α and β relaxation dynamics of a fragile plastic crystal ⊘

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We present a thorough dielectric investigation of the relaxation dynamics of plastic crystalline Freon112, which exhibits freezing of the orientational degrees of freedom into a glassy crystal below 90 K. Among other plastic crystals, Freon112 stands out by being relatively fragile within Angell's [*Relaxations in Complex Systems*, edited by K. L. Ngai and G. B. Wright (NRL, Washington, DC, 1985), p. 3] classification scheme and by showing an unusually strong β relaxation. Comparing the results to those on Freon112a, having only a single molecular conformation, points to the importance of the presence of two molecular conformations in Freon112 for the explanation of its unusual properties. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2180786]

I. INTRODUCTION

Glass phenomena occur when a dynamically disordered system (e.g., a liquid, plastic crystal, or paramagnet) freezes as a function of external temperature or pressure devoid of long range order. In this freezing process, one or more degrees of freedom of atoms or molecules continuously slow down, reaching the so-called glass transition when their dynamics has a characteristic time, generally chosen to be 10^2 s (for recent reviews on glass transition see, e.g., Ref. 1). Since in the liquid phase there are translational and orientational disorders, the glass transition of canonical glass formers is associated with the freezing of these two degrees of freedom. But a mesophase can exist between the completely ordered crystalline phase and the transitionally and orientationally disordered liquid phase, the so-called plastic phase or orientationally disordered (OD) phase.[2,3] In the plastic phase, the centers of mass of the molecules have spatial long range order, forming a lattice which generally has high symmetry (such as cubic, quasicubic, or rhombohedral[2–4]), but there is only short range order with respect to the orientational degrees of freedom.[5] As for glass-forming liquids, the typical phenomenology of a glass transition also can be realized in various plastic crystals when the temperature is decreased, but in this case only the orientational degrees of freedom are frozen, yielding the formation of a "glassy crystal,"[6] also called OD glass.

Concerning the dynamics of OD phases, dielectric spectroscopy has been revealed to be a useful tool to understand the complex dynamics of these phases.[7–13] Based on these works there seem to be some general dynamic features of OD phases and its glasses: They are rather strong (following the definition of Angell[14]) and they follow the Böhmer rela-

tion between nonexponentiality of the α relaxation and fragility.[15,16] On the contrary, the so-called Nagel scaling[17] does not seem to work for these phases.[7,11,18] In addition, there is only a weak or no β relaxation at all and the excess wing, showing up as a second power law at the high frequency flank of the α peak in many canonical glass formers,[17,19–21] is either absent in plastic crystals[11] or can be ascribed to a weak secondary relaxation.[7,9]

Among compounds forming orientational glasses, 1,2-difluoro-1,1,2,2-tetrachloroethane $(CFCl_2-CFCl_2)$, also named Freon112, has been revealed to be an exception to the aforementioned strongness of glassy crystals.[22] When cooled from the liquid phase, a bcc OD phase is formed,[23] which on further cooling yields a glassy crystal. The completely ordered phase, whose symmetry is not known, appears only after long waiting times (about 50 days at 77–160 K).[23] Freon112 has two energetically nonequivalent molecular conformations, namely, *trans* (with a C_{2h} symmetry) and *gauche* (with a C_2 symmetry).[24] The *trans* conformer is more stable than *gauche*, and while the latter has a dipolar moment of 0.26 D,[25] the *trans* conformer is nonpolar. The energy barrier (ΔH^*) and energy difference between the two conformers (ΔH) were determined using NMR, Raman, and far infrared spectroscopies and specific heat measurements,[23,26,27] yielding values of ΔH^* between 0.3 and 0.42 eV and $\Delta H = 0.005-0.008$ eV. In the specific heat measurements by Kishimoto *et al.*[23] a strong jump at 90 K showed up, which was assigned to the primary glass transition. Two additional thermal effects were observed at 60 and 130 K, ascribed to a secondary relaxation and the freezing of the *trans-gauche* transition, respectively. The primary glass transition temperature was also determined by Krüger *et al.*[28] taking into account the change in the slope of the temperature dependence of the refractive index and bcc lattice pa-

rameter leading to $T_g = 86$ K. Also dielectric data are reported in the latter work, although the actual spectra are not shown and only the temperature dependent curve of dielectric loss for a single frequency is given. Recently a molecular dynamics (MD) simulation has been performed on this compound,[29] in which, using a simplified model of Freon112, it was possible to obtain information on the "slow" dynamics of this compound (slow when compared to the time domain usually investigated in MD simulations) and therefore the simulation can be tested by dielectric spectroscopy results. In that work mode coupling theory[30] (MCT) was also successfully employed to interpret the results.

In the present work also the freon compound 1,1-difluoro-1,2,2,2-tetrachloroethane ($CCl_3 - CClF_2$, also called Freon112a) is investigated, which has the same overall molecular formula as Freon112, but with both fluorine atoms connected to one carbon. There is only one conformation of this molecule. Therefore, since it has a permanent dipolar moment, and it has no *trans-gauche* disorder, it is of interest to compare its properties with those of the Freon112 molecule. No information, either on the relaxation dynamics or on the polymorphism of this compound, are found in the bibliography.

II. EXPERIMENTAL DETAILS

Freon112 and Freon112a were purchased from ACBR company with a minimum purity of 99% and were used without further purification. Dielectric spectra were obtained by means of frequency response analysis using a Novocontrol-α analyzer in the frequency range 10 mHz $\leq \nu$ $\leq$ 1 MHz and by means of a reflectometric technique using a HP4291 impedance analyzer at 1 MHz $\leq \nu \leq$ 1.8 GHz.[31] Cooling and heating of the samples were performed using a nitrogen gas-heating system and a helium-based cryostat. The parallel-plate capacitors were filled in the liquid phase and, because of the high vapor pressure of these compounds, quickly cooled down in order to avoid sublimation. Prior to the measurements up to 1 MHz, the samples were cooled down to about 70 K with a typical rate of 5 K/min; for ν > 1 MHz the sample was quenched in liquid nitrogen. In both cases the measurements were performed under heating; the high frequency measurements were carried out above the glass temperature. A possible dependence of the dielectric behavior on history will be investigated in a future work.

Specific heat measurements were done by means of an ac technique using the physical property measurement systems (PPMS) from Quantum Design. The cell was filled with about 30 mg of the substance in the liquid phase. Contributions from the specific heat of the cell were subtracted from that experimentally determined. Additional calorimetric experiments were performed by a differential scanning calorimetry (DSC) using a Perkin Elmer DSC7 device with high pressure cells, because of the high vapor pressure of the substances.
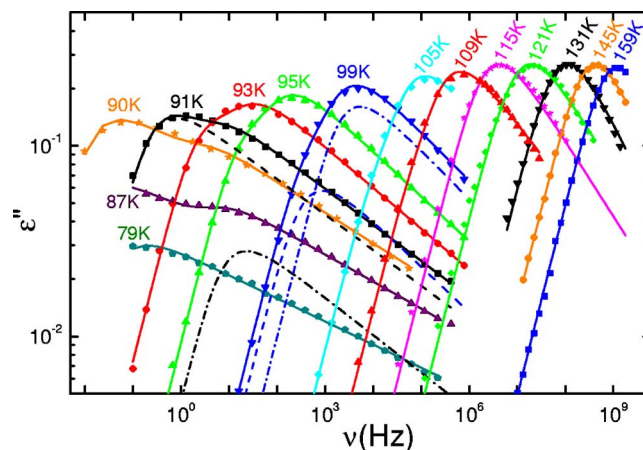

FIG. 1. (Color online) Dielectric loss for the compound Freon112. The lines show the fits using two ($79 < T < 130$ K) or one ($130 < T < 160$ K) CD function. The two CD functions used to fit the spectra in the first temperature range are indicated for 91 and 99 K by the dashed and dot-dashed lines.

III. RESULTS

A. Freon112

The main feature showing up in the spectra is a well-pronounced relaxation peak (Fig. 1).[32] Its continuous shift over many decades towards lower frequencies with decreasing temperature mirrors the glassy freezing of the orientational dynamics in this plastic crystal.[7] At higher temperatures, $T > 100$ K, a single peak is observed, which can be well described, e.g., by the empirical Cole-Davidson (CD) function (lines in Fig. 1). However, for $T < 100$ K a shoulder emerges at the low-frequency flank of the relaxation peak, which seems to increase strongly in intensity, and, with further lowering of temperature, develops into a separate peak with an amplitude even larger than that of the high-frequency peak. Tentatively we will denote the slow process as α relaxation and the faster process as β relaxation; at high temperatures, where both processes are merged, the term $\alpha\beta$ process is chosen. Overall, while in earlier works only a single relaxation process was reported,[22,28,29,33,34] obviously two processes appear in this compound, exchanging the role of the dominating one depending on temperature. In order to analyze the spectra, a single CD function was sufficient to fit the relaxation peaks for temperatures above 130 K. But it was impossible, either with a single CD or with a Havriliak-Negami (HN) function, to fit the spectra for $T < 130$ K. Instead for this temperature range, even for the curves between 105 and 121 K where the appearance of a low-frequency shoulder is not immediately evident, two CD functions had to be used to fit the spectra (for 91 and 99 K the two constituents of these fits are indicated by the dashed and dot-dashed lines). This finding provides further evidence for the existence of two separate relaxation phenomena in Freon112. Now the question arises why only a single relaxation phenomenon was reported in previous works.[22,28,29,33,34] Figure 2 shows the relaxation map including the results of the fits of Fig. 1 and those reported in the literature.[22,28,29,33,34] Obviously, all published data have been collected at temperatures too high to clearly resolve the second relaxation. Only in Ref. 28, values of τ obtained from dielectric measurements
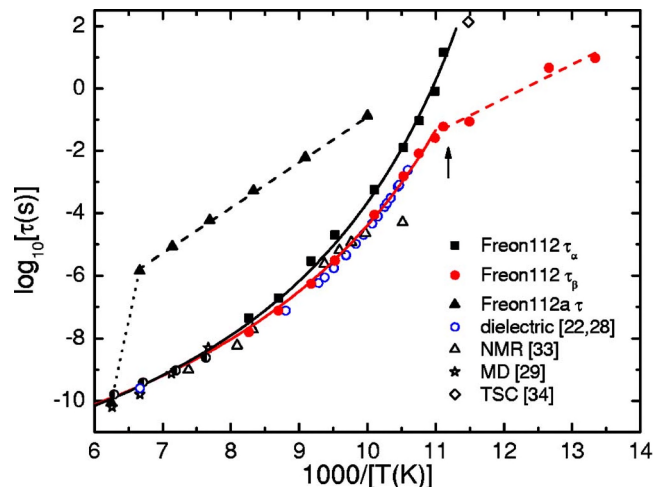
FIG. 2. (Color online) Relaxation time for α, β, and $\alpha\beta$ (half-filled circles) peaks in Freon112 and α peak for Freon112a. Dielectric spectroscopy data of Krüger *et al.* (Ref. 28) and Angell *et al.* (Ref. 22), NMR data (Ref. 33), TSC data (Ref. 34), and MD data (Ref. 29) are also shown. The solid and dashed lines are fits with the VFT law, Eq. (1), and an Arrhenius behavior, respectively. The arrow indicates the glass temperature.
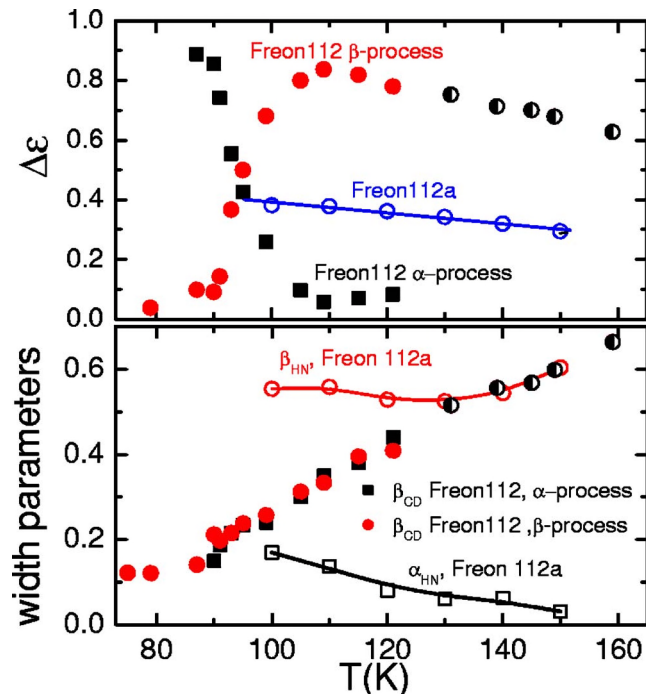

FIG. 3. (Color online) Relaxation strength and width parameters used to fit the Freon112 and Freon112a spectra. The parameters used to fit the single high temperature $\alpha\beta$ relaxation peak for Freon112 are shown as half-filled circles. The lines are drawn to guide the eyes.

were reported extending down to 95 K, where a small low-frequency shoulder of the loss peak should reveal the presence of a second relaxation process (Fig. 1). However, unfortunately in that work the data have not been analyzed in terms of frequency-dependent plots and the relaxation times were evaluated from the temperature-dependent data instead. As revealed by Fig. 2, the relaxation times obtained by Krüger *et al.*[28] correspond to the β relaxation, representing the dominant relaxation process in the temperature range investigated in this work.

The previously determined non-Arrhenius behavior of $\tau(T)$ for this compound is evident from the strong curvature in the Arrhenius representation of Fig. 2. In order to fit the relaxation time as a function of temperature, a Vogel-Fulcher-Tammann (VFT) equation was used (solid line),

$$\tau = \tau_0 \exp\left[\frac{D T_{\text{VF}}}{T - T_{\text{VF}}}\right], \quad (1)$$

with T_{VF} the Vogel-Fulcher temperature and D the strength parameter,[14] obtaining values of $\tau_0 = 6.2 \times 10^{-14}$ s, $T_{\text{VF}} = 68.8$ K, and $D = 10$. The relatively small value of the strength parameter already indicates the fragile character of this OD glass, which will be treated in more detail in Sec. IV. In order to determine the glass temperature we have adopted the general definition, i.e., the temperature for which the relaxation time is 100 s, leading to $T_g = 88$ K, in reasonable agreement with the previous calorimetric determinations ($T_g = 90$ K).[23,35] Concerning the β relaxation process, it also follows a VFT behavior for the temperature range above T_g ($\tau_0 = 7.2 \times 10^{-14}$ s, $T_{\text{VF}} = 64.9$ K, and $D = 10.9$). For lower temperatures $\tau_\beta(T)$ shows a transition into a much weaker Arrhenius-type temperature dependence. The "glass temperature" obtained for this second relaxation is about 70 K. In this context, it is interesting that in the specific heat measurements of Freon112 (Refs. 23 and 35) a "small heat-capacity anomaly at around 60 K has been attributed to the β relaxation." Since the determination of this temperature effect is

subjected to some error, and the slope of $\tau_\beta(T)$ in Fig. 2 depends on thermal history in this sub-T_g region, it seems reasonable that the aforementioned thermal effect could be related to the β relaxation observed by dielectric spectroscopy. The agreement of the glass temperature determined from the α relaxation time with that from specific heat measurements and the finding of a transition of $\tau_\beta(T)$ into Arrhenius behavior already at τ_β values much lower than 100 s corroborates the correct assignment of both relaxations as α and β relaxations. Obviously, despite the relaxation occurring at higher frequencies is the dominating one at high temperatures, it is the relaxation denoted as α relaxation that determines the glassy freezing in Freon112.

In Fig. 3 the remaining CD fitting parameters for Freon112 are shown. The results concerning the dielectric strength ($\Delta\varepsilon$) are especially interesting. When increasing temperature the dielectric strength of the α relaxation decreases quickly at about the glass transition temperature and remains constant for higher temperatures. Because in this temperature range the α relaxation only appears as a shoulder in $\varepsilon''(\nu)$, its dielectric strength could not be unambiguously determined, but the general trend should be correct. On the contrary $\Delta\varepsilon_\beta$ increases at the same temperature, that is, T_g. For temperatures above 130 K, only a single peak has been fitted, and therefore for this temperature range only $\Delta\varepsilon_{\alpha\beta}$ could be determined. With respect to the exponent of the high-frequency flank of the relaxation peaks, for both α and β relaxations this parameter is roughly the same and becomes extremely small for low temperatures. When considering these results, however, one should be aware that especially at high temperatures the determination of β_{CD} of
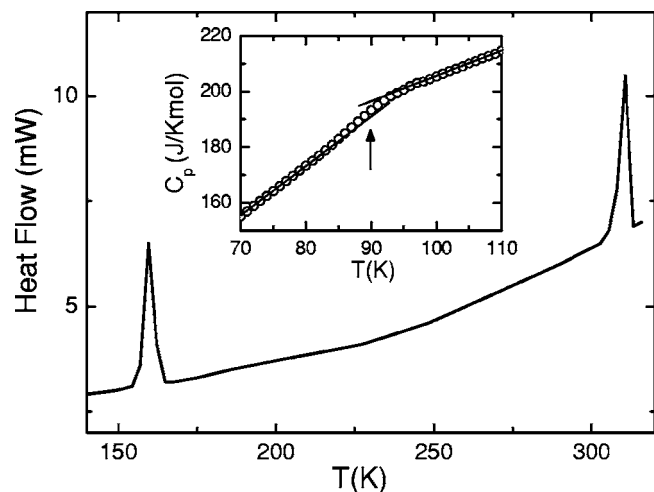
FIG. 4. DSC experiment showing the polymorphism of Freon112a. The inset shows the specific heat measurement performed on phase II (see text).

FIG. 5. (Color online) Dielectric loss for Freon112. The lines show the result of fits using the Havriliak-Negami relation.

the α process has a high uncertainty due to the strong overlap with the β process. In addition, one should mention that it is not so clear if a simple *additive* superposition of different contributions to $\varepsilon''(\nu)$ is really justified.[36,37] While alternative approaches may lead to somewhat different parameters, we believe that the overall trend of two broad relaxations exchanging the role of the dominating process depending on temperature will remain the same.

B. Freon112a

In contrast to Freon112, Freon112a (having the same molecular formula as Freon112) has only one molecular conformation exhibiting a permanent dipolar moment, which makes worthwhile the comparison of these two compounds. Since to our knowledge there are no information on the polymorphism of this substance in the literature, DSC experiments were performed to establish the phase sequence for this compound, revealing the existence of two phase transitions (see Fig. 4). The obtained melting temperature (T_m =309 K) and enthalpy change (ΔH=3.5 kJ mol^{-1}) lead to an entropy of fusion of ΔS=11.3 J(K mol)$^{-1}$. Following Timmermans criterion $[\Delta S_m < 21$ J(K mol)$^{-1}$ for a plastic phase],[38] this melting entropy value indicates that the solid phase just below the melting (from now on phase I) can be assigned as a plastic crystal, similar to the findings in Freon112. Preliminary neutron diffraction experiments have also been performed on this compound,[39] and the spectra could be fitted assuming a bcc lattice with a parameter close to that of the bcc phase of Freon112. However, unlike Freon112, Freon112a shows a second phase transition from the plastic phase to a more stable solid phase (from now on phase II) at T=158 K $[\Delta H$=3.4 kJ mol^{-1} and ΔS =21.6 J(K mol)$^{-1}]$. In Fig. 4 specific heat results obtained with an ac calorimeter in phase II (the only one showing a glass transition), and DSC experiments used to determine the polymorphism of the substance, are shown. The figure reveals a specific heat anomaly at 90±2 K, which can be assigned to a glass transition, its T_g coinciding with that for Freon112. Thus it seems that some disorder remains in phase
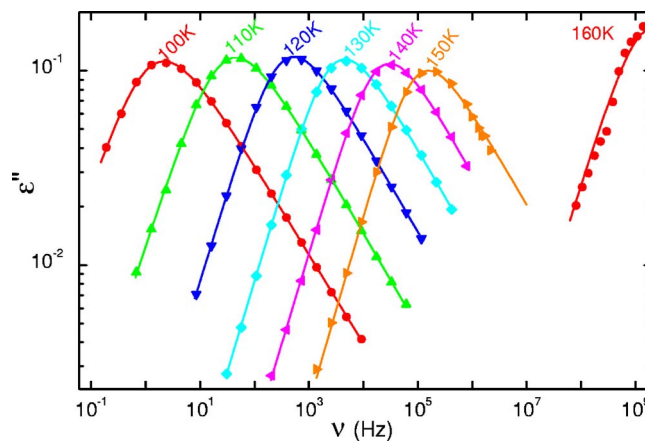
II, which finally freezes at 90 K. The situation is similar to that found in various other plastic crystals, e.g., some methylbromomethanes,[40] adamantanone,[7] and *ortho*-[41] and *meta*-carborane.[7] In these cases, typical glass phenomena occur in a phase allowing for restricted orientational motions only, in contrast to the high-temperature plastic phase where free reorientations of the molecules are possible.[40,42] A similar scenario can be tentatively attributed to Freon112a. As was already speculated in Refs. 23 and 35, it seems likely that in Freon112 the free rotator phase is conserved down to the lowest temperatures due to the *trans-gauche* conformational disorder arising below 130 K.

In Fig. 5, the dielectric loss spectra of Freon112a are shown. In phase II we observe the typical temperature-dependent shift of well-pronounced relaxation peaks over many decades of frequency, proving that indeed glassy freezing occurs in this phase. Comparing the peak at 160 K, which was measured in phase I, to that at 150 K in phase II reveals a strong slowing down of relaxation at the phase transition. A very similar behavior was also found in *ortho*- and *meta*-carborane and adamantanone and ascribed to the restriction of the reorientational motion in the low-temperature phase.[7,41] In contrast to the two successive relaxations found in Freon112 (Fig. 1), in Freon112a only one relaxation process seems to prevail. For all temperatures investigated, the loss peaks shown in Fig. 5 could well be fitted with a single HN function (lines). The resulting temperature-dependent relaxation time is shown in Fig. 2. In marked contrast to the finding in Freon112, $\tau(T)$ in phase II of Freon112a follows an Arrhenius behavior with an energy barrier of 300 meV. Interestingly, $\tau(160$ K$)$ measured in phase I of Freon112a matches the value obtained for Freon112 at the same temperature. The remaining relaxation parameters of Freon112a, showing a smooth and unspectacular temperature dependence, are given in Fig. 3.

IV. DISCUSSION

In Fig. 6, an Angell plot[43] of the temperature-dependent α relaxation time for the two investigated freon compounds is given, enabling the direct comparison of the temperature characteristics of τ to that of several other plastic crystals[7]
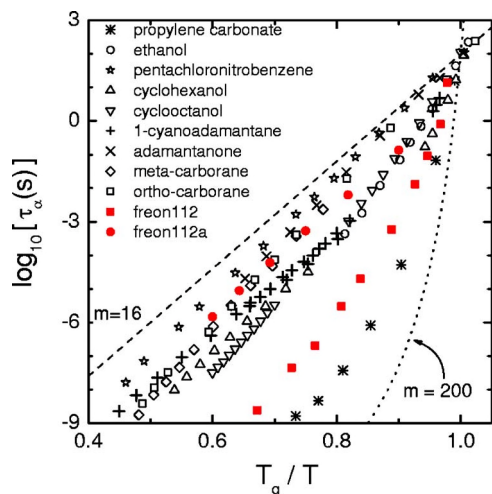
FIG. 6. (Color online) Angell plot of the α relaxation times for plastic crystals (Ref. 7). The results of the present work are presented as closed symbols. For comparison results on supercooled-liquid propylene carbonate are shown. The dashed and dotted lines show the behavior for maximal and minimal fragilities.

also shown in the figure. For comparison, also the curve for a typical fragile structural glass former, propylene carbonate, is given.[44] As was already predicted by Angell *et al.*[22,45] based on a rather restricted data set, Fig. 6 demonstrates that Freon112 indeed exhibits pronounced fragile characteristics and in fact it seems to be the most fragile plastic crystal known so far. As a quantitative measure of the fragility, the fragility parameter m was introduced in Refs. 46 and 47, defined by the slope at T_g in the Angell plot. From Fig. 6, we find $m=68$, characterizing Freon112 as a fragile glass former. In contrast Freon112a is revealed as rather strong, in agreement with the findings in most other plastic crystals. In Ref. 7, an explanation for the low fragility of plastic crystals in line with ideas[48] that relate the fragility to the form of the potential energy landscape in configuration space was considered. The typical properties of fragile and strong glass formers can be rationalized assuming that the density of minima in the potential energy landscape increases with increasing fragility. For plastic crystals, in Ref. 7 the lattice symmetry was presumed to lead to a reduced density of energy minima, which explains their relatively low fragility. Within this framework the higher fragility in Freon112 can be rationalized assuming that the strong *trans-gauche* conformational disorder in this material leads to an increased density of energy minima.

According to the well-established correlation between fragility and the width of the α relaxation peak at T_g,[15,49] fragile materials should have rather large α peak widths, corresponding to small values of the exponent β, characterizing the high-frequency flank of the α peak. Indeed, at low temperatures, β_{CD} in Freon112 becomes very small (Fig. 3). With a half-width of about 3.2, the α relaxation in Freon112 even seems too broad in view of this correlation. However, due to the overlap with the β relaxation, the determination of the α peak width at low temperatures has a rather high uncertainty and it is not possible to arrive at a definite statement concerning the validity of this correlation in Freon112.

The fragile character of Freon112 is not the only exceptional feature of this compound. Although plastic crystals often show a β relaxation, the dielectric strength of this process is usually much smaller than that of the α relaxation, and also smaller than the β process found in typical canonical glass formers.[7] That is not the case for Freon112, as becomes obvious in Fig. 3. At temperatures above the glass transition, the dielectric strength of the α relaxation decreases while that of the β process increases; the latter even becoming the dominating relaxation process at high temperatures. This unusual behavior, namely, a β process with an amplitude becoming comparable or even exceeding that of the α process at high temperatures, to our knowledge so far was never observed in any plastic crystal and is realized only in few canonical glass formers, e.g., toluene or polybutadiene.[21,37] In general, the occurrence of β relaxations is a common feature in canonical glass formers. Sometimes intramolecular motions are held responsible for β relaxations, but Johari and Goldstein[50] demonstrated that secondary relaxation processes also show up in relatively simple molecular glass formers, where intramolecular contributions seem unlikely. This led to the notion that these so-called Johari-Goldstein (JG) β relaxations are inherent to glass-forming materials in general. However, the microscopic processes behind this kind of β relaxations are still controversially discussed. With an Arrhenius behavior of τ_β below T_g, the β relaxation in Freon112 detected in the present work exhibits a typical feature of JG β relaxations found also in canonical glass formers.[21,50] Another typical property of JG relaxations is a correlation of the β relaxation time at T_g with the Kohlrausch exponent β_{KWW} promoted in Ref. 51, which was rationalized within the framework of the coupling model.[52] The fulfillment of this relation recently was even proposed as a criterion to distinguish genuine JG β relaxations (inherent to the glassy state of matter) from other types of secondary relaxations (e.g., due to intramolecular modes).[53] This relation was successfully tested for a variety of plastic crystals[7] and for toluene and polybutadiene,[51] which show a similar relaxation scenario as Freon112. However, using the predicted relation $\tau_\beta = t_c^{1-\beta_{KWW}} \tau_\alpha^{\beta_{KWW}}$ with $t_c = 2$ ps (Refs. 51 and 53) and the present $\beta_{KWW}(T_g) \approx 0.34$, calculated from $\beta_{CD} \approx 0.2$ (cf. Fig. 3),[54] we obtain $\tau_\beta(T_g) \approx 10^{-7}$ s, which is far off the actual relaxation time of about 0.1 s (see Fig. 2). Thus at first glance it seems that the observed β relaxation in Freon112 is not a JG relaxation.

In contrast to Freon112, Freon112a only shows a single relaxation process. As one of the main differences of both materials is the possibility of the first to have two molecular conformations, it is likely that the occurrence of two relaxations in Freon112 is somehow connected to this difference. The transition between the *gauche* and *trans* conformations in Freon112 corresponds to a rotation around the C–C axis. As this is a dipolar active motion, one may attribute the second relaxation in Freon112 to this intramolecular mode, but a corresponding mode of course is also possible in Freon112a. A more reasonable explanation arises considering the fact that only the *gauche* conformer has a dipolar moment, meaning that below 130 K (freezing temperature of the conformational disorder) the dielectric signal arises from

a solution of about 50% of dipolar molecules in a nonpolar medium.[55] A recent study of Blochowicz and Rössler[56] of molecules with high dipolar moment in an only weakly polar substance (50% 2-picoline in tristyrene) revealed dielectric spectra closely resembling the ones obtained by us: At low temperatures there is an extremely broadened α relaxation peak and a well-separated weaker β relaxation. For temperatures just above T_g there is a change of the relative dielectric strength of the primary and secondary relaxation, the latter becoming larger than the first. Comparing the properties of the β relaxation shown in this paper[56] with that of the secondary relaxation phenomenon of Freon112, we find that both processes show similar properties: The relaxation strength of the β process is almost constant for temperatures below T_g, the time constant follows an Arrhenius law for $T < T_g$, and the relationship between the activation energy of the β process and T_g [$\Delta H_a/(k_B T_g) \approx 25$], promoted in Refs. 21 and 57, is also accomplished taking into account the aforementioned uncertainty in the determination of ΔH_a because of nonequilibrium effects for $T < T_g$ [$\Delta H_a/(k_B T_g) = 30$ in our case]. Furthermore, for the 50% mixture of 2-picoline in tristyrene the correlation between the stretching exponent of the α relaxation and the β relaxation time[51] fails as in the case of Freon112, again because of the extremely small slope of the high-frequency flank of the primary relaxation peak. However, in Ref. 58 arguments were put forward that the broadening caused by concentration fluctuations in the mixture may prevent the width parameter of the α relaxation being directly determined from the frequency dependence of the loss. Such a scenario may also be in effect in the present case of polar Freon112 molecules with *gauche* conformation, "dissolved" in a nonpolar medium formed by the *trans* molecules. As the conformational transitions in Freon112 exhibit glassy freezing close to 130 K,[23,35] much higher than $T_g \approx 88$ K determined from $\tau_\alpha(T)$ of the α relaxation, the *gauche-trans* disorder can be regarded as static on the time scale of the α relaxation. Thus there is an effective substitutional disorder of *gauche* and *trans* molecules, which is the analog to the concentration fluctuations in the picoline/tristyrene mixture. Therefore the aforementioned large discrepancy of the experimental $\tau_\beta(T_g)$ from the one calculated using $\beta_{KWW}(T_g) = 0.34$ does not necessarily imply the failure of the correlation promoted in Ref. 51 or that the β relaxation in Freon112 is not a JG relaxation.[53]

Assuming that this β relaxation indeed is of JG type, one may speculate about a rationalization of its increased strength in the diluted case within the "islands of mobility" framework promoted, e.g., in Ref. 50. There it was suggested that JG relaxations in canonical glass formers arise from localized motions of a fraction of the molecules residing in regions of lower density, leading to reduced interactions among neighboring molecules and thus faster dynamics. It is reasonable that this effect is absent or much weaker in plastic crystals where density fluctuations are smaller, being generated by the orientational disorder only, which would explain the much weaker or even absent β relaxations in these materials.[7,11] The reorientational dynamics of the molecules in most plastic crystals can be assumed to be determined by dipolar and steric interactions with neighbors, which due to

the regular crystalline lattice show smaller spatial fluctuations than in canonical glass formers. However, the situation is different in conformationally disordered Freon112, where one could imagine regions of relatively isolated dipolar *gauche* molecules in a matrix of nonpolar *trans* molecules. These regions could correspond to the less dense regions considered in Ref. 50 for the explanation of the β relaxations in canonical glass formers: Due to the much reduced dipolar interactions, the reorientational motions in these regions should be faster, giving rise to the observed strong β relaxation in Freon112. However, one should be aware that the dipolar moment of Freon112 is rather small and no "islands" were invoked in the interpretation of the binary picoline system, which has a substantially larger dipole moment. Thus the scenario developed above is highly speculative.

V. CONCLUSION

In summary, we have performed a thorough dielectric investigation of plastic crystalline Freon112, comparing the results to those on Freon112a. In relation to other plastic crystals, Freon112 is exceptional in many respects: At first, despite that it is composed of rather asymmetric dumbbell-shaped molecules, it forms a plastic crystalline phase which can easily be supercooled; the transition to the completely ordered phase being extremely slow.[23,35] In addition, in contrast to other plastic crystalline materials,[7] the glassy freezing of the orientational dynamics in Freon112 exhibits typical fragile characteristics and in fact, with $m = 68$, to our knowledge Freon112 is the most fragile orientationally disordered material known so far. Finally, while other plastic crystals exhibit no or only weak secondary relaxations,[7,11] Freon112 shows a β relaxation with a dielectric strength comparable to that of the α relaxation and even becoming the dominant process at high temperatures. All these exceptional properties are not found in Freon112a, showing a transition into a phase with restricted reorientational motions only, strong relaxation characteristics, and neither a β relaxation nor an excess wing. It seems reasonable to ascribe the unusual findings in Freon112 to the presence of two molecular conformations in this system, in contrast to Freon112a, which has only a single one. At first, as was already considered in Refs. 23 and 35, the strong conformational disorder in Freon112, which is frozen on the time scale of the α relaxation, seems to prevent complete orientational order at low temperatures as this would imply all molecules transferring to the same conformation. In addition, the unusually high fragility may be ascribed to a higher density of minima in the potential energy landscape caused by the strong *trans-gauche* disorder. Finally, this *trans-gauche* disordered material may be regarded analogous to a solution of dipolar molecules in a nonpolar medium, shown to lead to a β relaxation scenario similar to the present observations,[56] which may be rationalized within the explanation of the JG relaxation in terms of islands of mobility.[50] Overall, certainly many of the proposed explanations of the unusual behavior of Freon112 revealed in the present work are speculative and need to be corroborated by further experiments as, e.g., NMR clarifying the details of the reorientational motions in this compound. However, it

seems likely that Freon112, with its unusual behavior standing out among all other plastic crystals, may be a key system to enhance our understanding of glassy dynamics in general and especially of the nature of the JG process. For this reason currently further investigations are being carried out in order to determine the conformational, long and short range orders in this compound as functions of temperature by means of neutron diffraction.

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