

High frequency dynamics of an orientationally disordered molecular crystal

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Abstract

The dynamic structure factor of the polycrystalline plastic crystal 1-cyanoadamantane has been measured in the THz frequency region by inelastic X-ray scattering as a function of the exchanged momentum Q in the range $1\text{--}10\text{ nm}^{-1}$ and as a function of the temperature in the two solid disordered phases: plastic crystal and glassy crystal. We find that the dispersion of the acoustic excitations is crystal-like in the two phases and that the attenuation $\Gamma(Q)$ shows a negligible T dependence similarly to structural glasses and a Q^α behavior with $1.15 < \alpha < 1.50$ at variance with structural glasses characterized by a Q^2 dependence.

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1. Introduction

One of the most challenging problem in modern condensed matter physics is the understanding of the relaxation dynamics in glass forming materials. When a liquid is cooled below its melting point, it usually crystallizes. Depending on the specific substance and on the cooling rate, however, it may avoid the crystalline phase sustaining a metastable liquid state, ultimately becoming a (disordered) solid at the glass transition temperature T_g . The above phenomenology usually involves structural degrees of freedom and we speak in terms of structural (α) relaxation leading to the formation of a structural glass. Besides these 'canonical' glasses, however, other classes of glassy systems exist. One of them, the 'spin glasses', is the class of glasses most studied by the theoretical point of view.

A possible practical realization of a 'spin glass' are the glassy crystals obtained by quenching plastic crystals. In these latter systems a temperature interval exists where the center of mass of the molecules lies on an ordered lattice, while the orientations are randomly distributed. On cooling the orientational degrees of freedom they undergo a first order phase transition and freeze in a fully ordered molecular crystal. Similarly to a glass-former liquid, when cooled fast enough, a plastic crystal can sustain orientational supercooling below its first order transition temperature, ending in a glass in which the orientational degrees of freedom are disorderly frozen. In structural glasses particular attention has been paid to understand the nature of acoustic excitation and in particular the mechanism of the propagation and attenuation of density fluctuations in the GHz and THz frequency region. This topic has been the subject of many studies of experimental [1–3] and numerical nature [4–6]. Structural glasses are true 'topologically' disordered systems. A glassy crystal can be viewed as a substitutional glass, i.e., an ordered system (molecular center

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of mass in a regular lattice) with disordered force constants. The study of the acoustic excitations in glassy crystals would bring important information on the role of topological vs substitutional disorder. With this purpose inelastic X-ray scattering (IXS) measurements on a prototypical plastic crystal, the 1-cyanoadamantane ($C_{11}H_{15}N$), have been performed to see how the dynamic structure factor is affected by the orientational disorder. This system at room temperature is in the plastic crystal (Rotator phase) with a fcc structure and molecular orientation almost isotropic (dynamic disorder of orientations). On decreasing the temperature it undergoes a transition at $T_{m-R} = 283$ K [7–10] to a fully ordered monoclinic crystal. On the contrary upon standard cryostat fast cooling (approximately 20 K/min), this crystal undergoes an orientational glass transition at $T_g^0 = 177$ K [7–10] becoming a glassy crystal (static disorder of orientations). In this work we present the results obtained by investigating the high frequency dynamics (THz frequency region) of 1-cyanoadamantane across the orientational glass transition, looking at the effect of the orientational disorder on the propagation and attenuation of density fluctuations.

2. Experimental method and results

Polycrystalline 1-cyanoadamantane (purity 97%) purchased from Sigma–Aldrich, has been hashed with a mortar to obtain a thin powder. The powder has been placed in a sample cell composed of a stainless still block with a cylindrical hole in the direction of the incident beam. Two kapton windows 250 μm thick were fixed at the two opposite extremities of the cylindrical hole through two

stainless still holder screwed on the metallic block. The experiment has been performed at the high energy resolution IXS beam-line ID28 at the European Synchrotron Radiation Facility. The instrument consists of a back-scattering monochromator and five independent analyzers held one next to the other with a constant angular offset on a 6.5 m long analyzer arm. The used configuration, obtained operating at the (111111) Si Bragg reflection of both monochromator and analyzers, gives an instrumental energy resolution of 1.8 meV full width half maximum (FWHM) and a Q offset of 3 nm^{-1} between two neighbor analyzers. Further details on the beam-line are reported elsewhere [11,12]. The scans have been done as a function of the energy at fixed momentum transfer Q . They have been obtained by varying the back-scattering monochromator temperature with respect to that of the analyzer crystals while each Q value has been selected by rotating the analyzer arm. Each scan took about 180 min and each spectrum at fixed Q was obtained by summing up to 2 scans with a total integration time of 120 s for each point. The measurements have been performed as a function of the temperature with a helium flux cryostat in the two solid disordered phases: plastic crystal ($T = 330$ K) and glassy crystal ($T = 150$ K) and for each T as a function of Q in the region 1–10 nm^{-1} . An example of the IXS spectra of polycrystalline 1-cyanoadamantane is shown in Fig. 1 in the two solid disordered phases and at two selected Q values ($Q = 2.5$ nm^{-1} , $Q = 5.5$ nm^{-1}). Well defined inelastic peaks are observed at both Q s in the different phases. At variance with the plastic crystal, the intensity scattered by the glassy crystal shows a more intense quasi-elastic contribution in the explored Q range. In Fig. 1 the experimental

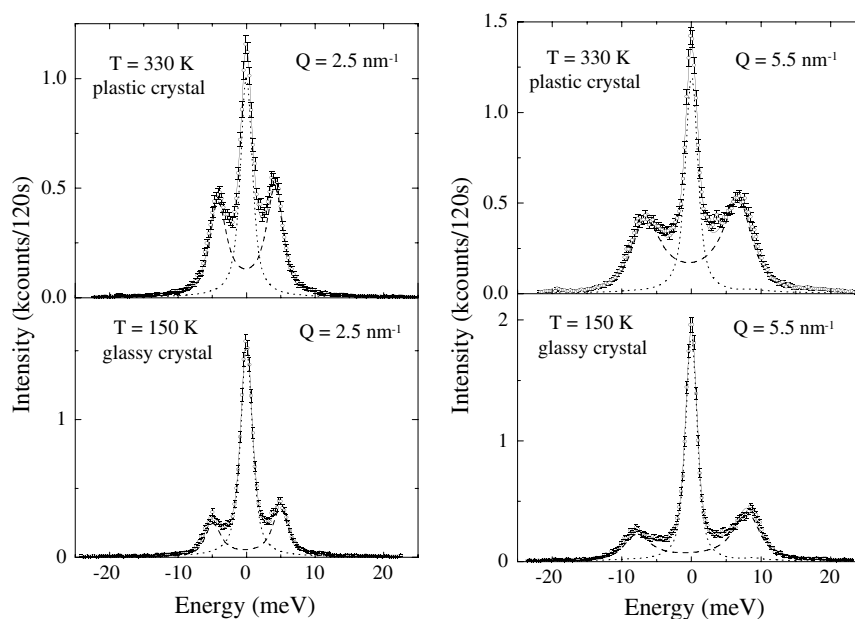


Fig. 1. IXS spectra of 1-cyanoadamantane at the indicated Q values and as a function of the temperature. The plastic crystal and glassy crystal phases are compared at the two indicated Q values. The experimental data (symbols) are reported together with the fits (full line); the elastic (dotted line) and inelastic (dashed line) contributions are individually shown.

data (points) are compared to the fits (full line). The fitting function is obtained from the generalized hydrodynamics using the memory function approach and applying the Markovian approximation which assumes a instantaneous decay of the molecular vibrations [13]. This approximation gives the following expression for the dynamic structure factor $S(Q, \omega)$:

$$\frac{S(Q, \omega)}{S(Q)} = \left\{ f(Q)\delta(\omega) + \frac{(1-f(Q))}{\pi} \frac{\Omega(Q)^2 \Gamma(Q)}{[\omega^2 - \Omega(Q)^2]^2 + [\omega \Gamma(Q)]^2} \right\}, \quad (1)$$

where the two terms represent respectively the quasi-elastic and inelastic part of the spectra; $f(Q)$ is the ratio between the elastic and total integrated intensity, $\Omega(Q)$ is the energy of the acoustic modes and $\Gamma(Q)$ is the sound attenuation related to the acoustic attenuation coefficient through the expression $\alpha = 2\pi\Gamma/hc$. To fit the spectra of Fig. 1 we used a function given by the convolution of the experimentally measured energy resolution $R(\omega)$ and $S(Q, \omega)$ corrected in order to satisfy the detailed balance:

$$I(Q, \omega) = I_0 R(\omega) \otimes [\beta \hbar \omega / (1 - e^{-\beta \hbar \omega}) S(Q, \omega)], \quad (2)$$

where I_0 is a normalization factor and $\beta = 1/K_B T$. The two parameters $\Omega(Q)$ and $\Gamma(Q)$ have been plotted as a function of Q in Figs. 2 and 3 respectively. The behavior of $\Omega(Q)$ vs Q in the two different solid phases reported in Fig. 2 is typical of a system in which the molecules are ordered in well defined lattice positions, this yields a dispersion curve with a sinusoidal shape characteristic of the Brillouin zones. At variance with a single crystal in which the longitudinal acoustic modes propagate along a well defined direction, here the dispersion curve is averaged over all the crystalline directions being the sample polycrystalline. In the low Q limit a linear dependence of $\Omega(Q)$ vs Q gives two different values of the sound velocity: $c_\infty = 2610$ m/s in the plastic

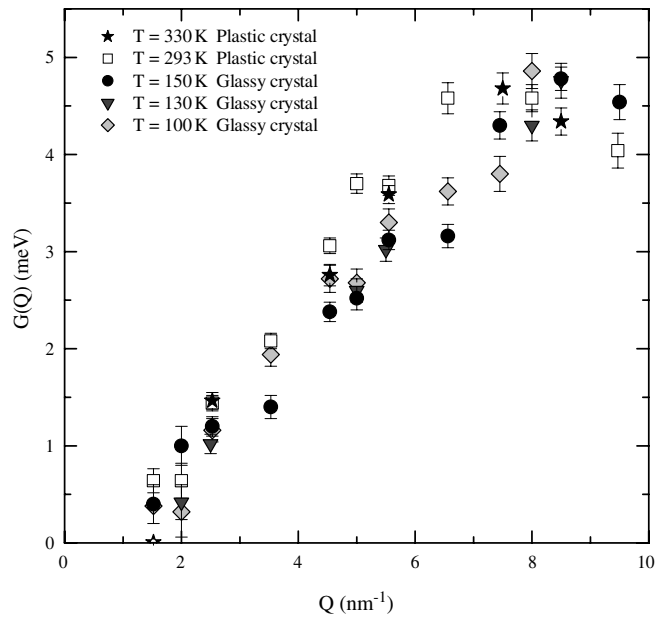


Fig. 3. Sound attenuation for 1-cyanoadamantane at the indicated temperatures in the plastic fcc crystal (stars, squares), and glassy crystal (circles, down triangles, diamonds).

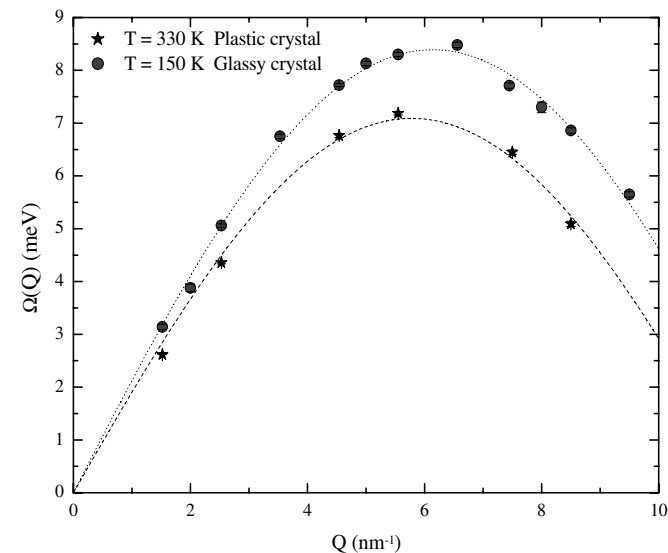


Fig. 2. Dispersion curves for 1-cyanoadamantane at the indicated temperatures in the plastic fcc crystal (stars) and glassy crystal (circles). The best fit with a sinusoidal function is reported for each phase.

crystal and $c_\infty = 3040$ m/s in the glassy crystal. The result for the glassy crystal is not surprising in fact, although the glass is disordered and frozen with respect to the orientational degrees of freedom, it presents a translational order which gives rise to a crystal-like dispersion curve. The sound attenuation parameter $\Gamma(Q)$ is reported in Fig. 3 as a function of Q and at five investigated temperatures ($T = 100$ K, 130 K, 150 K, 293 K, 330 K) three of which (the first three) in the glassy phase. It shows a negligible temperature dependence in the glassy phase as well as in the other two solid phases. This finding is in agreement with what found in many structural glasses [14] and crystals [3] investigated in the THz frequency region. At variance with the ‘canonical’ structural glasses which have a line-width parameter which shows a Q^2 dependence, this glassy crystal seems to follow a power law Q^α with $\alpha < 2$. In particular the following values have been found in the region $Q = 1\text{--}6.5$ nm $^{-1}$: $\alpha = 1.3$ ($T = 100$ K), $\alpha = 1.25$ ($T = 130$ K), $\alpha = 1.15$ ($T = 150$ K), $\alpha = 1.3$ ($T = 293$ K), $\alpha = 1.5$ ($T = 330$ K). In presence of a polycrystalline sample, in the low Q region, one expects $\alpha = 1$ since the non-vanishing width of the lines comes from the orientational average of different linear dispersion relations ($\Omega(Q) = c(\hat{Q}) \cdot Q$). This broadening can be calculated through the relation $\Delta\Gamma(Q) \simeq \Delta c \cdot Q$ where Δc is the difference between the lowest and the highest value of the sound velocity in different crystallographic directions. In 1-cyanoadamantane $\Delta c = c_L(111) - c_L(100) \simeq 100$ m/s as shown in Ref. [15] and the calculated values of $\Delta\Gamma(Q)$ in the range $1\text{--}10$ nm $^{-1}$ turn out to be about a factor ten smaller than that measured. We thus conclude that this effect is not relevant here. In addition the fact that we found $\alpha > 1$ (up to 1.5) indicates that we are in presence of a frustrated glass. In

fact in a recent numerical calculation [5] on three different classes of structural glasses it has been found that α spans from 1.5 to 4 depending on the degree of frustration of the glass and in particular that α decreases at increasing frustration. This experimental evidence is also supported by another numerical work in which the hypothesis of frustrated elastic domain in the supercooled plastic crystal of the cyanoadamantane family is proposed [16]. Concerning the $\Gamma(Q) \propto Q$ proportionality of the sound attenuation in disordered systems a microscopical interpretation is also given in Ref. [6].

3. Conclusions

In this work we have studied the dynamic structure factor $S(Q, \omega)$ of the polycrystalline plastic crystal 1-cyanoadamantane in the THz frequency region as a function of Q in the range $1\text{--}10\text{ nm}^{-1}$ and as a function of the temperature in the plastic crystal and glassy crystal phases. The data have been analyzed with the damped harmonic oscillator model according to the generalized hydrodynamics and assuming an instantaneous decay of the vibrational dynamics. The obtained dispersion curves, with a crystal-like behavior, allowed to extract the low Q limit sound velocities in all the investigated phases. The sound attenuation $\Gamma(Q)$ seems to have a negligible temperature dependence as all the structural glasses investigated in this frequency region. On the contrary in the low Q region it shows a Q dependence behavior following a Q^α power law with $1.15 < \alpha < 1.50$ at difference with structural glasses in which $\alpha = 2$ is commonly found. This experimental evidence is the indication of the fact that we are in presence of a frustrated glass.

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