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Angaben zur Veröffentlichung / Publication details:

Brand, Robert, Peter Lunkenheimer, and Alois Loidl. 1997. "Relaxations and fast dynamics of the plastic crystal cyclo-octanol investigated by broadband dielectric spectroscopy." *Physical Review B* 56 (10): R5713–16. <https://doi.org/10.1103/PhysRevB.56.R5713>.

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Relaxations and fast dynamics of the plastic crystal cyclo-octanol investigated by broadband dielectric spectroscopy

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(Received 19 May 1997)

The dielectric loss of cyclo-octanol has been investigated in a very broad frequency window of more than 17 decades. The relaxational response was traced in the plastic and the supercooled plastic phase, which are governed by the same relaxational dynamics. Experimental evidence is provided for two additional relaxational processes below the GHz region which contribute to the high-frequency wing of the α relaxation peaks. Near 100 GHz a loss minimum shows up which cannot be ascribed to a simple transition from the α relaxation to the infrared bands. As in supercooled liquids, additional fast processes seem to contribute to the dielectric response at these high frequencies. [S0163-1829(97)50134-2]

Broadband dielectric spectroscopy has proven to be an important tool in investigating the dynamic behavior of glass-forming liquids. Dielectric techniques have been used, e.g., to observe the well-known α - or structural relaxation process over a broad frequency and temperature range (see, e.g., Ref. 1). Recently, special interest in the dynamics at high frequencies, in the microwave, and submillimeter range has risen due to the predictions of some theoretical and scaling approaches elaborated in the past.²⁻⁴ Stimulated by this development investigations of the dielectric properties of glass-forming liquids in a frequency range of more than 18 decades up to some 100 GHz have been carried out.⁵ In the present paper our broadband dielectric experiments have been extended to the plastic crystal cyclo-octanol. In plastic crystals the centers of mass of the molecules form a regular crystalline lattice but the molecules are dynamically disordered with respect to the orientational degrees of freedom. Orientationally disordered crystals are often considered as model systems for structural glasses. It is the aim of the present paper to investigate the relaxation dynamics focusing on the high-frequency behavior also in this totally different class of glass-forming systems. In addition, we want to extend the recently published investigations of the α process in cyclo-octanol performed by Leslie-Pelecky and Birge,^{6,7} that were restricted to frequencies below 10 kHz. When cooled slowly, cyclo-octanol exhibits a transition from a phase, with fast and isotropic reorientations of the molecules, to a phase with restricted reorientations at 265 K and a further transition to a completely ordered state at 220 K.⁸⁻¹⁰ Both transitions can be supercooled, using cooling rates of >5 K/min,^{7,8} by which orientational disorder is preserved. We were especially interested if the same relaxation dynamics governs the supercooled as well as the plastic phase.

To cover a broad frequency range, various experimental setups were used, including a time domain spectrometer ($10 \mu\text{Hz} \leq \nu \leq 1 \text{ kHz}$), LCR-meters ($10 \text{ mHz} \leq \nu \leq 30 \text{ MHz}$), impedance analyzers (reflectometric technique, $1 \text{ MHz} \leq \nu \leq 10 \text{ GHz}$), and a network analyzer (transmission technique, $100 \text{ MHz} \leq \nu \leq 40 \text{ GHz}$). In addition, for frequencies $60 \text{ GHz} \leq \nu \leq 380 \text{ GHz}$, quasioptical measurements were performed employing a submillimeter spectrometer in a Mach-Zehnder setup.¹¹ A closed-cycle refrigerator

and a gas-heating system were utilized for cooling. In most of the experiments we used commercially available cyclo-octanol ($>99.3\%$ AppliChem, Darmstadt) without further purification. To check for a possible influence of impurities, we repeated some experiments using cyclo-octanol after purification using a distillation procedure, but obtained no significant difference to the results from the unpurified samples.

Figure 1 shows the frequency dependence of the dielectric loss ε'' for various temperatures. A well-developed α -relaxation peak is observed shifting through the frequency window. In addition, a minimum shows up at high frequencies in the transition region to the far-infrared resonances. At first we will analyze the α process. Between 200 and 240 K the samples reveal a time-dependent transformation to the ordered phases with a time constant comparable or smaller than the typical frequency sweep time. The α -relaxation peaks observed in the disordered state are absent in the low-temperature states.^{7,8} Therefore, it was not possible to obtain reliable results in this temperature range. In Fig. 1 the reduced peak height of the curves at 205 and 240 K can be explained, assuming that the samples partly reveal orientational order. It is important to note that in Fig. 1 below 205 K the α relaxation has been measured in the supercooled state, while the data above 240 K belong to the plastic (dynamically disordered) phase. As will be shown below, the relaxation characteristics are essentially the same for the two regimes. The spectral form and peak frequency ν_p of $\varepsilon''(\nu)$ agree well with the results of Leslie-Pelecky and Birge,^{6,7} obtained at frequencies 10^{-3} – 10^4 Hz in the supercooled region. The relaxation strength $\Delta\varepsilon = \varepsilon_0 - \varepsilon_\infty$ vs temperature, as extracted from the low and high-frequency limit (ε_0 and ε_∞ , respectively) of the real part of the dielectric constant ε' (not shown, Ref. 12) also agrees with results reported earlier^{6,7} and can be described approximately using a Curie law, $\Delta\varepsilon \sim 1/T$.

The solid lines in Fig. 1 are fits using the phenomenological Cole-Davidson- (CD-) function.¹³ Data and fits agree well below and about 2 decades above ν_p . At high frequencies clear deviations show up as it has been found in many glass-forming systems.⁴ We used the CD function because it leads to somewhat better fits at high frequencies, compared

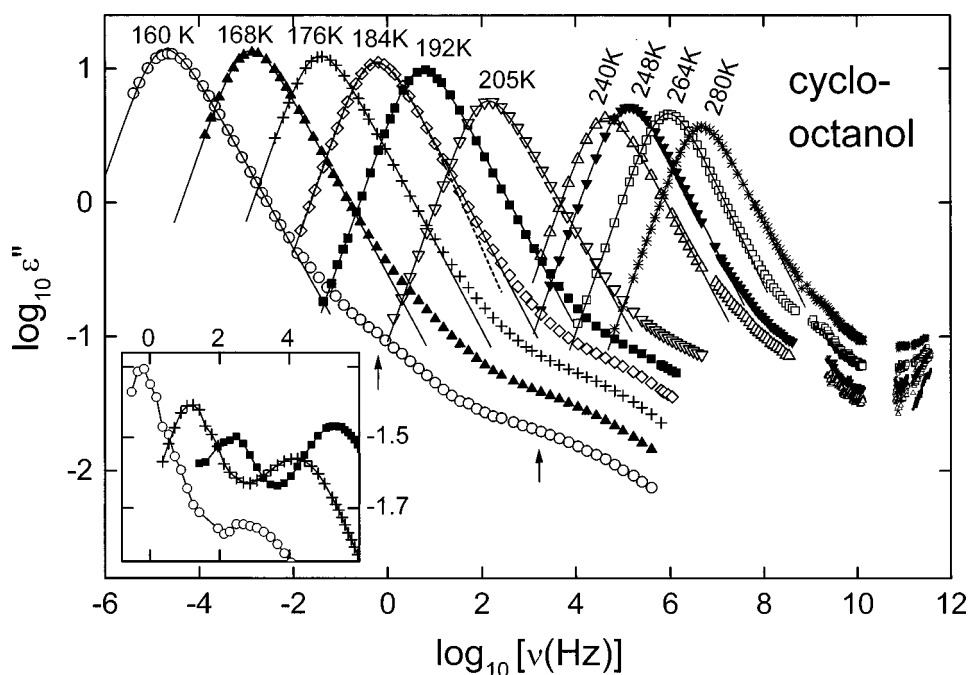


FIG. 1. Frequency dependence of the dielectric loss for various temperatures. The curves for $T \leq 205$ K have been taken during heating and the results above 240 K were taken during cooling. The solid lines are fits using the CD function. The dashed line represents a fit using the Fourier transform of the KWW function. The arrows indicate the existence of two additional relaxation processes for the 160 K curve. The inset shows the loss obtained after allowing the sample to transfer into the ordered state.

to the commonly used Fourier transform of a stretched exponential [Kohlrausch-Williams-Watts (KWW)] behavior. This is demonstrated for the 184 K curve where the dashed line represents the KWW-fit result. The width parameter resulting from the CD fits increases slightly from $\beta_{CD} = 0.62$ at 160 K to $\beta_{CD} = 0.75$ at 280 K.¹²

Figure 2 shows the temperature dependence of the average relaxation time $\langle \tau \rangle$ obtained from the CD fits in Arrhenius representation (open circles). The solid line is a fit using the Vogel-Fulcher law, $\langle \tau \rangle = \tau_0 \exp[B/(T - T_0)]$ which provides a good description of $\tau(T)$. The resulting parameters are $\tau_0 = 2 \times 10^{-15}$ s, $B = 3320$ K, and $T_0 = 82$ K, which agrees reasonably well with the results of Leslie-Pelecky and

Birge,^{6,7} keeping in mind the restricted dynamic range available to them. The inset of Fig. 2 represents an Angell plot,¹⁴ $\log_{10}(\tau)$ vs T_g/T . Here $T_g \approx 168$ K was estimated from the condition $\tau(T_g) = 100$ s. The fragility parameter m , defined as the slope in the Angell plot at T_g , is determined as $m = 33$, in agreement with the analysis of Leslie-Pelecky and Birge.^{6,7}

Taking a closer look at the high-frequency wing of the α -relaxation peak in Fig. 1, the existence of two additional relaxational features can be detected as indicated by the arrows for the 160 K curve. While the first process (called β process in the following), which is located near some Hz for 160 K is barely visible for higher temperatures, the second process (called γ process) is rather well pronounced and clearly shifts to higher frequencies with increasing temperature. As mentioned above, the α process is suppressed in the ordered states of cyclo-octanol. The inset of Fig. 1 shows $\varepsilon''(\nu)$ for three temperatures, after the sample has transformed into the ordered state, by keeping the temperature at 230 K for 24 h. In the orientationally ordered state the β - and γ -relaxation peaks show up rather clearly shifting to higher frequencies with increasing temperature. The peak positions can be taken as a good approximation of the inverse relaxation times. In Fig. 2 the relaxation times for the β and γ process are included. They show a thermally activated behavior. The energy barrier E and the preexponential factor τ_0 are determined as $E = 0.51$ eV, $\tau_0 = 1.8 \times 10^{-17}$ s for the β process and $E = 0.47$ eV, $\tau_0 = 2.9 \times 10^{-19}$ s for the γ process. Indications for a secondary relaxation process in cyclo-octanol have also been found by Fuchs *et al.*,¹⁵ using nuclear magnetic resonance and thermally stimulated current measurements, and by Stockhausen and Hornhardt¹⁶ in the liquid phase, using dielectric experiments. In addition, Shablakh

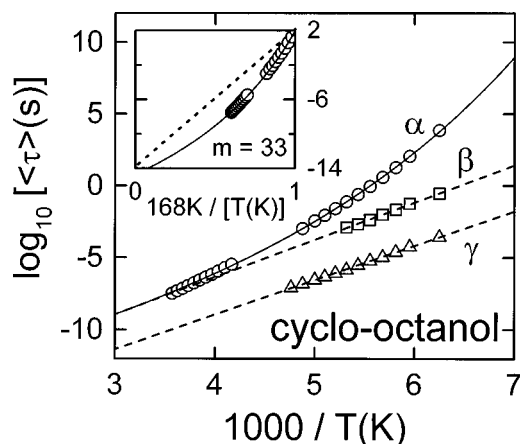


FIG. 2. Relaxation time of α , β , and γ relaxation in Arrhenius representation. The solid line is a fit using the Vogel-Fulcher law, the dashed lines are fits assuming thermally activated behavior. The inset represents an Angell plot (Ref. 14) for the α -relaxation time. The dotted line demonstrates maximal strong behavior.

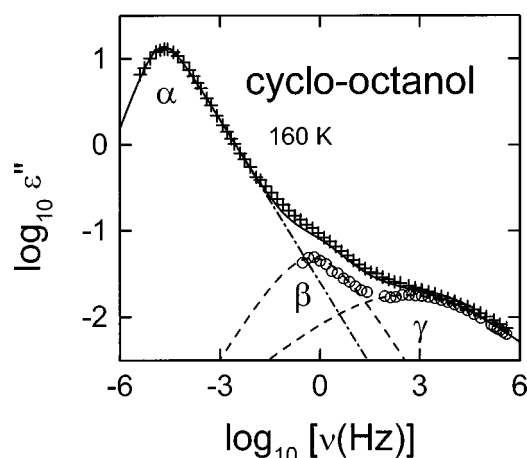


FIG. 3. Dielectric loss at 160 K in the supercooled orientationally disordered phase (+) and in the ordered phase (O). The dash-dotted line is a fit of $\varepsilon''(\nu)$ near the α -peak maximum using the CD function. The dashed lines have been calculated with the CC function. The solid line is the sum of the dashed and dash-dotted lines.

*et al.*⁸ reported a relaxation process in the ordered state of cyclo-octanol from their dielectric measurements. A detailed comparison will follow in a future paper.¹²

The occurrence of secondary relaxation processes, exhibiting thermally activated dynamics, is a common feature seen in many glass formers and often is explained in terms of an internal change of the molecular conformation, e.g., the movement of a side-chain in a polymer. Johari and Goldstein¹⁷ have demonstrated that these secondary processes also show up in simple molecular glass formers. This finding has led to the assumption of a more fundamental explanation of these so-called Johari-Goldstein β processes, which are possibly intrinsic to all glass-forming liquids. In addition, it has been found that for high temperatures the time scales of primary and secondary relaxations often merge,^{1,17} which is also demonstrated in the present work for the case of the α and β relaxation times of cyclo-octanol (cf. Fig. 2). This finding suggests a common mechanism for both processes and a possible explanation is given in Refs. 17 and 18. Alternative explanations for additional relaxation processes in cyclo-octanol, in terms of side-band effects or conformational changes, could be transitions between the six possible three-dimensional shapes of the *C*-octagon or transitions between the two possible orientations of the hydroxy group.^{8,9} As the β and γ processes show up in the ordered phase as well, it seems rather clear that both relaxations are due to single-molecule conformational changes and possibly could be explained by the latter mechanisms.

In Fig. 3 the 160 K curves for the supercooled and the ordered states are replotted. The dashed lines have been calculated, using the empirical Cole-Cole (CC) function,¹⁹ in order to give a description of the β - and the γ -relaxation peaks. The dash-dotted line is the fit of the α -peak region, using the CD function. The solid line represents the sum of these three contributions and gives a remarkably good fit of the measured $\varepsilon''(\nu)$ data in the supercooled region over 11 decades of frequency. A similar evaluation can also be performed for the other temperatures. From these results, it becomes obvious that (i) the β and γ processes are only negligibly influenced by the phase transition into the ordered state

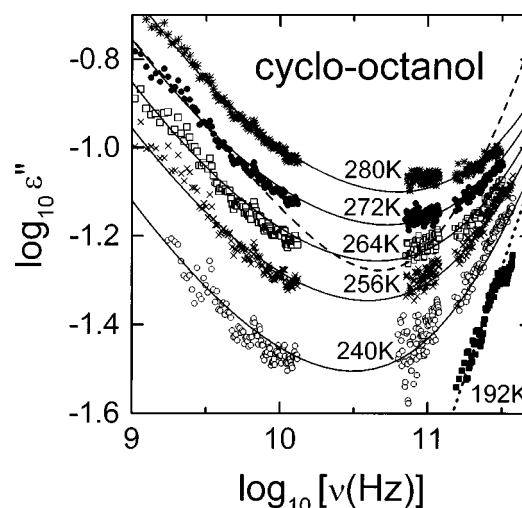


FIG. 4. Magnified view of the high-frequency region of $\varepsilon''(\nu)$. The dotted line demonstrates a slope of 1. The dashed line was calculated using $\varepsilon''(\nu) = c_1 \nu^{-b} + c_2 \nu$, the solid lines are fits with $\varepsilon''(\nu) = c_1 \nu^{-b} + c_2 \nu + c_3$.

and (ii) the high-frequency wing of the α peak is strongly influenced by these secondary relaxation processes. Therefore it is difficult to compare high-frequency dielectric data on cyclo-octanol to the predictions of the scaling formalism introduced by Dixon *et al.*⁴ These authors have shown that by an appropriate scaling of the x and y axis of the $\varepsilon''(\nu)$ curves, the data of a variety of different materials can be scaled onto one master curve. However, as stated by these authors, loss data that are influenced by secondary relaxations should not be compared to their scaling approach.

Finally, we will subject our attention to the dielectric behavior in the region above GHz as shown in Fig. 4. Despite the existing experimental gap in the investigated frequency range between 15 and 60 GHz, the existence of a minimum in $\varepsilon''(\nu)$ is clearly revealed. The amplitude of the minimum ε_{\min} diminishes for decreasing temperature, and its position ν_{\min} seems to shift to lower frequencies as it has also been observed for the structural glass formers investigated so far.⁵ The occurrence of a minimum by itself is not surprising as absorption processes can be expected in the infrared region, too. It is reasonable to assume a linear behavior for the increase of $\varepsilon''(\nu)$ to these infrared bands. Indeed for the lowest temperature investigated (192 K) a linear behavior (dotted line) is approached, as it was also found in our previous investigations of some structural glass formers.⁵ However, the dashed line in Fig. 4, which has been calculated with $\varepsilon''(\nu) = c_1 \nu^{-b} + c_2 \nu$, demonstrates that it is not possible to describe the data at higher temperatures by assuming a simple transition from a power law decrease to a linear increase. If one accepts that this simple additive superposition of both processes is correct, it seems that additional contributions to ε'' near the minimum region are important. The simplest approach to take account of this behavior is to add a constant to the above formula leading to $\varepsilon''(\nu) = c_1 \nu^{-b} + c_2 \nu + c_3$. The solid lines in Fig. 4 are fits using this expression, which provides a good description of the minimum region for all temperatures. One has to state clearly that there is no theoretical justification for the addition of c_3 . However, such a constant loss behavior has been predicted early

by Angell and co-workers¹ for glass-forming systems by combining low-frequency dielectric and high-frequency infrared data. It is interesting that the structural glass formers investigated, show a very similar behavior concerning the occurrence of a rather broad minimum.⁵ In these materials, the mode coupling theory (MCT) of the glass transition² provides a reasonable description of the high-frequency behavior near the minimum.⁵ Further experimental work is necessary to check if MCT as developed for structural glass formers may also be applied for plastic crystals as cyclo-octanol.

In conclusion, we have investigated the dielectric response of the plastic crystal cyclo-octanol in an extremely

broad frequency range. In addition to the α -relaxational response, there is evidence for two further relaxational processes. The fact that the high-frequency wing of the α -relaxation peak is strongly affected by these processes, prevents a proper comparison of the dielectric results in cyclo-octanol with the scaling form found by Dixon *et al.*⁴ At frequencies around some 10 GHz a minimum in $\epsilon''(\nu)$ has been detected. This minimum reveals similar characteristics compared to our published results in structural glasses,⁵ and cannot be ascribed to a simple transition from the α relaxation to the infrared bands. As in glass-forming liquids, additional high-frequency processes have to be assumed to describe the experimental data.

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