collective character. We present here a computer simulation which was primarily intended to confirm this description of plastic molecular crystals.

B) We used the molecular dynamics technique for a two dimensional model which is an idealization of the sodium cyanide (NaCN). Real sodium cyanide shows a high temperature plastic phase (phase I) with the fcc rocksalt structure (space group O_h^5 , Z = 1) where the overall cubic symmetry is ensured through the orientational disorder of the CN^- dumbbells which align preferentially along the (1,0,0) direction ([3-7]). A critical softening of the shear elastic constance C_{44} is observed ([6]) at the transition towards the phase II

which is a clear evidence for the importance of the phonon reorientation coupling. The use of a two dimensional model makes the computational work faster (there are only five degrees of freedom in each formular unit), and allows the simulation of a relatively large sample (10 x 10 unit cell in our case) which is necessary if one wants to investigate the collective behavior of the reorientational process.

Our model ([8]) includes only a simple set of pair interactions: Coulomb interactions plus short range repulsive forces between each end of the dumbbell CN^- and the surrounding Na^+ ions. For the Coulomb interaction CN^- is considered as a monopole located at the center of mass, the higher moments of the charge distribution being neglected so that the electrostatic part of the potential is independent of the molecular orientations. The model includes no direct interaction between the orientations of neighbouring cyanides.

The low temperature structure corresponding to this model is not exactly known and may be very complicated. However, starting from an unstable square symmetric struture, we found that a ferroelastic shear distortion of the unit cell leads to a structure which is dynamically stable at least in the harmonic approximation. In this structure the basis vector of the Bravais lattice have equal length and form an angle of 82°, the CN^- dumbbell being aligned along the longest diagonal of the unit cell.

We present here the results outcoming from two distinct simulations of a square 10 x 10 sample. The first one (Run A) corresponds to a kinetic temperature of 300 K and the inertial moment of the dumbbells was assigned a numerical value such that the mean librational frequency (about 120 cm^{-1}) matches with the frequency range of the zone boundary phonon. In the second one (Run D) at 400 K, the inertial moment was raised so that librational frequencies match with the acoustical phonon branches near the zone center.

II - Structural disorder and single particle rotational dynamics

The results concerning the structural aspect of the orientational disorder and the single particle rotational dynamics have been published elsewhere ([8]) and can be summarized as follows.

- The orientational probability function presents two equivalent maxima for the orientations (1,1) and $(1,\bar{1})$ of the dumbbell with respect to the square samples axes.

- The average structure of the simulated sample has a square symmetry, but its instantaneous configuration presents a pattern of local distortions which tend to reproduce locally the low temperature ferroelastic structure. This is reflected in the Debye Waller factors $< U^2_{CN} >$ and $< U^2_{Na} >$ which, in our computation, exceeds by a factor of two, the corresponding harmonic phonon contribution. The remaining part of these Debye Waller factors represent the quasi static contribution, related to the local deformation of the CN^- environment.

- The individual rotational dynamics appears as a sequence of time intervals during which the dumbbell has a librational motion interrupted by large amplitude reorientational motions. The lifetime of librational interval (or mean residence time, τ_R) can be roughly estimated from the shape of the individual rotational correlation function to be about 1,3 pcs for the first run and 2,25 pcs for the second one.

- The orientational self-correlation functions also reveal a broad librational band: ω_L = 100 cm^{-1}, FWHM = 100 cm^{-1} for the first run, and ω_L = 35 cm^{-1}, FWHM = 30 cm^{-1} for the second one. This lineshape arises essentially from an inhomogeneous broadening effect due to the disorder, each molecule of the sample experiencing a different potential well at a given time.

III - Collective dynamics

The collective static and dynamical behavior of the simulated crystal can be studied from the Fourier transforms of various correlation functions such as

$$S_r(\bar{q},\omega) = \int e^{i\omega t} < (\sum_L e^{i\bar{q}\bar{R}_L} \sin 2\theta_L(0)) (\sum_{L'} e^{-i\bar{q}\bar{R}_{L'}} \sin 2\theta_{L'}(t)) > d\omega$$

or

$$S_t^{\alpha s}(\bar{q},\omega) = \int e^{i\omega t} < (\sum_L e^{i\bar{q}\bar{R}^s_L} U^\alpha_{Ls}(0)) (\sum_{L'} e^{-i\bar{q}\bar{R}^s_{L'}} U^\alpha_{Ls}(t)) > d\omega$$

where θ_L is the angular coordinate of the CN^- ions in the L cell

U^α_{Ls} is the cartesian component of the displacement $\bar{U}_{Ls}$ of the (L_s) atom from its equilibrium quadratic position $\bar{R}_{Ls}$

The $\bar{q}$ wave vectors available in our molecular dynamics simulation form a sublattice, the spacing of which is one tenth of the reciprocal Bravail lattice.

A) The translational correlation functions $S_t^{\alpha s}(\bar{q},\omega)$ exhibit underdamped phonon resonances with sometimes rather important linewidths. The overall aspect of the corresponding dispersion curves look very much like those of the ordered ferroelastic structure (*Fig. 1*). This can be explained as follows: the dispersion of the phonon branches arise essentially from the long range Coulomb interactions which do not depend much of the local detailed structure. Thus, the influence of the disorder appears mostly through the short range repulsive interactions; their effects of the phonon spectra can be estimated, through the frequency difference between phonons of the ferroelastic phase corresponding to perpendicular wave vectors, and this frequency difference remains actually small compared with the coulombian dispersion. As expected the phonon linewidth of the simulated sample is, for each $\bar{q}$ value,

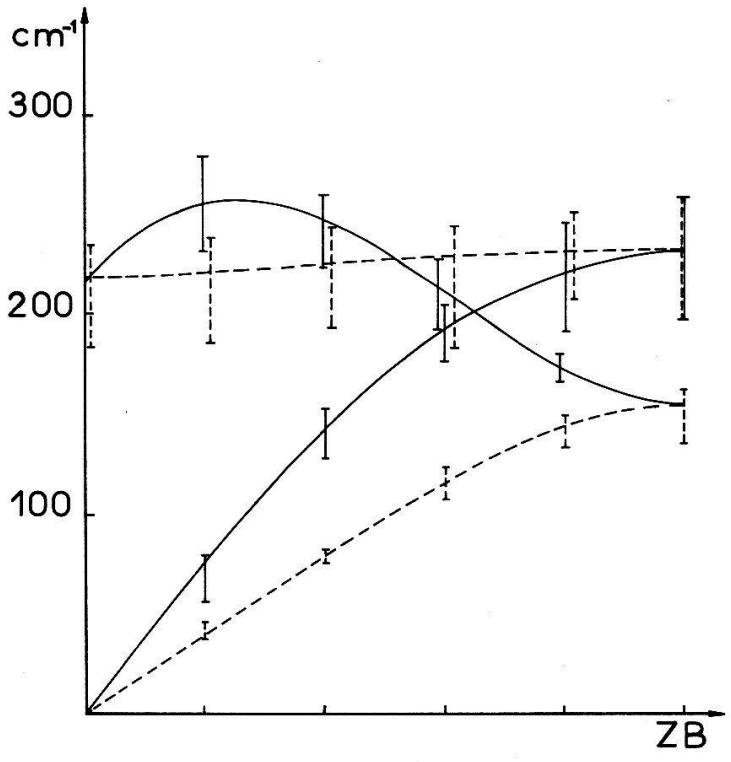

Fig. 1 Phonon dispersion curve for $\bar{q}$ // (1,1)

For each polarization, the curves have been obtained from an harmonic phonon calculation in the ferroelastic phase, for the (1,1) and (1,$\bar{1}$) directions through

$$\omega = \{ \frac{1}{2} [\omega_{11}^2 + \omega_{1\bar{1}}^2] \}^{\frac{1}{2}}$$

The vertical bars represent the FWHM for each phonon, as obtained in the simulation; ——— : L phonons; ----: T phonons.

approximately proportional to this difference. In conclusion, meaningful dispersion curves can be drawn for the translational phonons, and their linewidths arise essentially from disorder effects (Note that, due to the large value of τ_R, life time effects merely contribute to the computed linewidths).

B) Static orientational correlations functions $S_r(\bar{q}, t = 0)$ or, in direct space, $S_r(L, t = 0)$ have been computed. They show strong ferro-orientational correlation in rows parallel to the (1,0) and (0,1) directions of the crystal. However the simulated sample appears to be too small to allow a meaningful evaluation of the corresponding correlation length in this direction.

C) The collective behavior of the orientational processes appears in the wave vector dependence of the rotational correlation $S_r(\bar{q},\omega)$ and a comparison can be made with the corresponding self correlation functions (*see Fig. 2 which has been drawn for the run D*). All these reorientational correlation functions exhibit a low frequency peak, but the correlation time appears to be significatively larger for $\bar{q}$ vectors along the direction (1,0)

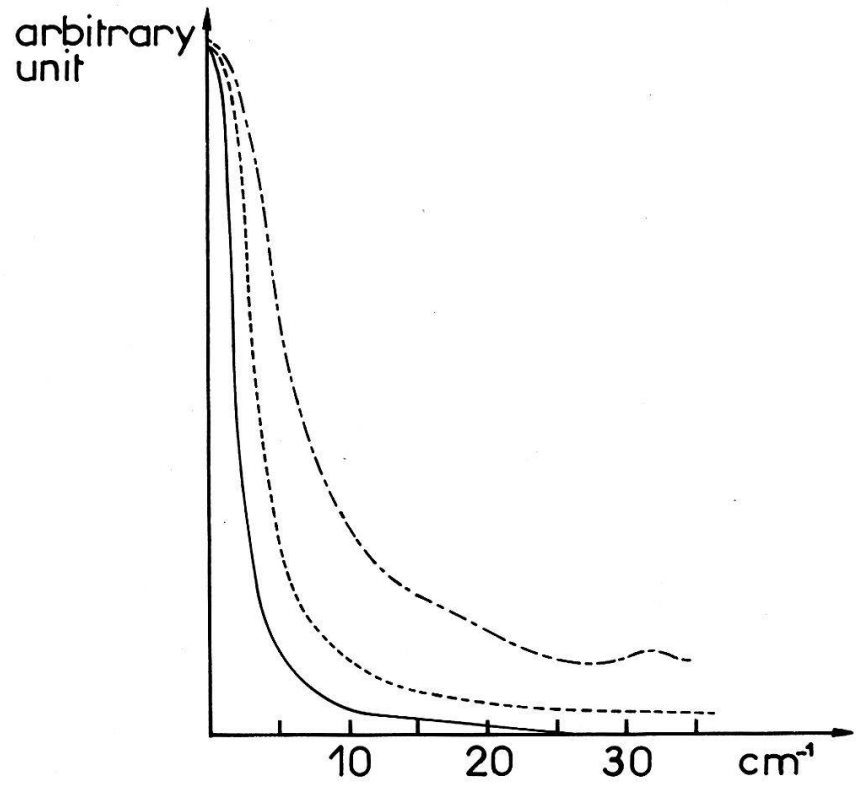

Fig. 2 Fourier transform correlation function for the angular variable sin2θ (Run D).

— — $S_r(\bar{q},\omega)$ for $\bar{q} = \frac{2\pi}{a}$ (0.1,0)

----- Self correlation function

— - — $S_r(\bar{q},\omega)$ for $\bar{q} = \frac{2\pi}{a}$ (0.1,0.1)

and (0,1) which are precisely the directions of the static orientational correlation. The coupling between the orientational processes and the lattice modes exhibits itself through the presence of a low frequency peak in some translational correlation function $S_t(\bar{q},\omega)$, the linewidth of which is equal to that of the corresponding $S_r(\bar{q},\omega)$. Reorientational processes seem to be mostly coupled to the transverse displacement of the sodium atoms for wave vectors $\bar{q}$ parallel to (1,0). For this direction, the correlation time $\tau(\bar{q})$ corresponding to the low frequency peak does not depend on the value of $\bar{q}$ (*see Table I*). This coupling is related to the ferroelastic character of the local distortion, an orientational correlation along a (1,0) direction implying a corresponding transverse displacement of the neighbouring Na ions.

Qx	0.1	0.2	0.3	0.4	0.5
τ	2.6	2.5	2.3	1.8	1.3
Sr	58	50	47	47	27
St	2.9	0.7	0.3	0.1	0.1

Table I Correlation time $\tau(\bar{q})$ (in 10^{-12} s) and integrated intensity of the low frequency peak for $S_r(\bar{q},\omega)$ (reorientational correlation function) and $S_t(\bar{q},\omega)$ (transverse displacement of Na^+), for $\bar{q}$ along (1,0) (result concerning Run D).

The strength of this coupling can be estimated from the integrated intensity of the low frequency peak in $S_t(\bar{q},\omega)$. In the case of Run A , this intensity increases slowly from the zone center to the zone boundary; on the contrary in the case of Run D this intensity decreases rapidly as soon as q goes away from the zone center. This behavior seems to be correlated to the spectral density of the libration modes in each case; we are thus led to propose that the reorientation phonon coupling is in our system mediated by the librations of the molecules.

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