Is There an Excess Wing in the Dielectric Loss of Plastic Crystals?

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The plastic crystals ortho- and meta-carborane and 1-cyanoadamantane are investigated by dielectric spectroscopy for frequencies $10^{-3} \leq \nu \leq 10^9$ Hz, paying special attention to the spectral shape of the loss peaks. For the carboranes, we provide clear experimental evidence that the high-frequency wing follows a single power law over many decades in frequency. The excess wing, which shows up in a variety of glass-forming liquids as a second power law at high frequencies, is completely absent in the carboranes. In 1-cyanoadamantane, a weak excess wing shows up which can be ascribed to a Johari-Goldstein β process. We conclude that the excess wing is a property of supercooled liquids only. [S0031-9007(99)08525-7]

The investigation of the relaxation dynamics is an important aspect in the research on glass-forming materials [1]. Dielectric spectroscopy has proven to be an important tool for the investigation of the relaxation behavior due to the extremely broad dynamic range (more than 18 frequency decades [2]) accessible. In the frequency dependence of the dielectric loss, $\varepsilon''(\nu)$, the well known α-relaxation peak appears. The microscopic origin of its spectral shape which deviates from the simple monodispersive Debye behavior is still unclear in many respects. Maybe the most intriguing feature is the occurrence of an excess wing (also called "high-frequency wing" or "tail") which shows up as a high-frequency excess contribution to the power law $\nu^{-\beta}$ commonly found at $\nu > \nu_p$ (ν_p being the peak frequency). This excess wing, which will be simply called "wing" in the following, was already noted in the early work of Davidson and Cole [3] and seems to be a universal feature of glass-forming liquids [4–7] at least if a β relaxation is absent (see below). Until now, the microscopic origin of the wing remains unclear, and it is commonly felt that an explanation for this puzzling phenomenon would widely enhance our understanding of glass-forming materials. It is the goal of the present Letter to contribute to its clarification by checking for the presence of the wing in a totally different class of disordered materials, the plastic crystals.

Usually phenomenological functions as, e.g., the Cole-Davidson (CD) function [3] or the Fourier transform of the Kohlrausch-Williams-Watts (KWW) function [8] are used to describe the dielectric loss peaks in glass-forming liquids. However, these empirical functions which extrapolate to a power law, $\varepsilon'' \sim \nu^{-\beta}$, provide good fits of the experimental data at best up to three decades above the peak frequency, only. At higher frequencies, the excess wing appears which can reasonably well be described as a second power law, $\varepsilon'' \sim \nu^{-b}$ with $b < \beta$ [5–7]. In many cases, it is possible to describe the α peak including the wing using a model of dynamically correlated domains [9], but for low temperatures and extremely broadband data

deviations show up [10]. Also, the frustration-limited-domain model is able to describe the wing at least partly [11]. A possible description of the wing by an additional relaxation process was assumed not to provide the correct picture [5]. Such secondary processes, usually termed β processes, can often be ascribed to an internal change of the molecular conformation. As the wing exhibits universal properties [4], it cannot be ascribed to this type of β relaxations which depend on the specific molecular structure. The finding that secondary relaxation processes can show up also in simple glass formers led to the assumption of a more fundamental reason for these so-called Johari-Goldstein β processes [12]. Also, recent theoretical developments within the coupling model [13] may point in the direction of a universal β relaxation, closely connected to the α process [14]. It cannot be fully excluded that the wing and these possible intrinsic β relaxations are manifestations of the same microscopic mechanism. However, in the following, we will treat them as independent phenomena.

Another very successful description of the wing is given by the so-called Nagel scaling [4,15] where the $\varepsilon''(\nu)$ curves for different temperatures and even for different materials can be scaled onto one master curve. This extraordinary scaling behavior strongly suggests a correlation between the α process and the wing. Some criticism of the Nagel scaling arose concerning its universality [16,17] and accuracy [17,18], and minor modifications of the original scaling procedure have been proposed [17]. However, it is still commonly believed that the Nagel scaling is of significance for our understanding of glass-forming liquids, and many efforts have been made to check its validity in a variety of materials [15,16,18].

The question arises if the wing phenomenon is a universal feature of all disordered materials. For example, if a β peak is present, a wing is difficult to detect (assuming that wing and β process are different phenomena). This is the case for many glass-forming liquids and especially for polymers where well developed β processes are

universally present. In this context it is of interest, if the wing appears also in plastic crystals (PCs) [19]. In PCs (also called rotor or glassy crystals) the centers of mass of the molecules form a regular crystalline lattice but the molecules are dynamically disordered with respect to their orientational degrees of freedom. PCs are often considered as model systems for structural glass formers (SGFs) and much simpler to treat in theoretical and simulation approaches to the glassy state. In addition, recent experimental work on ethanol in its plastic and crystalline phases revealed the importance of orientational degrees of freedom also for SGFs [20]. Unfortunately, there are only a few experimental papers until now that report results concerning the wing in PCs. In a recent paper on the PC cyclooctanol (c-OCT), Leslie-Pelecky and Birge [19] reported the occurrence of a wing. However, some of the present authors showed [21] that secondary relaxation processes prevail in the wing region in c-OCT, and therefore the intrinsic nature of the observed wing can be doubted [22]. In two recent papers [23,24], the appearance of a wing was reported in the PC phase of ethanol. However, the ethanol molecule has many internal degrees of freedom. Therefore a β-relaxation process cannot be excluded as a reason for the apparent wing, which is consistent with the evaluation performed in [24]. Prototypical rigid molecules forming a plastic-crystalline phase are the fullerenes, C_{60} [25]. No indication for a wing was found in the dielectric spectra of C_{60} [26], but the experiments were hampered by the weak coupling of dielectric spectroscopy to the reorientational motions in C_{60}.

The aim of the present work is to investigate the high-frequency response in PCs which have a rigid molecular structure without any internal degrees of freedom. Of course, the occurrence of a Johari-Goldstein β process cannot be excluded, but it was found that these processes are much weaker in PCs compared to SGFs [27]. As sample materials, we have chosen ortho-carborane (o-CA), meta-carborane (m-CA), and 1-cyanoadamantane (CNA). We want to clarify the presence of the wing and possible Johari-Goldstein processes and check for the applicability of scaling in these materials.

The carborane molecule, $B_{10}C_2H_{12}$, forms an almost regular shaped icosahedron whose corners are occupied by ten boron and two carbon atoms. The icosahedron is surrounded by 12 outward bonded hydrogen atoms. For o-CA, the two carbon atoms occupy adjacent positions; for m-CA they are separated by one boron atom. Overall, the carborane molecules are nearly spherically shaped and therefore experience little steric hindrance for reorientational processes. A detailed dielectric study of o-CA has been published recently [28], but no information concerning the wing was provided. Both carboranes are well characterized as PCs [28,29]. For the phase transitions occurring in these materials and the possible reorientational modes, see [30]. In CNA ($C_{10}H_{15}CN$), the carbon atoms form a rigid cage, and the free bonds are saturated by hy-

drogen atoms and one cyano group. It is also well characterized as PC [31]. Information on phase transitions and reorientational modes can be found in [31,32]. The only internal degree of motion possible in this molecule, the bending motion of the C—C≡N group, was shown to be much too fast to have any influence on dielectric measurements [33]. There are various reports on dielectric measurements on CNA [27,34]. However, no information concerning the wing was provided.

In the experiments, commercially available carborane and CNA powders were used and pressed into pellets. Both sides of the samples were covered with silver paint. Various experimental setups were used, including a time domain spectrometer (10 μHz $\leq \nu \leq$ 1 kHz), LCR meters (10 mHz $\leq \nu \leq$ 30 MHz), and impedance analyzers (reflectometric technique, 1 MHz $\leq \nu \leq$ 1.8 GHz). For cooling, a closed-cycle refrigerator and a gas-heating system were utilized.

Figure 1 shows $\varepsilon''(\nu)$ of o-CA for various temperatures. Well developed loss peaks show up, accompanied by the typical relaxation steps in the real part $\varepsilon'(\nu)$ (inset). The unusual increase of the relaxation strength with temperature, revealed in the inset, indicates cooperative motion of the molecules as discussed in [28]. For frequencies below and above ν_p, the loss peaks exhibit well defined power laws. The power law for $\nu > \nu_p$ extends over eight decades for the lowest temperature. Clearly, there is no indication of a wing or a β process up to the highest frequencies investigated. The solid lines are fits with the CD function which provides an excellent description of the real and the imaginary parts in the whole frequency range. For comparison, fits using the Fourier transform of the KWW function are shown at 181 and 224 K. Clearly, the KWW function is unable to fit the data at high frequencies. Despite the fact that the KWW function is more widely used nowadays, in the authors' experience, $\varepsilon''(\nu)$ data are often described much better by the CD function [2,21,35,36]. Figure 2 shows the same plot for m-CA. Again, it is clearly seen that the wing is absent and there
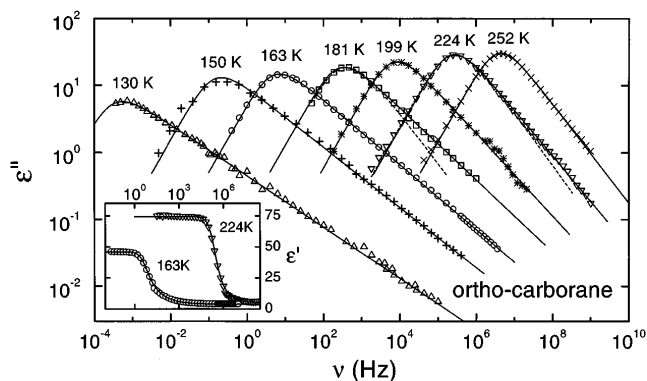

FIG. 1. $\varepsilon''(\nu)$ and $\varepsilon'(\nu)$ (inset) of o-CA for various temperatures. The solid lines are fits with the CD function. The dashed lines are fits with the Fourier transform of the KWW function.
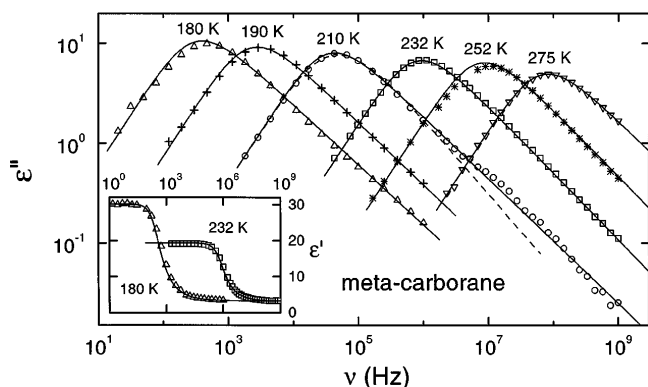
FIG. 2.   Same as Fig. 1, but for *m*-CA.

is no β relaxation present. The CD function gives a good description of the data.

Figure 3 shows the results for CNA. The data at 300 K are well fit by the CD function. For the lower temperatures, above some 10 MHz, upward deviations of $\varepsilon''(\nu)$ from the CD fits appear. However, they are significantly smaller than those caused by the wing in SGFs and almost invisible in $\varepsilon'(\nu)$ (see inset). Most probably, these deviations can be ascribed to a Johari-Goldstein β process that was deduced from the appearance of a β peak near 100 K in the kHz range [27]. Extrapolating the $\tau(T)$ behavior, reported in [27], to 260 K, this β process should show up just where the deviations from CD behavior are seen in Fig. 3. Also, the very small amplitude of this process is in agreement with that found in [27]. In contrast, the wing in SGFs seems not to develop into a β peak at low temperatures [5].

In order to compare quantitatively the deviations from CD behavior seen in CNA with those observed in SGFs, we have applied the Nagel scaling to the data [4]. In Fig. 4, scaled curves for CNA and two typical SGFs (glycerol [2] and propylene carbonate [36]) are shown. The curves for the SGFs almost coincide [37] and closely stick to the master curve of Nagel and co-workers [4] (not shown). Clearly, the scaled curves for CNA deviate from the SGF
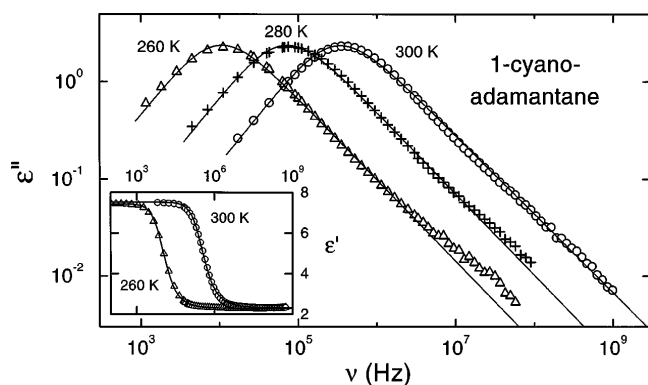
curves (see the inset of Fig. 4). This shows that the slight deviations from CD behavior found for CNA (Fig. 3) cannot be identified with the wing phenomenon seen in the SGFs. The scaled curves for *o*-CA and *m*-CA exhibit clear deviations from the SGF behavior also (Fig. 4). In addition, the various curves for the PCs deviate from each other. This can be rationalized considering that their $\varepsilon''(\nu)$ curves all follow more or less well a CD behavior and that different CD curves do not scale in the Nagel plot [15]. A modification of the Nagel scaling was recently proposed by Dendzik *et al.* [17] and demonstrated to enable a scaling of different CD curves onto one master curve. Indeed, using the modified procedure, all curves for the PCs scale onto one master curve [37].

We now will summarize the results concerning the wing in PCs obtained so far in our and other groups. (i) *c*-OCT: In this material clearly secondary relaxation processes contribute to $\varepsilon''(\nu)$ at high frequencies [21]. As some of the present authors have shown [21], the complete $\varepsilon''(\nu)$ curves can be rather well explained assuming a sum of CD (for the α process) and two Cole-Cole functions (for the β and γ process). Therefore it seems likely that a pure CD function is sufficient for the description of the α relaxation in *c*-OCT up to highest frequencies and that there is no such wing as in the SGFs. In a recent paper [23], a very weakly frequency dependent loss ($\varepsilon'' \sim \nu^{-0.09}$) was detected in *c*-OCT in its glassy crystalline state at low temperatures and interpreted as indication of a wing. However, in our opinion, it cannot be excluded that this contribution is the high-frequency tail of one of the secondary relaxations. (ii) Ethanol: Concerning the plastic phase of ethanol, where a wing was reported recently [23,24], intramolecular excitations cannot be excluded, as discussed above. Further work is necessary to clarify this point. (iii) C_{60}: Because of the small intensity of the $\varepsilon''(\nu)$ peaks only data in a limited frequency range are
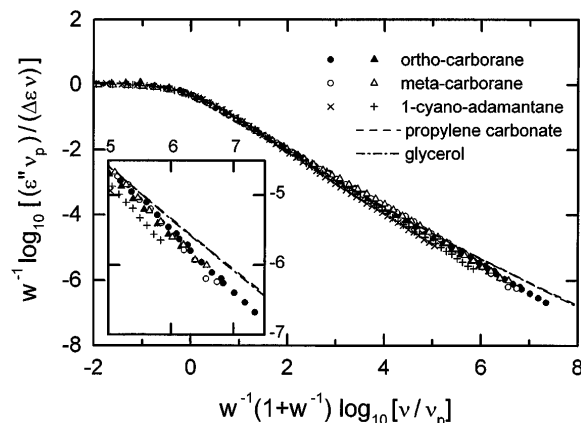

FIG. 3. $\varepsilon''(\nu)$ and $\varepsilon'(\nu)$ (inset) of CNA. The lines are fits with the CD function.

FIG. 4.   Nagel plot of the $\varepsilon''(\nu)$ results on *o*-CA ($\bullet$: 130 K; $\blacktriangle$: 150 K), *m*-CA ($\circ$: 200 K; $\triangle$: 210 K), CNA ($\times$: 280 K; $+$: 300 K), propylene carbonate [36] (dashed line: 158 K), and glycerol [2] (dash-dotted line: 195 K). The inset shows a magnified view of the high-frequency section. For the meaning of the axis labels, see Ref. [4].

available. No wing is observed [26] but a conclusive statement cannot be made. (iv) CNA: In this PC, minor deviations from CD behavior show up, which are of much smaller amplitude than in the SGFs and can be ascribed to a weak Johari-Goldstein β process. (iv) o-CA and m-CA: Also no wing is present. The CD function describes the data perfectly well. The power law $\varepsilon'' \sim \nu^{-\beta}$ extends up to eight decades above ν_p, a finding which was never seen in any glass-forming material before.

We conclude that the wing is not a universal feature for PCs. Therefore, there are limitations for considering PCs as model systems of SGFs. The wing, in the form as seen in many SGFs, may even be universally absent in this class of materials which suggests that it is connected to the translational disorder in SGFs. Especially for theories that predict a wing [9,11], implications can be expected. Hopefully, the present results will contribute to a clarification of the mysterious high-frequency-wing phenomenon in the dielectric response of glass-forming materials.

[1] See, e.g., special issue on *Relaxations in Complex Systems,* edited by K. L. Ngai, E. Riande, and G. B. Wright [J. Non-Cryst. Solids **172–174** (1994)].

[2] See, e.g., U. Schneider *et al.,* J. Non-Cryst. Solids **235–237**, 173 (1998).

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