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Ultrasonic attenuation in glassy crystalline cyclohexanol (*)

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Résumé. — On rapporte des mesures d'atténuation ultrasonore à 100 MHz sur la phase réorientationnelle du cyclohexanol. Les résultats confirment qu'au refroidissement le désordre orientationnel des molécules dans le réseau cristallin est gelé progressivement en suivant un mécanisme de relaxation.

Abstract. — Ultrasonic attenuation measurements at 100 MHz on the orientationally disordered crystalline phase of cyclohexanol are reported. The results provide additional evidence that the freezing process of the orientational disorder of the molecules in the crystal lattice is a relaxational phenomenon.

1. Introduction.

It is well known that cyclohexanol belongs to the group of organic compounds which exhibit an orientationally disordered phase immediately below their melting point [1, 2]. This crystalline phase is characterized by rapid rotational motions of molecules and is known to be plastic according to Timmermans' criterion [1]. Furthermore, the orientationally disordered or plastic crystals can be supercooled into a glass-like state [3, 4].

Previous studies of cyclohexanol [5] show that the higher temperature plastic phase (phase I) is stable between 265 and 298 K and it is easily supercooled. A moderate cooling rate of 6 K/min. is sufficient to prevent the transformation into the stable phase II. The supercooled phase I shows some characteristic features of the glass transition : a discontinuous specific heat at the glass transition temperature T_g of 150 K and a residual entropy at 0 K. Slow relaxation processes covering a wide frequency range, from 10^{-3} to 10^5 Hz, are responsible for the reported dielectric relaxations [6, 8]. Motional narrowing effects observed around T_g in nuclear magnetic resonance experiments [7, 8] show that the molecular reorientations become progressively slower when the temperature is decreased below T_g . At low temperatures some properties similar to those found in ordinary glasses have been observed in this rotational glass [10]. In order to better describe the freezing process of the molecular reorientations and their importance at low temperatures we have studied the ultrasonic loss in the disordered phase I of cyclohexanol above liquid helium temperatures.

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2. Experimental.

Ultrasonic measurements were performed between 60 and 200 MHz on samples of cyclohexanol of commercial purity (Baker Co.). Because of the high ultrasonic attenuation of liquid cyclohexanol the attenuation measurements had to be performed on very thin specimens using the buffer-rod method described in [11]. The inset of figure 1 shows a schematic illustration of the sample mounting. A film of liquid cyclohexanol (C) was placed at room temperature between two Z-cut quartz delay rods (Q) of dimensions $4 \times 4 \times 25.4 \text{ mm}^3$ and $4 \times 4 \times 12.5 \text{ mm}^3$ with optically polished and parallel end faces. The two rods were separated by a thin copper ring spacer (S) of calibrated thickness. The whole assembly was placed inside the channel of a brass sample holder (Sa) and good thermal contact was established by means of copper-beryllium springs. The temperature was determined by means of calibrated thermocouples and carbon resistors (T) firmly attached to the sample holder. Longitudinal ultrasonic waves were generated and detected by means of a polyvinylidene fluoride (PVF₂) transducer bonded with flexible adhesive (Oxford Instruments) to the longer delay rod. Using a standard pulse-echo technique the detected echo pattern consists of two distinct trains associated with the delay paths of the elastic waves in the rod-sample assembly.

Fig. 1. — Attenuation E_R/E_T in dB as a function of temperature for four samples of cyclohexanol (0 dB corresponds to the values measured at 4 K). The experimental curves (a), (b), (c) and the filled circles were taken during cooling from 300 to 100 K at a rate of 6 K/min. Circles and crosses correspond to measurements on the same sample : ● during supercooling to 80 K (run 1), ○ subsequently heated from 4 K at a rate of 0.8 K/min. (run 2), × after further heat treatment and annealing (see text), during heating at 0.8 K/min. (run 3). The dashed curves (e) and (d) are calculated from equation 4 with activation energies of 1 500 and 1 560 K and τ_0 of 1 and 13×10^{-13} s, respectively. The inset shows the experimental arrangement for the buffer-rod technique described in the text.

The first detected echo of amplitude E_R corresponds to the reflection from the long quartz-cyclohexanol interface. The second detected echo, associated with the reflection from the free end surface of the short quartz, has its magnitude E_T considerably attenuated by its double path in the cyclohexanol film. By comparing the amplitude ratio E_R/E_T for films of different thicknesses

d or for different frequencies the intrinsic attenuation coefficient α of cyclohexanol can in principle be determined from

$$E_R/E_T = Z(e^{2\gamma d} - 1) \quad (1)$$

where $Z = r/(1 - r^2)^2$, r is the reflection coefficient of the quartz-cyclohexanol interface, assumed here to be constant, and $\gamma = \alpha + i\phi$ is the complex propagation constant in the film with the phase constant ϕ given by

$$\phi = 2\pi Fd/v, \quad (2)$$

here F is the frequency and v is the sound velocity in cyclohexanol. Equation 1, where the relatively small attenuation of the quartz rods has been neglected, contains multiple-beam interference terms which occur when the film thickness becomes comparable to the sound wavelength and which would produce oscillations in E_R/E_T with frequency or film thickness making a direct determination of α difficult. We find, however, that since αd is small in the liquid phase [12] expanding $\text{Ln}(E_R/E_T)$ in powers of αd gives

$$\text{Ln}(E_R/E_T) = 2\alpha d + (\alpha d)^2 O(\phi) + P(Z, \phi) \quad (3)$$

where $P = 2 \text{Ln}(2Z \sin \phi)$ is nearly independent of T and the second term is less than 10 % of the first for liquid film of 40 μm and $F \lesssim 100$ MHz (it is about 20 % and 35 % for 150 and 190 MHz, respectively). Thus for the lower experimental frequencies $\text{Ln}(E_R/E_T)$ reflects reasonably well the temperature dependence of the attenuation coefficient. This approximation becomes better as the temperature (and the attenuation in the solid phases) is decreased. Furthermore, by normalizing the measured attenuation for different frequencies to its value at 4 K (corresponding to 0 dB in Fig. 1) we suppress the effect of the oscillating term P on the temperature dependence of α .

Measurements of the amplitude ratio E_R/E_T in decibels, which we call here the attenuation, were performed with a Matec 2470 Automatic Attenuation Recorder. An intrinsic attenuation coefficient of 188 dB/cm was deduced for liquid samples at 300 K from measurements in three films 80, 130 and 160 μm thick at 60 MHz. This value is in good agreement with the results reported by Plass [12]. From measurements as a function of frequency in 80 μm -thick films at 77 K we found that the attenuation oscillates with a frequency of approximately 20 MHz. This provides, through equation 2 an estimate of 3×10^5 cm/s for the longitudinal sound velocity in solid cyclohexanol.

All solid cyclohexanol samples were prepared by cooling the liquid films in a helium atmosphere from 300 to 100 K at a rate of 6 K/min. and from 100 to 80 K at a slower rate of 1 K/min. The samples were subsequently cooled to 4 K. Attenuation measurements as a function of temperature were possible and reproducible for different frequencies for solid films about 80 μm thick by recording the amplitude ratio E_R/E_T in dB as the temperature was changed. Various attempts with solid films thicker than 100 μm were unsuccessful due to a drastic deterioration of the echo pattern as the temperature was decreased. For all reported frequencies the temperature dependence of the attenuation was measured during the (super) cooling cycle to 80 K at the rates given above. In order to characterize the low temperature contribution to the attenuation due to the orientational disorder different cycles of measurements at each frequency were performed from 4 K to about 150 K on the same samples supercooled firstly below T_g and then annealed at 160 K.

The sequence of measurement followed is illustrated in figure 1 by the data taken at 100 MHz. (Run 1) first the data (full circles) were taken upon supercooling to 80 K at the rates given above. (Run 2) then the measurements (open circles) were taken on the supercooled sample from 4 K to 160 K at a heating rate of 0.8 K/min. (Run 3) the sample was then cooled down to 80 K in about 10 hours and subsequently cooled to 4 K, and finally the data (crosses) were taken from 4 K to 180 K at the same heating rate of 0.8 K/min.

3. Results.

Figure 1 shows the experimental attenuation in cyclohexanol as a function of temperature for four samples and four different frequencies (run 1). For clarity the experimental results for slow heating (run 2) and after sample annealing (run 3) are shown only at 100 MHz, but the same general features were observed at all frequencies.

Upon fast cooling (run 1) the attenuation of the supercooled phase I shows two different temperature regimes :

(i) a high temperature regime occurring above the characteristic temperature $T_g = 150$ K in which the attenuation of the supercooled phase I is very high. Around 200 K its magnitude measured at 60 MHz is comparable to that found for the liquid at 300 K and too high to be measured at higher frequencies. Two maxima centred at 150 K and 210 K are observed at 60 MHz, and at all frequencies the attenuation decreases very rapidly below T_g . From measurements performed at 15 MHz we observed the same behaviour around T_g . The 150 K peak is well resolved but the experimental conditions were not as good as at 60 MHz and did not permit to extend measurements above 190 K. For clarity the results taken at this frequency are not shown in figure 1.

(ii) a low temperature regime occurring below T_g in which the attenuation shows a broad peak centred around 80 K and has a small magnitude. This regime is only shown for 100 MHz in figure 1 and corresponds to full circles below 120 K and open circles below 80 K.

Upon slow heating from 4 K the attenuation vs. temperature curves are very similar for both the unannealed (run 2) and annealed (run 3) samples but are somewhat different above 100 K from those obtained during supercooling (run 1). In neither case does the attenuation recover its value in the supercooling cycle, the difference at 100 MHz being as large as 10 dB.

In all annealing treatments we observe that the echo train transmitted through the cyclohexanol film is lost when the temperature increases above 190 K and it is not recovered when the temperature is again decreased. This is probably due to cracks produced in the film by differential thermal stresses and seems to indicate that the plasticity of the film is reduced by slow heating. As a consequence it has not been possible to study the acoustic properties after thermal annealing above 200 K.

The most remarkable conclusion of our results is that there is a continuous decrease of the ultrasonic attenuation of the supercooled phase I of the cyclohexanol as the temperature is reduced through the characteristic temperature T_g , where a discontinuity in the specific heat has been observed [5, 8]. The experimental results indicate that, for rapidly cooled samples, the behaviour of the ultrasonic attenuation above T_g must be associated with the dynamic disorder of the molecules in the supercooled phase I and that a gradual freezing of the molecular motions occur when temperature decreases below T_g . The results of figure 1 cover a small frequency range but nevertheless information on the relaxation process which governs the freezing of the reorientational disorder in phase I may be obtained. The peak observed at 210 K for 60 MHz is well resolved and can be reasonably described by a Debye relaxation

$$A \sim \frac{\omega^2 \tau_1}{1 + (\omega\tau_1)^2} \quad (4)$$

where ω is the angular ultrasonic frequency and τ_1 is the relaxation time $\tau_1 = 1.3 \times 10^{-12} \exp(1560/T)$ (s) deduced from NMR experiments [7]. The peak at 150 K, observed at 60 MHz, is not as well resolved at higher frequencies. The attenuation around T_g increases with frequency but not linearly. As discussed above the phase terms in expression 3 become important corrections at high frequencies and temperatures and the measured temperature dependence of the attenuation around T_g is only qualitatively related to that of α . The activation energy of the 150 K relaxation peak cannot be directly extracted from our results because of the limited frequency

where it is well resolved. Nevertheless, the experimental results can be roughly fitted at 60 MHz by a Debye curve and a relaxation time τ_2 with an activation energy of 1 500 K and a pre-exponential factor of 10^{-13} s (curve *e* in Fig. 1). This should only be taken as a qualitative indication. The drastic decrease of the attenuation observed for all frequencies below T_g may be indicative that we are entering a regime where $\omega\tau_2$ becomes greater than one.

Finally, we comment on the ultrasonic attenuation of the thermally treated cyclohexanol films. It is well known that thermal annealing above 200 K causes the transformation of the supercooled phase I of the cyclohexanol into the ordered phase II [5]. Transformations into different metastable crystalline phases have also been observed below 200 K by differential thermal analysis measurements on bulk samples [5]. It has also been pointed out that between 170 and 200 K the supercooled phase I tends to recrystallize into phase II [7, 8]. In the light of these observations and due to the difficulties we encounter when measuring the ultrasonic attenuation after a thermal annealing above 200 K, because of the mechanical failure of the cyclohexanol film, it is undetermined whether our samples annealed to about 160 K were in a metastable mixed crystalline phase or in the stable phase II. However, we note that below 80 K the temperature dependence of the attenuation in the disordered phase I (open circle in Fig. 1) is quite similar to that observed after thermal treatment at 160 K (crosses in Fig. 1).

4. Conclusions.

The present ultrasonic results give evidences that the freezing process occurring in the supercooled plastic phase of cyclohexanol is a relaxational phenomenon. An activation energy corresponding to 1 560 K in good agreement with the value previously deduced from NMR experiments has been obtained. No additional ultrasonic losses with respect to those found in the phase annealed around 160 K have been observed in the orientationally disordered phase at liquid helium temperatures.

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