Molecular reorientation in *ortho*-carborane studied by dielectric spectroscopy

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The dielectric properties of *ortho*-carborane have been investigated in a broad frequency range of 20 Hz$\leq\nu\leq$1 GHz and at temperatures 10 K$\leq T\leq$380 K. At $T>$275 K the *ortho*-carborane molecules undergo fast and isotropic reorientations with frequencies larger than 1 GHz. Below a phase transition at $T_c\approx$275 K the reorientation is partly restricted and the dynamics of the remaining reorientational motion is reduced. At 160 K, the dielectric results reveal a small anomaly which we assign to a second phase transition. At temperatures 150 K$<T<$275 K the dipolar active orientational degrees of freedom freeze in on the time scale of the measuring frequencies. The corresponding peaks in the frequency dependence of the dielectric loss can well be described using the Fourier transform of the Kohlrausch–Williams–Watts (KWW) function with a stretching parameter $\beta\approx$0.8. However, for frequencies well above the peak maximum we find significant deviations from KWW behavior. In the temperature and frequency range investigated, the dynamics of the dipolar relaxation process behaves thermally activated with an activation energy of 0.52 eV. In the classification scheme of Angell *et al.* the fragility of *ortho*-carborane can be estimated as $m\approx$20 characterizing it as a strong glass former. *Ortho*-carborane fits well into the correlation scheme of Böhmer *et al.* where polydispersivity and fragility are related to each other. At high temperatures and low frequencies conductivity processes (hopping) dominate the dielectric response of *ortho*-carborane. © *1996 American Institute of Physics.* [S0021-9606(96)50110-4]

I. INTRODUCTION

The *ortho*-carborane molecule, $B_{10}C_2H_{12}$, forms an almost regular shaped icosahedron whose corners are occupied by ten boron and two adjacent carbon atoms. The icosahedron is surrounded by 12 radially outward bonded hydrogen atoms. Due to its high symmetry, which implies little steric hindrance, and due to a relatively weak intermolecular bonding, the *ortho*-carborane molecules undergo fast and almost isotropic reorientations above 273 K.[1–4] This finding characterizes *ortho*-carborane as a so-called plastic crystal, in which the centers of mass of the molecules form a regular crystalline lattice but where the molecules are dynamically disordered with respect to the orientational degrees of freedom.

So far the reorientational motion of *ortho*-carborane has been studied by NMR,[1–5] specific heat[1,6] and Raman spectroscopy.[7,8] These investigations reveal a phase transition near 270 K where the reorientational motion changes from almost isotropic to (strongly) anisotropic. However, the results are at variance to each other concerning the low temperature behavior of *ortho*-carborane. Near 160 K, a second phase transition has been detected by Raman spectroscopy[7,8] and adiabatic calorimetry.[6] The entropy of this transition amounts $R\times$ln 3,[6] indicating a partial restriction of the reorientational motion.[6–8] However, this transition has not been observed in NMR experiments.[1–5] In addition, the existence of a further phase transition at 200 K was deduced from NMR measurements by Reynard *et al.*[4,5] These authors argue that the inner boron and the outer hydrogen cage reorient independently, the boron cage being stationary at $T<$200 K while the protons still exchange positions. Bukalov *et al.*[7,8]

concluded from Raman experiments that, when cooled at a "normal" rate of 10 K/h, at 165 K *ortho*-carborane freezes into a disordered state, similar to an orientational glass. However, when cooled slowly (0.1 K/h) complete orientational order is achieved at 167 K. A disordered state at low temperatures seems also to be in accord with the results of Westrum *et al.*[6] who infer from their specific heat experiments that *ortho*-carborane may have a residual entropy of $R\times$ln 2 at $T=$0 K.

Similar behavior has recently been found in the fullerite C_{60} where the freezing of the reorientational motion of the fullerene molecules could be observed over some 15 decades of frequency[9–11] using various techniques including dielectric spectroscopy.[10–12] While in C_{60} the dipolar moment is induced by neighboring disordered molecules, *ortho*-carborane is characterized by an intrinsic dipole moment of 4.4 D.[13] Therefore, dielectric spectroscopy seems ideally suited to get information about the reorientational dynamics of this material. However, to our knowledge, there are only two, not very detailed dielectric studies on this material[14,15] which are restricted to a very small frequency range of only 2 decades and temperatures above 100 K.

We performed a detailed dielectric investigation of *ortho*-carborane in a broad frequency range. The main scopes of this investigation were (i) to get information about the phase transition near 270 K, (ii) to provide experimental evidence for the existence of additional phase or glass transitions at temperatures below 270 K, and (iii) to investigate the dynamics of the reorientational motion. Here, it is of special interest to determine the temperature dependence of
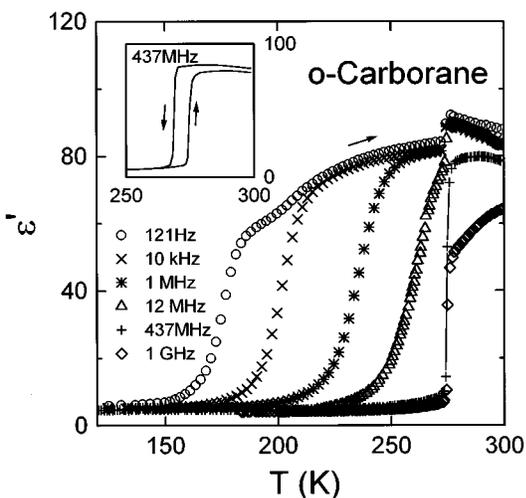
FIG. 1. Temperature dependence of the dielectric constant, ϵ', for various measuring frequencies as obtained on heating. The inset shows the heating and cooling curves near T_c for 437 MHz.

FIG. 2. Temperature dependence of the real part of the conductivity, σ', for various frequencies. The frequencies are (from top to bottom): 1 GHz, 331 MHz, 110 MHz, 36 MHz, 12 MHz, 6.9 MHz, 2.3 MHz, 1 MHz, 499 kHz, 167 kHz, 67 kHz, 27 kHz, 11 kHz, 4.5 kHz, 1.9 kHz, 735 Hz, 299 Hz, 121 Hz, and 49 Hz. The arrow indicates the anomaly near 160 K.

the relaxation rates and to characterize the distribution of relaxation times.

II. EXPERIMENTAL DETAILS

Commercially available *ortho*-carborane which has been used without further purification has been pulverized and pressed to pellets with typical areas of 10 mm^2 and thicknesses of 1 mm. As contacts both sides of the samples have been covered with silver paint. The measurements have been performed using different experimental setups: For frequencies 20 Hz$\leq\nu\leq$1 MHz a standard four-point technique with an autobalance bridge (HP4284) has been employed. For frequencies $\nu\geq$1 MHz an impedance analyzer (HP4191) has been used which measures the complex reflection coefficient of a coaxial line at the end of which the sample is mounted to bridge the inner and outer conductor.[16] After a proper calibration to determine residual reflections and phase shifts, the impedance can be calculated from the reflection coefficient. For cooling, a He closed cycle refrigerator (10 K$<T<$300 K) and a N$_2$ gas heating system (100 K$<T<$600 K) have been used. As carboranes exhibit a high sublimation pressure[6] we restricted the measurements in the latter device to temperatures below 380 K.

III. RESULTS AND DISCUSSION

A. Phase transitions and reorientational motion

Figure 1 shows the temperature dependence of the real part of the dielectric constant ϵ' for temperatures below room temperature and various frequencies. On heating, at $T_c=275$ (±1) K a phase transition shows up, characterized by a significant step in ϵ'. As is demonstrated in the inset, the phase transition exhibits a hysteresis of approximately 6 K, the signature of a first order phase transition. These findings are in accord with published data where phase transition temperatures between 263 and 277 K and hysteresis widths of 5
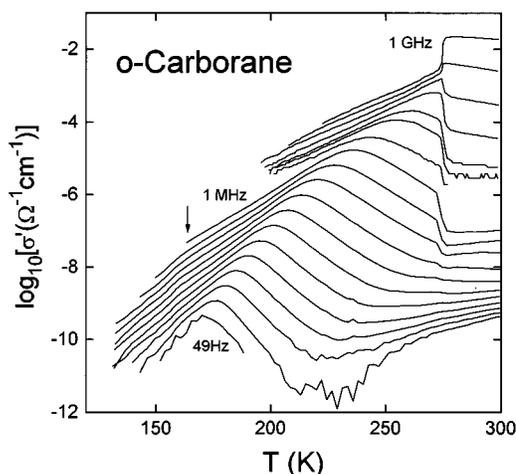
K have been reported.[1–8,13,14] Below T_c, $\epsilon'(T)$ exhibits a steplike decrease which is shifted to smaller temperatures for smaller frequencies. This behavior is in good agreement with the findings of Bartet *et al.*[14] and Pilet *et al.*[15] who performed dielectric measurements in the kHz range. It is the fingerprint of a relaxational process with a rate that slows down in the frequency and temperature range set by the experiment. At low temperatures a limiting value of $\epsilon_\infty=4.5$ (±0.5) is reached. To check for the intrinsic nature of these findings, several measurements have been performed on different samples which have been subjected to different grinding procedures and pressures during the preparation of the pellets. The characteristic features as shown in Fig. 1 have been found in all samples, e.g., the step in ϵ' at the phase transition, the value of T_c, the temperature dependence of the relaxation rate, and the value of ϵ_∞. However, the height of the relaxational step below T_c and the slope of $\epsilon'(T)$ above T_c varied significantly (about 50%), a finding for which we have no explanation at the moment.

Figure 2 demonstrates that the steps in $\epsilon'(T)$ are accompanied by well developed loss peaks in the temperature dependence of the real part of the conductivity which is proportional to the imaginary part of the dielectric constant, ϵ''. The position of the peak roughly marks the temperature where the inverse relaxation time of the reorientation process is equal to the circular frequency $\omega=2\pi\nu$. Similar to the findings in Fig. 1, the phase transition at 275 K shows up as a step in the temperature dependence of σ'. However, with decreasing frequencies, the steps change direction from upwards to downwards and finally vanish at frequencies below the kHz range. At low frequencies and at temperatures well above the peak maximum, $\sigma'(T)$ increases with increasing temperature and is not affected by the structural phase transition. This increase continues up to the highest temperatures investigated (380 K, not shown) and is due to charge transport, i.e., to conduction processes (see Sec. III C). Obviously,

the phase transition affects the relaxation process only. Again, these features were found in several measurements on different samples, the only difference being the absolute value of the conductivity dominated part of $\sigma'(T)$.

The steps in $\epsilon'(T)$ and $\epsilon''(T)$ at T_c can well be explained assuming that the relaxation process becomes faster for $T > T_c$ and hence, that the loss peaks shift to lower temperatures. Figure 2 reveals that even at the highest frequencies the peak in $\sigma'(T)$ is not located above T_c which makes the determination of the relaxation times above T_c impossible. A shift of the relaxation feature to low temperatures corresponds to an instantaneous decrease of the relaxation time when heating above T_c. We propose the following explanation for this finding. At temperatures $T > T_c$ where isotropic reorientation prevails, the molecules are able to use the optimal "path" when reorienting in response to the field, i.e., they can avoid as much steric hindrance as possible. However, below T_c, the reorientation paths are restricted which forces the molecules to overcome higher potential barriers and results in a longer relaxation time. It follows that a rotation around, at least, one axis which is not parallel to the direction of the dipolar moment should be restricted. However, the restriction of the molecular reorientations below T_c still allows the molecules to fully respond to the field. Hence, the peak height and the height of the relaxation step in $\epsilon'(T)$ are almost unaffected of the phase transition, as observed in Figs. 1 and 2.

Now we want to address the question of additional phase transitions. At first there is an anomaly in $\epsilon'(T)$ at $T \approx 190$ K and 121 Hz (Fig. 1). However, as this feature is seen at low frequencies only and as there is no corresponding anomaly in $\sigma'(T)$ (Fig. 2) we think it cannot be taken as the indication of a phase transition. Another anomaly seems to show up, independent of frequency, at 160 K in $\sigma'(T)$ (Fig. 2, indicated by arrow). Interestingly, there are various reports of an anomaly in this region from Raman,[7,8] NMR,[4] and specific heat[1,6] measurements. From the Raman results, a transition at 165 K into a metastable statically disordered state has been suggested,[7,8] while the specific heat results point towards a first order phase transition at a slightly lower temperature of 158 K.[6] At first glance the dielectric constant reveals no anomaly at this temperature (Fig. 1). However, at 160 K, ϵ' is mainly determined by its high-frequency limit, ϵ_∞. We therefore subtracted ϵ_∞ from ϵ'. The results are shown in Fig. 3 in a semilogarithmic scale. Indeed, at 160 K an anomaly shows up (arrow in Fig. 3), which we observed in all samples investigated. The cooling rates during the various measurements varied between 0.2 and 1 K/min with no effect on the temperature of the anomaly at 160 K. This finding, together with the fact that a freezing of reorientational motion should show up as a pronounced relaxational effect in the dielectric properties, makes it questionable to characterize the anomaly at 165 K as a glasslike transition as suggested by Bukalov *et al.*[8] An alternative explanation would be a phase transition where the rotation around an axis parallel (or nearly parallel) to the dipolar moment is restricted which would explain its small effect on the dielectric properties. The inset of Fig. 3 demonstrates the absence of any anomaly in $\epsilon'(T)$ at lower
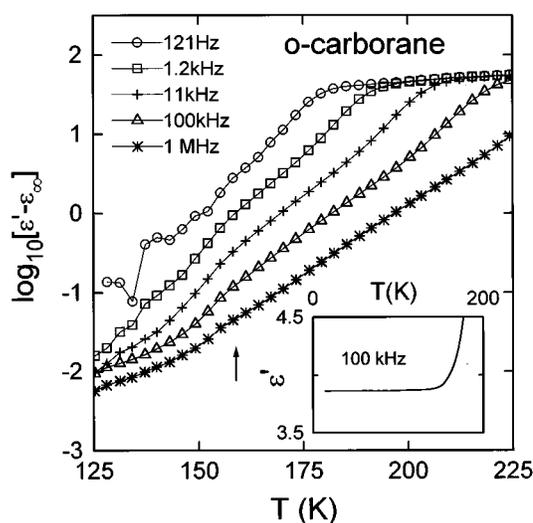
FIG. 3. Temperature dependence of the dielectric constant, ϵ', subtracted by the high-frequency/low-temperature limit of the dielectric constant, ϵ_∞. ϵ_∞ has been determined by extrapolation of each curve to low temperatures. The arrow indicates the anomaly near 160 K. The lines connect the data points. The inset shows the temperature dependence of ϵ' for 100 kHz at temperatures down to 12 K.

temperatures down to 10 K which has been found for all frequencies investigated. Obviously, on the time scale given by the measuring frequencies all dipolar active reorientational motions of the *ortho*-carborane molecules have completely frozen at temperatures below the relaxation step.

B. The relaxation process

In this section, we want to characterize the relaxation feature in *ortho*-carborane in more detail. Figure 4 shows the frequency dependence of the imaginary part of the dielectric constant, ϵ'', for various temperatures in a semilogarithmic plot. As expected from the temperature dependences of ϵ' and σ', for $T < T_c$, well developed loss peaks show up which shift through the frequency window with changing temperature. The peaks are significantly broader than expected for a monodispersive and/or single-exponential relaxation process and exhibit an assymetric shape. At temperatures above T_c (282 K in Fig. 4) only an increase of ϵ'' can be observed
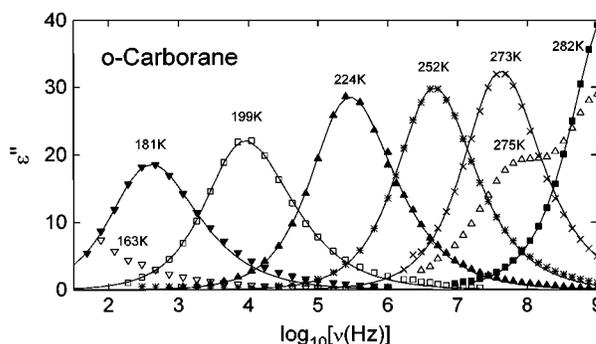
FIG. 4. Frequency dependence of the loss, ϵ'', for various temperatures. The lines are the results of fits using the Fourier transform of the KWW function.
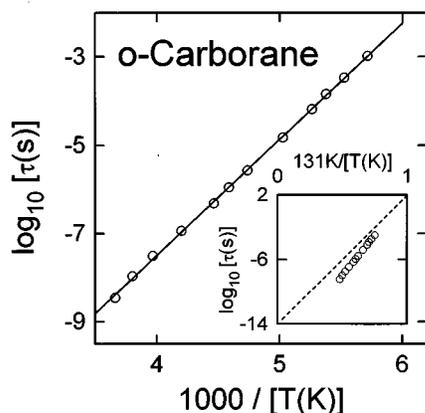
FIG. 5. Temperature dependence (Arrhenius representation) of the relaxation time τ_{KWW} as obtained from fits of $\epsilon''(\nu)$ with the Fourier transform of the KWW function. The solid line is the result of a fit using the Arrhenius law. The inset demonstrates the deviations of the relaxation times of *ortho*-carborane from maximal strong behavior (dashed line).

which exhibits the same slope as seen at the left side of the loss peaks below T_c. At the highest frequencies investigated indications of a saturation show up. These findings are indicative for a steplike decrease of the relaxation time when increasing the temperature above T_c as already suggested in the previous section. The frequency sweep performed at 275 K, i.e., very near the phase transition, obviously can be explained by a coexistence of both phases which leads to a double-peak structure.

In the physics of disordered materials loss peak data are usually described by the Fourier transform of the Kohlrausch–Williams–Watts (KWW) function, $\phi(t) = \phi_0 \exp(-t/\tau_{KWW})^\beta$. β is the stretching exponent, characterizing the nonexponential behavior. The value of β determines the width and assymetry of the relaxation peak. The results of fits using this function are shown as solid lines in Fig. 4. A good agreement of fit and data could only be achieved up to frequencies approximately 1.5 decades above the peak maximum. At higher frequencies the fit clearly underestimates the measured loss, a finding which has also commonly been observed in structural glasses.[17]

Figure 5 shows the temperature dependence of the relaxation rate τ_{KWW} in an Arrhenius representation. In the temperature and frequency range investigated, the relaxation dynamics behaves thermally activated with an energy barrier of 0.52 eV and an unphysically high attempt frequency of 2×10^{17} Hz. The value of the energy barrier is in good agreement with the value of 0.53 eV found by Pilet *et al.*[15] but in marked disagreement to the findings from NMR measurements[1–5] where values between 0.19 and 0.42 eV have been reported. However, if the relaxation process has polydispersive character as is suggested by our results (see below) the determination of the energy barrier from the temperature dependence of the spin–lattice relaxation time, T_1, should be restricted to the high temperature wing of the T_1 minimum. The resulting value of 0.38 ($\pm$0.05) eV still is significantly lower than the 0.53 eV found by us. This can be explained having in mind, that in dielectric experiments only

energy barriers connected to "dipolar active" reorientations of the molecules contribute, while the NMR results monitor all reorientations.

At first glance, the finding that the relaxation time of the reorientational motion of *ortho*-carborane behaves thermally activated over a relatively broad frequency range seems to characterize this material as "strong" glass former in the strong-fragile classification scheme of Angell.[18] However, the unphysically high attempt frequency of $\tau_0 = 2 \times 10^{17}$ Hz makes it highly probable that there are deviations from Arrhenius behavior at higher temperatures. To plot the temperature dependence of the relaxation time in the scheme given by Angell [i.e., $\log_{10}(\tau)$ vs T_g/T, T_g the glass temperature] we estimated the glass temperature T_g from an extrapolation of $\tau(T)$ to $\tau_g = 100$ s. In the inset of Fig. 5, we show the resulting plot. The dashed line indicates pure Arrhenius behavior with the minimum fragility parameter of 16,[19] the circles show our dielectric results. Despite some uncertainty concerning the determination of the glass temperature it becomes clear from the inset of Fig. 5 that *ortho*-carborane deviates significantly from the maximum strong behavior as represented by the dashed line. A fragility parameter of $m \approx 20$ can be estimated from the slope of the curve[19] which characterizes *ortho*-carborane still as a strong glass former. Böhmer *et al.*[19] have recently demonstrated that the fragility is related to the nonexponentiality of the relaxation process in a variety of glass formers. With $m \approx 20$ and $\beta \approx 0.8$ (see below), *ortho*-carborane fits very well into the correlation found by Böhmer *et al.*[19] This is in contrast to the findings in most orientationally disordered crystals, which are usually mixed crystals. In these systems, the observed deviations from the above mentioned relation is usually ascribed to the existence of random fields due to substitutional disorder.[20] This is supported by the finding that *ortho*-carborane and cyclo-octanol,[21] which are pure materials, fit well into the scheme found by Böhmer *et al.*[19] However, in C_{60} a very broad but symmetric distribution of relaxation times has been found[10–12] while its relaxation dynamics behave thermally activated over a broad frequency and temperature range.[9–11]

The remaining fitting parameters, the stretching exponent β and the relaxation strength $\epsilon_s - \epsilon_\infty$ are shown in Fig. 6. β clearly is smaller than 1 at all temperatures, i.e., the relaxation process is of polydispersive character. In addition, β decreases with decreasing temperature, a behavior which commonly is found in supercooled liquids. The relaxation strength exhibits a marked increase with temperature (lower frame of Fig. 6). This finding points towards cooperative motions of molecules or even to the onset of long-range orientational order. Cooperative reorientational motion in *ortho*-carborane has already been suggested by Baughman[1] on the basis of the finding that the intermolecular nearest neighbor distance is significantly smaller than the molecular diameter. In addition, the temperature dependence of the relaxation strength seems to reveal an anomaly near 230 K. However, this anomaly most probably is due to a not perfect matching of high (>1 MHz) and low frequency (<1 MHz) results which gives the highest error of fitting parameters
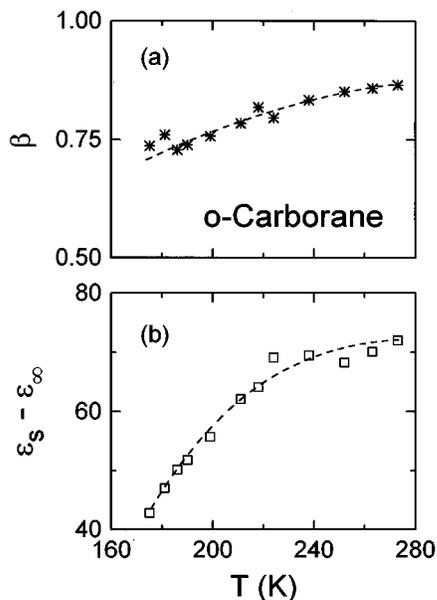
FIG. 6. Temperature dependence of the stretching parameter β (a) and of the relaxation strength $\epsilon_s - \epsilon_\infty$ (b) as obtained from fits of $\epsilon''(\nu)$ using the Fourier transform of the KWW function. The lines are drawn to guide the eyes.

FIG. 7. Frequency dependence of the real part of the conductivity, σ', for various temperatures above 238 K. The inset shows the frequency dependence of the dielectric constant, ϵ', for 350 and 381 K. The lines are the results of fits using the UDR, performed simultaneously on $\sigma'(\nu)$ and $\epsilon'(\nu)$.

when the peak is located near 1 MHz as is the case for 230 K.

Now we want to address the question if the transition into an orientationally disordered state claimed to be found by Bukalow *et al.*[7,8] at 165 K would be consistent with our findings of an orientational slowing down of dipolar degrees of freedom. It is suggestive to assume that the relaxational process detected in the present work is due to the same freezing of orientational order as the transition found by Bukalow *et al.* The temperature of this transition should depend on the time scale given by the measurement procedure. While in our dielectric experiments the characteristic time scale is set by the measuring frequency we can assume that in the Raman experiments of Bukalow *et al.* it is set by the cooling rate. In order to compare the time scales of both experimental methods, we assign a characteristic time τ_c to the cooling rate by employing the empirically found relation that 10 K/min corresponds to $\tau = 200$ s.[22] This leads to $\tau_c \approx 1.2 \times 10^4$ s for a cooling rate of 10 K/h as used by Bukalow *et al.*, which should give a measure for the dynamics of the dipoles at 165 K. However, from $\tau(T)$ as determined in the present work (Fig. 5) the relaxation rate at 165 K can be estimated as 10^{-2} s. Therefore, we conclude that the anomaly at 165 K found by Bukalow *et al.* is not connected with the orientational freezing observed in our dielectric experiments.

C. Charge transport

As already mentioned above, at low frequencies and high temperatures the electric response of *ortho*-carborane is dominated by conduction processes. In Fig. 7, we show the frequency dependence of σ' or for $T > 238$ K in a double-logarithmic plot. Two characteristic behaviors can be observed: At low temperatures (238 and 271 K), $\sigma'(T)$, reveals
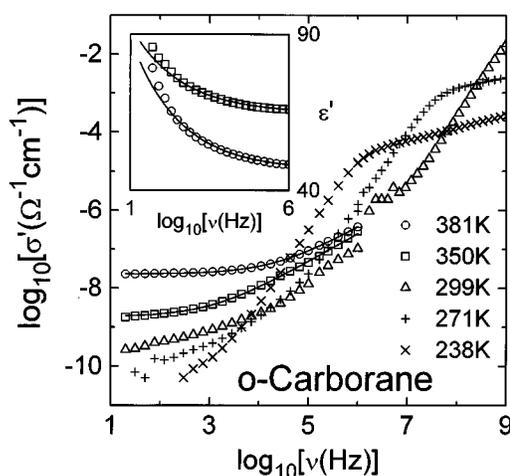
a well defined change of slope at high frequencies. For these temperatures and frequencies $\nu > 1$ kHz, $\sigma'(T)$ can be represented by two power laws. The frequency where the slope changes abruptly corresponds to the peak position in the $\epsilon''(\nu)$ representation (Fig. 4). At higher temperatures, $\sigma'(T)$ approaches a constant, frequency-independent saturation value at low frequencies and increases with constant slope for higher frequencies (ac conductivity). This behavior, seen nicely for 350 and 381 K in Fig. 7, is usually found in disordered conductors like amorphous semiconductors or ionic conductors and is the fingerprint of charge transport by hopping processes.[23,24] It can be parameterized according to $\sigma' = \sigma_{dc} + \sigma_0 \nu^s$ for which the expression "universal dielectric response" (UDR) has been termed.[24] σ_{dc} denotes the dc conductivity leading to a saturation of $\sigma'(\nu)$ at low frequencies. Using $\sigma'' = \epsilon_0 \epsilon' \omega$ and the Kramers–Kronig relation, the dielectric constant is given as $\epsilon' = \tan(s\pi/2)\sigma_0 \nu^{s-1} + \epsilon_p$. Here, ϵ_p has been added which denotes the contributions due to nondiffusive processes and which, in the case of *ortho*-carborane, for high temperatures is determined mainly by the dipolar reorientation of the molecules. The lines included in Fig. 7 and in the inset of Fig. 7, showing $\epsilon'(\nu)$ at high temperatures, are the results of fits using the UDR. A reasonable good agreement of data and fit has been obtained. The resulting exponent s has a value of 0.72 for both curves fitted (real and imaginary parts have been fitted simultaneously) which lies in the range found in other hopping systems.[23,24] However, to get detailed information about the hopping process involved, measurements at higher temperatures are necessary.

IV. CONCLUSIONS

We have investigated the dielectric properties of *ortho*-carborane in a broad frequency range. At 275 K, we find clear indications for a phase transition which has been observed already by other techniques.[1–8] Above 275 K, the

ortho-carborane molecules undergo fast and almost isotropic reorientations with a frequency larger than 1 GHz. At $T_c \approx 275$ K, the reorientation is partly restricted and the dynamics of the remaining reorientational motion is reduced. At temperatures below T_c, the remaining dipolar active reorientational degrees of freedom freeze in on the time scale of the measuring frequencies which leads to well developed relaxation features in real and imaginary part of the dielectric constant.

The dielectric response can be presented using the KWW function which describes the nonexponential decay in the time domain. However, at frequencies well above the peak maximum of $\epsilon''(\nu)$, we find marked deviations from KWW behavior, a characteristic feature found in many glass forming liquids.

At 160 K, the dielectric properties reveal a small anomaly that has also been observed with other techniques.[6-8] Presumably, in this low-temperature phase transition molecular reorientations around an axis parallel (or almost parallel) to the dipolar moment become restricted. According to the results of Bukalov *et al.*,[7,8] *ortho*-carborane freezes into a metastable, disordered state at low temperatures. The dynamics of the dipolar relaxation process behaves thermally activated over 6 decades of frequency with an energy barrier of 0.52 eV. Our findings are not compatible with the 165 K reported as glass temperature by Bukalov *et al.*,[7,8] a discrepancy for which we have no explanation.

An unphysically high attempt frequency of 2×10^{17} Hz points towards deviations from pure Arrhenius behavior. In the classification scheme of Angell *et al.*[18] the fragility index[19] can be estimated as $m \approx 20$ characterizing *ortho*-carborane as strong glass former ($m = 16$ Arrhenius behavior). The relaxation process is moderately polydispersive with a width parameter β_{KWW} of approximately 0.8. With these values for m and β_{KWW}, *ortho*-carborane fits well into the correlation scheme of Böhmer *et al.*,[19] where the polydispersivity and fragility are related to each other.

From the high temperature and low frequency results, we found that hopping processes lead to macroscopic charge transport in *ortho*-carborane, similar to the findings in C_{60} and C_{70}.[10,11] However, to get more detailed informations about the hopping mechanism, further experiments are necessary.

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