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« Glassy » and plastic crystals of cyanoadamantane : a Brillouin scattering investigation

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Résumé. — Nous avons mesuré les constantes élastiques du cyanoadamantane dans ses phases plastique et « cristal vitreux ». L'évolution en température de C_{11} et l'atténuation du mode correspondant ont été étudiées tout particulièrement. La comparaison avec les résultats en neutrons montre une forte dispersion à température ambiante. La variation en température de C_{11} dans la phase plastique peut être expliquée par l'apparition d'un ordre local moléculaire de type antiferro.

Abstract. — The elastic constants of cyanoadamantane have been measured in the plastic and « glassy » crystal phases. A special attention has been given to the temperature evolution of C_{11} as well as to the damping of the corresponding mode. Comparison with neutron results shows a strong dispersion at room temperature. The temperature dependence of C_{11} in the plastic phase has been explained by the setting-up of a local antiferro ordering of molecules.

1. Introduction.

Cyanoadamantane ($C_{10}H_{15}CN$) is a cubic (Fm3m) plastic crystal between 285 and 458 K. Its low temperature phase is monoclinic. This crystal has extensively been studied in its plastic phase by X-Ray [1], Incoherent Quasi-elastic Neutron Scattering [2], NMR [3], Coherent Inelastic Neutron Scattering [4], Raman [5] and dielectric techniques [6].

A very interesting property of cyanoadamantane is the existence of a glassy crystal phase [7] below a glass transition at $T_g = 170$ K. Up to now this phase has essentially been studied in the cyclohexanol case [8-11]. The glassy crystalline phase obtained by quenching of the plastic phase, may be described as the superposition of the translational order characteristic of the plastic phases and some orientational frozen-in disorder. In this sense it may be called an « orientational glass ».

In the high temperature plastic phase, cyanoadamantane molecules undergo two types of motion [2, 3] : i) a fast rotation around the C-CN axis which may be well approximated by a rota-

tional diffusion (the step between two equilibrium positions is 30°) and ii) a slow motion where the 3-fold axis of the molecule (C_{3v} symmetry) reorientates between the six orientations lying along the 4-fold axes of the crystal lattice.

The fast rotation is known to persist in the glassy crystal phase [3], so that the glassy transition is likely due to the freezing of the slow reorientational degree of freedom.

2. Experimental results.

We report here a Brillouin scattering investigation from 80 to 435 K on a single crystal of about $3 \times 3 \times 8 \text{ mm}^3$. This temperature range covers the plastic crystal phase at $T > 285 \text{ K}$, the undercooled plastic crystal in the range 250 K to 285 K and the glassy crystal state below $T_g \simeq 170 \text{ K}$. Temperatures between 250 K and 285 K were reached from the plastic phase by slowly cooling down the sample. Due to the possible recrystallization into the monoclinic phase, stable below 285 K, measurements were not attempted in the range from 170 K to 250 K. In order to get the glassy crystal state, the sample has rapidly been quenched by setting it into an optical cryostat at liquid nitrogen temperature. The temperature range from 80 K to T_g was covered by stepwise heating of the sample. Recrystallization was effectively observed above T_g .

The experimental set-up has been described elsewhere [12]. Measurements were made at $\lambda = 4880$ and 5145 \AA in back-scattering configuration for the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions giving the elastic constants C_{11} and $C' = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$, respectively. 90° scattering was used for the study of the transverse waves leading to the determination of the C_{44} constant ($\langle 110 \rangle$ direction). Unfortunately the intensity of the transverse Brillouin component is very weak and our measurements were only possible in a limited range (273 to 363 K).

The calculation of elastic constants from Brillouin scattering measurements of sound velocity needs the knowledge of density and refractive index. X-ray determination of the cell parameter a in the range 240-340 K shows a linear variation with a slope of $10^{-3} \text{ \AA K}^{-1}$. Values of a in the glassy crystal state were taken from previous results [13]. We have also measured the refractive index n in the temperature interval 280-360 K, its value at 294 K is 1.559. Extrapolation to lower and higher temperatures was made by using the Lorenz-Lorentz formula.

The values of the elastic constants C_{11} , C_{12} and C_{44} as a function of temperature are given in table I. The variation of C_{11} in the glassy crystalline state and in the plastic phase is shown in figure 1.

Table I. — *Elastic constants of cyanoadamantane.*

T (K)	C_{11} (10^9 Nm^{-2})	C' (10^9 Nm^{-2})	C_{44} (10^9 Nm^{-2})	C_{12} (10^9 Nm^{-2})
273	8.08	—	1.79	—
294	7.79	8.01	1.88	4.47
303	7.67	7.82	1.88	4.21
333	7.21	7.35	1.82	3.85
363	6.60	7.06	1.74	4.04
393	5.88	6.46	—	—

The attenuation of the hypersonic phonons propagating along the $\langle 100 \rangle$ direction was also measured within the same range of temperature. The inverse mean free path l^{-1} of the phonon is deduced from the half-width at half-height, Γ , of the Brillouin line through the expression $l^{-1} = 4\pi\Gamma v^{-1}$ where v is the velocity of the phonon. The results are presented in figure 2.

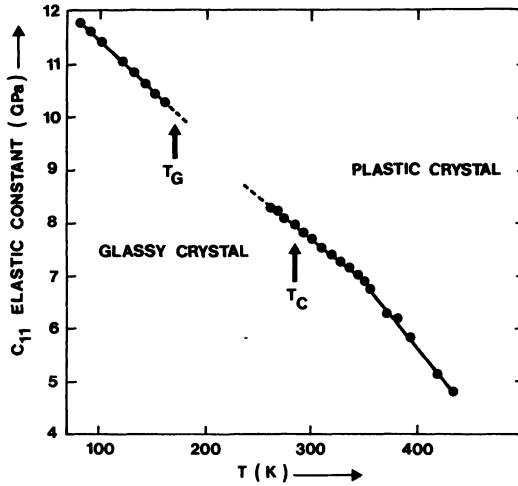


Fig. 1. — Variation of the C_{11} elastic constant as a function of temperature in the glassy and plastic crystals of cyanoadamantane.

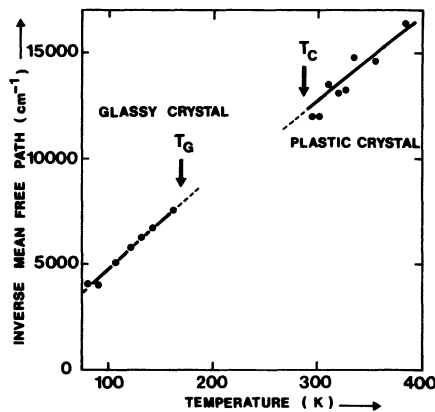


Fig. 2. — Variation of the inverse mean free path of the LA mode as a function of temperature in the glassy and plastic crystals of cyanoadamantane.

3. Discussion.

The comparison between our values of the C_{ij} 's at room temperature and those determined by coherent inelastic neutron scattering [4] shows the evidence of a very strong dispersion.

The neutron data are from reference [4] : $C_{11} = 11.17$, $C' = 11.66$ and $C_{44} = 2.56$ (all values in $10^9 Nm^{-2}$). Such a strong ω -dependence of the elastic constants was already observed in adamantane [14, 15].

The relaxation times (and the geometrical aspect) of the rotation around the C-CN axis in cyanoadamantane and of the overall molecular rotation in adamantane being very comparable, we believe that the process giving rise to dispersion is of the same nature in these two materials, i.e. a coupling of phonons with this type of rotation.

This coupling and the resultant dispersion could also explain the curvature of the C_{11} elastic constant clearly shown in figure 1. Such a curvature has also been noticed for C' . Using the value

of the fast rotation relaxation time deduced from neutron scattering ($\tau = 3.54 \times 10^{-33} e^{1000/T_S}$) [2], the regime $\omega\tau = 1$ is found to occur at ~ 190 K, outside the high temperature experimental range (the same value is obtained from a relaxation time deduced from NMR measurements [3]). This result is thus not consistent with the change in slope of the C_{11} vs. T curve appearing near 350 K. Furthermore, examination of figure 2 does not show any anomalous feature of the attenuation in the whole high temperature part of the curve. This continuous variation of the attenuation may mean that the process giving rise to the deviation of C_{11} from linearity is static. This explanation is supported by the results of dielectric and X-ray studies. The temperature variation of the dielectric constant ($d\epsilon/dT > 0$) and the value of the Kirkwood g factor ($g < 1$) indicates a local antiferro ordering of the CN dipoles existing all along the undercooled and stable cubic phase [6].

Diffuse X-ray scattering experiments performed in the glassy crystal show the apparition of narrow diffuse spots at the X boundary points of the Brillouin zone during annealing below T_g (Fig. 3). This also reflects the existence of a local antiferro-ordering, which is a long-ranged property in the low temperature monoclinic phase [16].

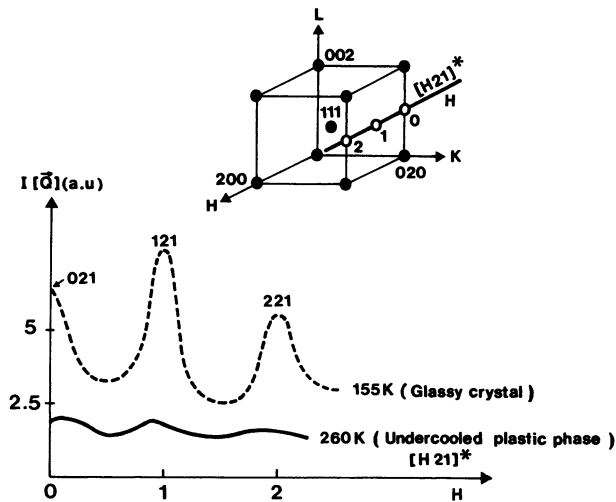


Fig. 3. — Diffuse X-ray scattering. Q scan along $[H21]^*$ in the glassy and undercooled plastic crystals of cyanoadamantane.

X-ray as well as dielectric experiments show that this local order strongly varies with temperature and we think that the curvature of C_{11} may be explained by this progressive loss of intermolecular correlations as T is increasing.

The observation of figure 2 shows that the attenuation displays a continuous decrease when going from the plastic to the glassy crystalline phase. Keeping in mind that the reorientational motion is frozen below T_g , we can infer that the process responsible for the attenuation is not related to this type of motion. However, it must be noted that the fast rotation around the dipolar axis is conserved below T_g . So that cyanoadamantane keeps a « plastic » character with respect to this particular motion. This can explain the strong temperature variation of the elastic constant C_{11} (C_{11} varies of a factor 2.5 between 80 and 430 K). In the plastic phase the average slope of the L -velocity versus temperature $\Delta v/\Delta T$ is approximately $3.5 \text{ ms}^{-1} \text{ K}^{-1}$ a usual value for a plastic crystal. (We have the values 4.5 for succinonitrile [17], 3.8 for cyclohexanol [18].) In the glassy crystal $\Delta v/\Delta T$ is found to be $2.3 \text{ ms}^{-1} \text{ K}^{-1}$ a relatively high value presumably related to the fast rotation.

So the very large variation of C_{11} may be considered as a normal characteristic of plastic phases. This effect appears here considerable because of the large temperature interval involved : it includes the plastic phase, the metastable phase and the glassy crystal considered here with its « plastic » character.

We may notice the high value of the attenuation which also appears as characteristic of the plastic phase. Comparable values were indeed found in succinonitrile [17] and cyclohexanol [18]. Down to 80 K the attenuation is much stronger than in a great variety of materials : ionic crystals NaCl and KCl [19], molecular crystal α -sulfur [20], amorphous polymer PMMA [21] and glass LASF7 [22].

The present work gives evidence of a strong dispersion effect, most likely related to the fast molecular rotation. The dependence of C_{11} as a function of the temperature seems to be normal for a plastic phase but the striking result of a variation of 2.5 for C_{11} between 80 and 430 K is essentially due to the very large temperature range where molecular rotation exists. We have also observed an anomalous curvature of C_{11} in the plastic phase, which we believe to be of static origin. Ultrasonic measurements and low temperature neutron scattering would be worthwhile for the understanding of the dispersion mechanism. We are aware that the measurements performed close to T_g include a part of annealing whose effect on the local order has recently been shown [23]. The study of the particular effect of the heat treatment on the acoustic properties is underway.

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