Two glass transitions in ethanol: a comparative dielectric relaxation study of the supercooled liquid and the plastic crystal

1998 J. Phys.: Condens. Matter 10 8155

(http://iopscience.iop.org/0953-8984/10/37/005)

J. Phys.: Condens. Matter **10** (1998) 8155–8171. Printed in the UK PII: S0953-8984(98)94347-8

Two glass transitions in ethanol: a comparative dielectric relaxation study of the supercooled liquid and the plastic crystal

S Benkhof, A Kudlik, T Blochowicz and E Rössler
Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany

Received 14 May 1998

Abstract. Ethanol is known to form two different kinds of glassy state, namely a structural glass and a glassy crystal, both showing the same glass transition temperature T_g. The molecular dynamics in the different phases (supercooled liquid/plastic crystal) and during the corresponding phase transition is studied by dielectric spectroscopy in the frequency range 10^{-2} Hz–3×10^{9} Hz (30 K–250 K). Extracting the time constant, width parameter and relaxation strength of the main relaxation (the α-process), very similar dielectric loss is found in both phases, including also the high-frequency wing. Comparing the temperature dependence of the time constants τ_α, the plastic crystal exhibits a less fragile behaviour. Additionally, a secondary relaxation is detected, again essentially the same in the two glassy states. We conclude that the motional mechanisms probed in the plastic crystal and in the supercooled liquid state are very similar.

1. Introduction

More than 20 years ago, Haida *et al* [1] performed a detailed thermodynamic study of ethanol, and found that besides the monoclinic ordered crystal ($T_m = 159$ K) another metastable phase exists, which will be called crystal II in the following. A small entropy of fusion for the transformation from the liquid to this phase together with a glass transition phenomenon at $T_g = 97$ K led them to the assumption that crystal II is a plastically crystalline phase. This means that the molecules exhibit rotational motion on a lattice formed by their centres of mass.

As experience shows, at least two different molecular properties favour the formation of a plastically crystalline phase. First, sterical hindrances for reorientation should be small. This is the case when the molecules have high symmetry, like benzene. Also, approximately centrosymmetric planar molecules (e.g. hexasubstituted benzenes [2, 3]), or globular molecules (e.g. cyanoadamantane [4], polar substituted ethanes [5]) exhibit a high tendency to perform reorientational processes in the crystalline solid. Second, systems with intrinsic disorder, for example due to different molecular conformers as in the case of cyclic alcohols [1, 6], often tend to form plastic crystals. In the special case of ethanol, both molecular properties mentioned are present. The shape of the molecule is approximately globular and there are different conformers. In the light of this, it seems to be no longer surprising that ethanol forms a plastically crystalline phase, and indeed in the past direct experimental evidence was found: NMR relaxation measurements [7] proved the existence of rotational motion in crystal II and x-ray experiments [8] showed that crystal II is a crystal with cubic symmetry, like most plastic crystals. Crystal II is metastable with respect to crystal I, the latter being a normal ordered crystal phase with a monoclinic lattice and space group Pc [9].

On cooling a plastic crystal, the rotation of the molecules on the lattice points slows down and becomes frozen at low temperatures. In the case of highly symmetric molecules like benzene this frozen state cannot be distinguished from an ordered crystal, as all accessible sites are energetically equivalent. On the other hand, systems with slightly reduced molecular symmetry, in the sense that different accessible orientations are energetically distinguishable [10], may lead to static disorder at low temperatures. In these cases, corresponding to the freezing in supercooled liquids, the transition from dynamic to static orientational disorder is called a glass transition and consequently the plastic crystal below T_g is called a glassy crystal [11]. Like for structural glasses, the glass transition temperature T_g is defined via a step in the specific heat. Here the system falls out of equilibrium, i.e. it cannot relax on typical experimental timescales. In the case of ethanol the remarkable scenario is found that a structural glass as well as a glassy crystal can be formed, the two forms having the same caloric glass transition temperature $T_g = 97$ K [1].

As noted, glassy crystals in general are metastable phases. There always exists a more stable ordered crystal. This situation is similar to that for structural glasses and so we believe that glassy crystals are very promising as regards improving the understanding of the physical phenomena associated with the glass transition. In contrast, both orientational glasses, which are always mixed crystals, and spin glasses have no ordered ground state. In this context molecular dynamics simulations on systems comparable to plastic crystals—for example, those described in [12], where infinitely thin hard needles fixed to a regular fcc lattice were studied—are interesting. Increasing the needle length leads to a divergence of the correlation times describing the decay of orientational correlations, a behaviour that can be interpreted as a glass transition. The scenario of this glass transition is found to be very similar to that observed in structural glasses, and it is a purely dynamical feature, since the static properties of the system are known to be independent of the needle length.

The possibility of comparing two different glassy states, the structural glass and the glassy crystal, of a given substance under the same thermodynamic conditions is very attractive for both theoreticians and experimentalists, and several interesting comparative studies of ethanol have been published. Ramos *et al* [13–15] showed that the low-temperature specific heat $c_P(T)$ in the glassy crystal is quite similar to that of the structural glass of ethanol and shows all the peculiarities typically found in disordered systems: a linear increase of $c_P(T)$ below 3 K ascribed to tunnelling states and a maximum in $c_P(T)/T^3$ at higher temperatures ($T \approx 5$ K). This excess density of states is rediscovered in inelastic neutron scattering data as the so-called boson peak at around 1 THz in both structural glass and glassy crystal [16]. The cubic structure of the plastically crystalline phase was verified in neutron diffraction experiments [17] and a detailed study of static orientational and translational correlations [18] revealed that intermediate-range order in the structural glass arises mainly from positional correlations; orientational correlations are confined to next-nearest neighbours, at most. A pressure-dependent phase diagram of ethanol was published in [19].

Although thermodynamic and structural aspects of the different phases of ethanol have been thoroughly examined, knowledge about the rotational motion of the molecules in crystal II remained poor. Surprisingly, neither relaxation times, nor the spectral shape of the relaxation are published, although Haida *et al* [1] have stated in their work on glassy crystalline ethanol: '… dielectric measurements for both glassy liquids and glassy crystals will illuminate the nature of vitrification'. In the present contribution we present data on the dielectric relaxation of ethanol for the liquid, the supercooled liquid, crystal II ($T > T_g$)

and the two glassy states ($T < T_g$) in order to reveal information about the reorientational motion in the different phases. As far as we are aware, this is the first dielectric relaxation study comparing the glass transition in the liquid and the plastically crystalline state in one and the same substance. Other studies of liquid and supercooled ethanol with dielectric spectroscopy can be found in references [20–24] but apparently no spectra for around T_g have been published.

2. Experimental details

The experiments were performed using a frequency response analyser, SI 1260 (Solartron), in connection with a current-to-voltage converter (Novocontrol; 10^{-2} Hz–10^7 Hz). The sample was filled into a capacitor consisting of two glass plates covered with gold as described in [25]. At higher frequencies (3×10^6 Hz–10^9 Hz) the reflection coefficient of a coaxial transmission line terminated with a plate capacitor filled with ethanol was measured with an HP 8753C network analyser. As the device under test is not a perfect capacitor it was necessary to perform an open/short compensation. The ethanol (CH_3CH_2OH) was purchased from Merck (99.9%) and used without further purification.

Ethanol can be easily supercooled only down to 140 K. In order to bypass crystallization below 140 K, we quenched the sample from room temperature to 30 K with cooling rates >50 K min^{-1} [16]. Then we made measurements up to $\approx$110 K, before crystallization occurs. Following reference [16], the plastically crystalline phase (crystal II) is formed by annealing the sample in a narrow temperature interval around 105 K after a quench below the glass transition temperature T_g of the supercooled liquid and reheating.

3. Results and analysis

3.1. Dielectric spectra and the phase transition

Figure 1 shows the dielectric loss (i.e. the imaginary part of the relative permittivity $\hat{\varepsilon}(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$) of ethanol in the liquid, the supercooled liquid and the structural glass as a function of frequency. As the temperature is lowered, the main relaxation peak shifts to lower frequencies, starting from 1 GHz [22] at room temperature and reaching 0.01 Hz at $T_g = 97$ K. Around 80 K a broad secondary relaxation process emerges in our frequency window.

As already mentioned in the experimental section, the plastic crystalline phase is formed by annealing the sample in a narrow temperature interval around 105 K. In figure 2 the temporal development of the dielectric loss at 105 K is shown. Starting from the supercooled liquid state with a loss peak situated at 3 Hz, a shoulder on the low-frequency side develops and after ten hours the transformation into crystal II is complete with a new main relaxation peak at around 0.1 Hz. Besides a change of the time constant, the spectra for the two phases are very similar, already indicating that the molecular dynamics of the plastic crystal and that of the supercooled liquid probed by dielectric spectroscopy are essentially the same. As $\varepsilon''(\nu, t)$ during the transformation can be described by a weighted superposition of the two limiting spectra (cf. figure 2), namely the main relaxation of the supercooled liquid and that of neat crystal II,

$$\varepsilon''(\nu, t) = N(t)\varepsilon''_{\text{liquid}}(\nu) + (1 - N(t))\varepsilon''_{\text{plastic crystal}}(\nu) \tag{1}$$

we conclude that during the transformation from the supercooled liquid to the plastic crystal two coexisting phases are present, which can be seen directly in the data as all of the spectra

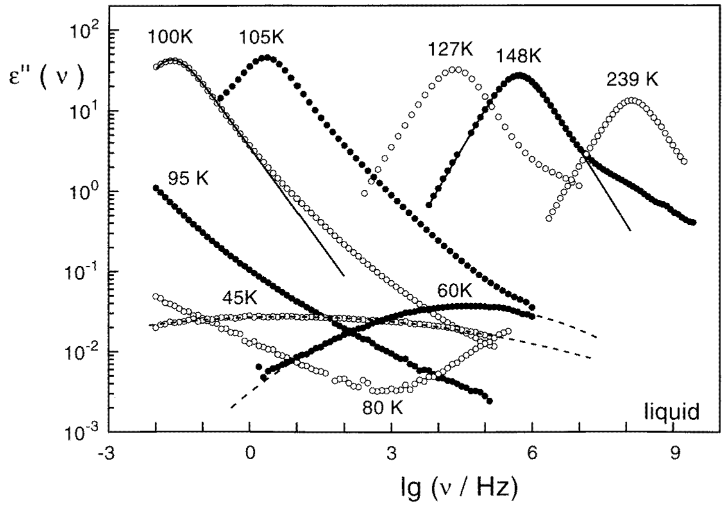

Figure 1. The imaginary part $\varepsilon''(\nu)$ of the dielectric susceptibility of ethanol as a function of frequency ν in the liquid, supercooled and glassy states (selected data). The solid lines are fits obtained using a Cole–Davidson function to describe the main relaxation; the dashed lines are fits obtained using a Gaussian distribution of activation enthalpies (equation (6)) for the secondary relaxation.

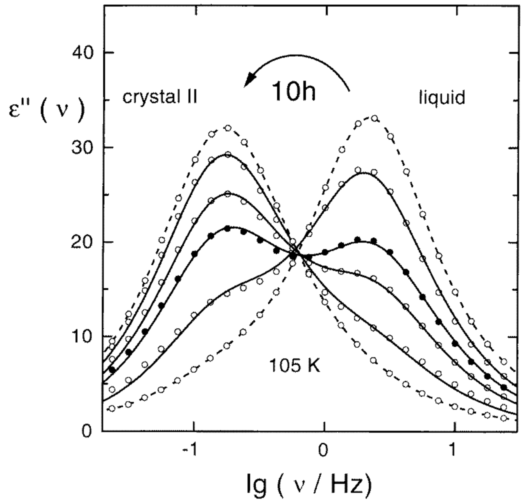

Figure 2. The development of $\varepsilon''(\nu)$ with time at 105 K (circles). During the transformation the spectra can be described as a weighted superposition (solid lines) of the spectra of the supercooled liquid and the plastic crystal (dashed lines). After 10 h the transformation from the supercooled liquid to crystal II is complete.

have a common point. The weighting factor $N(t)$ specifies the fraction of the molecules which are in the supercooled liquid phase. The results of the analysis of our data are shown in figure 3. The transformation curve is non-exponential and not at its steepest at shortest times, an observation that may indicate that a nucleation process is involved in the formation of crystal II. The inset of figure 3 shows the transformation times τ_T

($N(\tau_T) \equiv 0.1$) from our experiments compared with those (identically defined) of Fischer *et al* [26] derived by applying neutron scattering. There is a good agreement between the results of the different techniques, and so we conclude that the phase transition observed with dielectric spectroscopy does indeed show the growth of crystal II. Taking together the transformation times from both experiments and assuming thermally activated behaviour, a formation energy of 37.4 kJ mol^{-1} is found. This value explains the small temperature window, where the transformation can be followed experimentally.

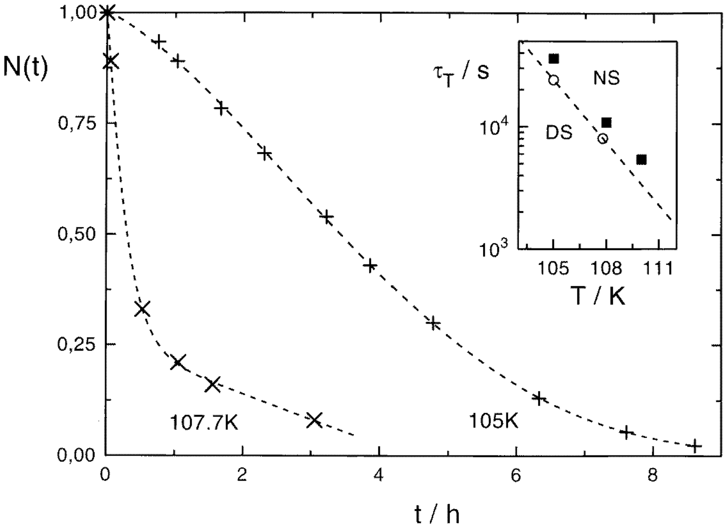

Figure 3. The weighting factor $N(t)$ which specifies the fraction of the molecules which are still in the supercooled liquid phase for two different temperatures. The dashed lines are guides for the eye. In the inset, typical transformation times τ_T ($N(\tau_T) = 0.1$) from our experiments (DS) compared with the results of Fischer *et al* [26] derived from neutron scattering (NS) are shown. Here the dashed line represents a fit assuming thermally activated behaviour.

Crystal II is stable with respect to the ordered crystal I on typical timescales of a DSC experiment (2 K min^{-1}) up to 129 K [19], but at around 110 K we already observed a slight tendency to transform on long timescales (hours). This explains why the dielectric spectra of the plastically crystalline phase of ethanol (cf. figure 4) are restricted to temperatures up to 119 K, where already a large portion of the sample has transformed to the ordered crystal I as can be seen by the loss of signal. Below T_g, like in the structural glass, a broad secondary relaxation is observed (cf. figure 4).

In the next two sections the temperature evolution of the main and the secondary relaxation in both disordered phases is discussed.

3.2. *The main relaxation*

Before discussing the spectra of the main relaxation, we want to make some general remarks concerning dielectric spectroscopy in crystalline solids. Here the question arises of how to interpret experiments on powder samples, as in our case of crystal II, where we have a polycrystalline sample. In general, the complex relative permittivity $\hat{\varepsilon}(\nu)$ of crystals is anisotropic as the rotation of the molecules is anisotropic. In this case it is necessary to use single crystals for the experiment, because in powder samples an average of the different lattice directions is measured. The only exception are cubic lattices, where in most cases the molecules rotate isotropically and here dielectric relaxation experiments on polycrystalline samples give direct information about the dielectric properties of the substance studied [27]. So, because of the cubic lattice the spectra of crystal II can be easily interpreted.

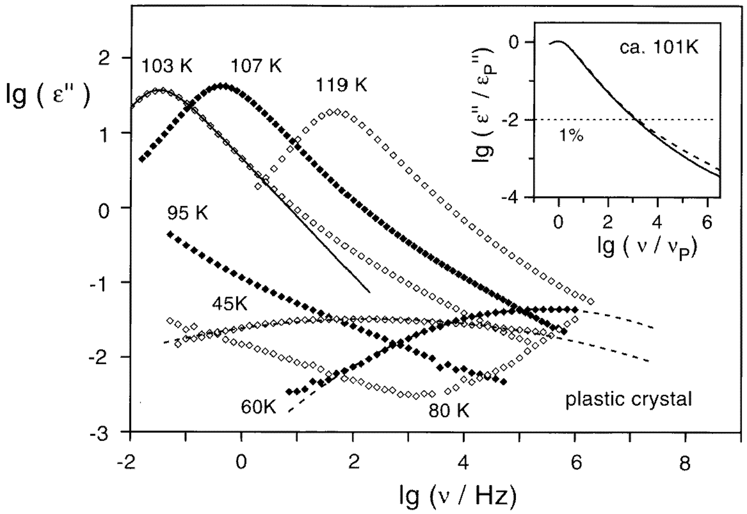

Figure 4. The imaginary part $\varepsilon''(\nu)$ of the dielectric susceptibility of ethanol in the plastically crystalline and glassy crystalline states (selected data). The solid lines are fits obtained using a Cole–Davidson function to describe the main relaxation; the dashed lines are fits obtained using a Gaussian distribution of activation enthalpies (equation (6)) for the secondary relaxation. In the inset the spectra of the supercooled liquid (solid line) and the plastic crystal (dashed line) at $\simeq$101 K after normalizing the relaxation peak are shown.

In order to analyse the development of the main relaxation with temperature, we applied the empirical *ansatz* of Cole and Davidson (CD) [28, 29], often used to interpolate dielectric spectra in supercooled liquids:

$$\varepsilon''(\nu) = -\mathrm{Im}(\Delta\varepsilon_\alpha/(1 + \mathrm{i}\,2\pi\nu\tau_{CD})^{\beta_{CD}}). \tag{2}$$

This function gives a fair description of $\varepsilon''(\nu)$ at around the maximum, but certainly fails to describe the high-frequency wing. In any case, it gives a good estimate for the correlation time $\tau = \tau_{CD}\beta_{CD}$ and the relaxation strength $\Delta\varepsilon_\alpha$. Figures 1 and 4 show some typical fits of the CD function (solid lines) and in figures 5 and 6 the temperature dependences of its parameters, namely the correlation time τ, the width parameter β_{CD} and the relaxation strength $\Delta\varepsilon_\alpha$, are presented.

3.2.1. The correlation time τ. Starting from room temperature where ethanol has a correlation time of around 160 ps [22], the time constant of the main relaxation of liquid ethanol (cf. figure 1) follows an Arrhenius law over a large temperature range (145 K $< T <$ 293 K), explicitly $\tau(T) = \tau_0 \exp(E_a/RT)$ with $E_a = 17.5$ kJ mol^{-1}. Only below 145 K is a stronger, non-Arrhenius slowing down observed, leading to a fragility parameter

$$m = \left.\frac{\mathrm{d}\,\mathrm{lg}(\tau)}{\mathrm{d}(T_g/T)}\right|_{T=T_g} \cong 60 \tag{3}$$

which lies in the intermediate-fragility range, and is comparable to that of glycerol. The high-temperature Arrhenius law is typical of monohydroxy alcohols [21], whereas for most other organic glass formers a Vogel–Fulcher–Tammann behaviour $\tau \propto \exp(B/(T - T_0))$ describes the data over a large temperature range.

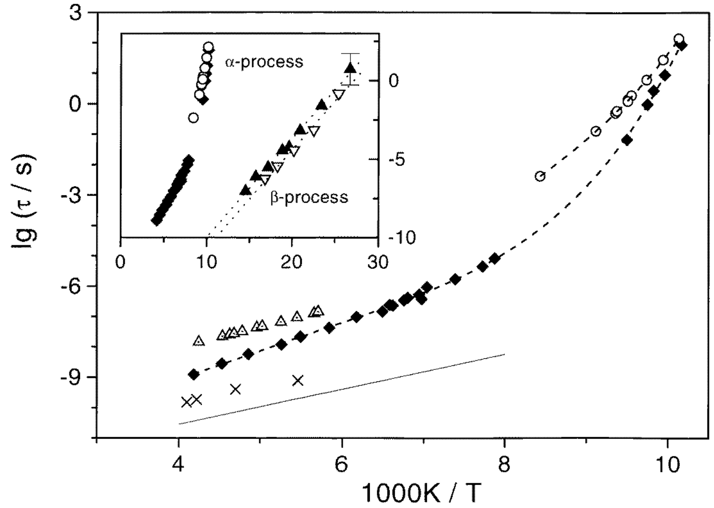

Figure 5. The time constants τ as a function of the inverse temperature for the main relaxation in the supercooled liquid (full diamonds) and for the plastically crystalline state (open circles). For comparison, relaxation times derived from mechanical relaxation [30] (crosses), from viscosity measurements [33] (dotted triangles) and ^{1}H-NMR [7] (solid line) are also shown. Dashed lines are guides for the eye. The inset shows $\langle \lg(\tau_\beta) \rangle$ for the secondary relaxation for both phases (open triangles: glassy crystal; filled triangles: structural glass). Here the dotted lines represent thermally activated behaviour.

Comparing the correlation times at a given temperature obtained from other relaxation methods (^{1}H-NMR [7], mechanical relaxation [30]) with those from dielectric spectroscopy, differences of more than two decades are found (cf figure 5). Also, the activation energies measured for the high-temperature Arrhenius behaviour determined with various techniques (viscosity [31–34], self-diffusion [35–37], ultrasound [30] and NMR [7, 38, 39]) are generally smaller (12.5 ± 2 kJ mol^{-1}) than the value 17.5 ± 0.4 kJ mol^{-1} found with dielectric spectroscopy (this work, [20, 24]). Here we just want to stress that the physical origin of the main relaxation in primary alcohols is controversial. In the discussion section, this question will be considered in detail.

Inspecting the correlation times $\tau(T)$ of the plastic crystal, we find that crystal II is less fragile ($m \cong 40$) than the supercooled liquid and that the $\tau(T)$ curves for the two supercooled phases intersect at approximately 97 K, which is exactly T_g as derived from specific heat measurements for both glassy phases [1]. Ethanol is not the only substance for which both glass transition temperatures are identical. The same scenario is found for cyclohexane [40], and for all other cases known differences of less than 15 K have always been found (1, 3-diphenyl-1, 1, 3, 3-tetramethyldisiloxane [41], 2-methyltetrahydrofuran [42]). Inspecting $\tau(T_g)$ we find $\simeq$500 s for both phases, a value only slightly higher than those typically found for simple organic glass formers, but lower than the atypical value $\tau(T_g) \approx 10^4$ s estimated for liquid 1-propanol [25].

3.2.2. The spectral shape of $\varepsilon''(\omega)$. β_{CD}, the width parameter of the CD function, is similar for the two phases studied, being around 0.8 at T_g and approaching 1 at high temperatures (figure 6(b)). At least in the fluid regime, this is typical of primary alcohols where usually a Debye relaxation ($\beta_{CD} = 1$) is observed [20]. In the well studied case of 1-propanol, also near the glass transition, $\beta_{CD} = 1$ is found [25], but for other alcohols, deviations from the Debye behaviour are reported [23]. Remarkably, the width parameter β_{CD} as derived with ultrasonic absorption studies is significantly smaller; explicitly, $\beta_{CD} = 0.4$ [30].

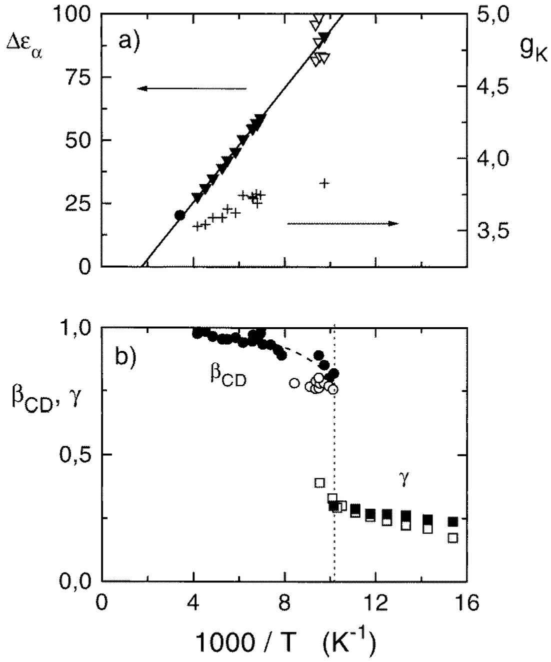

Figure 6. The parameters of the Cole–Davidson function as a function of $1000/T$. (a) Left-hand axis: the relaxation strength $\Delta\varepsilon_\alpha$ for the supercooled liquid (full triangles) and the plastic crystal (open triangles). The data point at room temperature (filled circle) has been derived from an evaluation of the data in [22]. The straight line represents the behaviour $\Delta\varepsilon_\alpha(T) = a + b/T$. Right-hand axis: the temperature dependence of the Kirkwood correlation factor g_K (+) as given by equation (5). (b) The width parameter β_{CD} (circles) and the exponent γ (squares) of the high-frequency power law of the main relaxation for the plastic crystal (open symbols) and the supercooled liquid (full symbols). The dotted line indicates T_g.

As mentioned, the CD function fails to describe $\varepsilon''(\nu)$ at high frequencies for both phases (cf. figures 1 and 4). These deviations have been known of for a long time [29], and since the work of Dixon *et al* [43] this so-called high-frequency wing has been assumed to be an intrinsic feature of $\varepsilon''(\nu)$ in glass-forming systems, although its origin is not yet understood. The high-frequency wing can be described as an additional power law with the exponent $\gamma < \beta_{CD}$, and one can interpret it [44] as the von Schweidler law [45, 46]. However, whether in the case of alcohols the spectral shape of the main relaxation including the high-frequency wing can be attributed to one single-relaxation process or whether there are two distinguishable contributions was in the case of n-propanol the subject of recent discussions [47, 25] (cf. also the discussion section).

Since, in contrast to many organic liquids, ethanol exhibits timescales of the main and secondary relaxation that are separated (cf. below), the high-frequency wing below T_g is not hidden by the secondary process over a broad temperature range and shows up as a power-law behaviour $\varepsilon''(\nu) \propto \nu^{-\gamma}$ with $\gamma < \beta_{CD}$. In order to evaluate our data in this regime we analysed the derivative $\mathrm{d}(\lg(\varepsilon''))/\mathrm{d}(\lg(\tau))$, and the such found exponent γ is shown in figure 6 as a function of temperature. Slight differences between the glassy crystal and the structural glass have to be stated. Coming from low temperatures, γ increases continuously, which is in contrast to the behaviour found for many structural glasses (e.g. glycerol) [44], for which γ is found to be independent of temperature when the sample has fallen out of equilibrium ($T \ll T_g$). Above T_g in crystal II, γ starts to increase more quickly with temperature, as observed for several other glass-forming substances [44], whereas in the supercooled liquid it cannot be determined, as, there, $\varepsilon''(\nu)$ is still curved at high frequencies. In order to compare the lineshape of the main relaxation in this temperature regime also, we plotted $\varepsilon''(\nu)$ for crystal II and the supercooled liquid around 101 K normalized to the relaxation peak (see the inset in figure 4). The two spectra are very similar; only in the high-frequency regime are small differences found. All in all, besides some minor differences in describing the high-frequency wing, we can state that the lineshapes of the main relaxation peaks for the supercooled liquid and the plastically crystalline phase are very similar. Finally we note that at T_g both exponents describing the spectral shape of the main relaxation at high frequencies can be determined unambiguously and we find $\beta_{CD}(T_g) = 0.8$ and $\gamma(T_g) = 0.3$ for both phases. Following Kim and Mazenko [48], a relationship between these two exponents can be derived, if one assumes the validity of the scaling procedure developed by Dixon *et al* [43]:

$$\frac{1+\gamma}{1+\beta_{CD}} = 0.72. \tag{4}$$

Indeed, equation (4) is fulfilled for ethanol at T_g.

3.2.3. The relaxation strength $\Delta\varepsilon_\alpha$.

The temperature dependence of $\Delta\varepsilon_\alpha$ is shown for both phases in figure 6(a). Discussing first the relaxation strength in the liquid phase, we find that $\Delta\varepsilon_\alpha(T)$ can be well described by $a + b/T$ ($a < 0$), a behaviour found for many organic glass formers, including alcohols [20]. Besides the temperature dependence, the absolute value of $\Delta\varepsilon_\alpha$ is of interest. It is mainly determined by the number density $N(T)$ of the molecules participating in the relaxation and their dipole moment μ, but also orientational correlations described by the Kirkwood correlation factor g_K [49] have an influence on the strength of the relaxation. $g_K(T)$ can be derived from the experimental $\Delta\varepsilon_\alpha(T)$ by applying the Kirkwood–Fröhlich equation:

$$g_K(T)\frac{1}{\varepsilon_0}\frac{N\mu^2}{9kT} = \frac{\Delta\varepsilon_\alpha(2\Delta\varepsilon_\alpha + 3\varepsilon_\infty)}{(\Delta\varepsilon_\alpha + \varepsilon_\infty)(\varepsilon_\infty + 2)^2}. \tag{5}$$

g_K is larger than 1 when the molecules tend to direct themselves with parallel dipole moments and smaller than 1 when anti-parallel ordering is preferred. For the evaluation of our data we assumed that the refraction index $n(T)$ is proportional to the mass density $\rho(T)$. Explicitly we used [50]

$$\rho(T)/(\mathrm{kg\ m^{-3}}) = 1043 - 0.866\ \mathrm{K^{-1}}\ T$$

and [31]

$$\mu = 5.5 \times 10^{-30}\ \mathrm{C\ m}.$$

ε_∞ was derived via the Maxwell equation $\varepsilon_\infty = n(T)^2$. For the absolute value of ε_∞, $n(297\ \mathrm{K})^{3\,\mathrm{THz}} = 1.4$ was used [51]. In the case of ethanol we find $g_K > 3.5$ below room temperature (figure 6), indicating strong ferroelectric correlations in the supercooled liquid, which presumably persist below T_g. The origin of these correlations can tentatively be connected with the presence of hydrogen bonds, as for many liquids with OH groups (e.g. glycerol) similar high values of g_K are reported [20]. On the other hand another interpretation for the high value of g_K might be the existence of additional transient dipole moments, formed for example by hydrogen bonds. In this case one of the assumptions leading to the Kirkwood–Fröhlich equation would not be fulfilled, namely that the dielectric susceptibility is only due to the reorientation of the molecule's permanent dipole vector; thus g_K would not be a measure for orientational correlations.

In figure 6 the relaxation strength $\Delta\varepsilon_\alpha$ of crystal II is shown and found to be the same as $\Delta\varepsilon_\alpha$ for the supercooled liquid within experimental error (≈10%). The scatter of the data points for crystal II reflects three different experimental runs where the phase transformation was followed. Again this indicates very similar motions for the two disordered phases.

3.3. *Secondary relaxation*

As already mentioned, we observed a secondary relaxation peak for the structural glass as well as for the glassy crystal. In figure 7 these data are shown on a linear $\varepsilon''(\nu)$ scale. Recalling the work of Johari and Goldstein [52, 53], who studied many organic glass formers below T_g, we want to stress that they came to the conclusion that the secondary or β-relaxation is an intrinsic feature of the glass transition. This has often been doubted [54, 55], but recently Kudlik *et al* [25, 56] gave new evidence for some general properties of the β-relaxation. For example, the mean activation enthalpy $\langle\Delta H_\beta\rangle$ of the β-process found for many glass-forming systems can be approximated by

$$\langle\Delta H_\beta\rangle \cong 24RT_g.$$

Therefore the β-relaxation seems to be of intermolecular origin, which is supported by the fact that rigid molecules like toluene or 3-fluor-aniline [25, 56] also show this process. However, there exist glass formers (e.g. glycerol) which do not exhibit a discernible β-process at all. Keeping these facts in mind we will now discuss the secondary relaxations of ethanol in the two glassy phases.

We analysed our data by assuming thermally activated Debye processes with a broad Gaussian distribution $g(\Delta H_\beta)$ of activation enthalpies ΔH_β [25, 54, 57, 58], which leads to the following approximation [54]:

$$\varepsilon''(\nu) = \Delta\varepsilon_\beta \frac{\sqrt{\pi}}{2W\ln(10)} \exp\left[-\left(\frac{\lg(\nu)-\lg(\nu_P)}{W}\right)^2\right]. \tag{6}$$

Here it is assumed that the distribution of correlation times is broad compared with the width of the Debye relaxation, an assumption that works well in the cases where $W > 2$ is found. W is the halfwidth of the loss peak on the logarithmic frequency scale, depending on the width σ of the activation enthalpy distribution via $W = \sigma/(RT\ln(10))$. ν_P denotes the position of the loss peak. $\langle\lg(\tau)\rangle = -\lg(2\pi\nu_P)$ defines an average logarithmic correlation time which is connected to the mean activation enthalpy $\langle\Delta H_\beta\rangle$ of $g(\Delta H_\beta)$ via

$$\langle\lg(\tau)\rangle = \lg(\tau_0) + \langle\Delta H_\beta\rangle/\ln(10)RT. \tag{7}$$

We emphasize that $\langle\lg(\tau)\rangle$ is not identical with $\lg\langle\tau\rangle$, where $\langle\tau\rangle$ is the correlation time defined via the integral over the correlation function. Equation (6) yields a satisfactory description of the spectral shape of the secondary relaxations for both phases (cf. figure 7). At high temperatures a power law was added to equation (6) in order to describe the whole

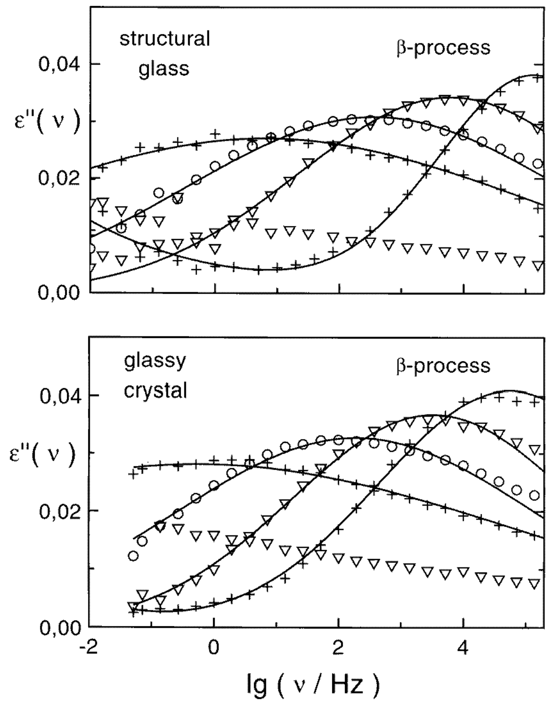

Figure 7. The imaginary part $\varepsilon''(\nu)$ of the dielectric susceptibility of ethanol in the structural glass (29 K, 43 K, 48 K, 53 K, 64 K) and the glassy crystalline state (29 K, 39 K, 45 K, 50 K, 55 K) showing the secondary relaxation process. The solid lines are fits to equation (6). At high temperatures an additional power law was added in order to take account of the high-frequency wing.

of the spectra including the high-frequency wing of the α-relaxation, which is also present below T_g.

Figure 5 shows the temperature dependence of $\langle \lg(\tau_\beta) \rangle$ for the structural glass and the glassy crystal and an Arrhenius temperature dependence of $\langle \lg(\tau_\beta) \rangle$ with an activation enthalpy of 11.7 ± 0.7 kJ mol^{-1} ($=14.6RT_g$) and 11.6 ± 1.2 kJ mol^{-1} ($=14.4RT_g$) and prefactors $\lg(\tau_0/\mathrm{s})$ of -16 ± 0.7 and -16.6 ± 1.4 are found, respectively. These values of the mean activation enthalpy are much lower than $24RT_g$, the value often found for the β-process, but the prefactor τ_0 is of the same order of magnitude as is found for many structural glass formers [56, 59], being smaller than the time constants usually observed for single particle dynamics. Comparing the timescales of the main and secondary relaxation, it becomes obvious that no merging of the two processes occurs, even at the highest temperatures. Thus it remains to be clarified whether the secondary relaxation in ethanol can be identified with a Johari-type β-process. Remarkably, in the organic glass former TPP (triphenyl phosphite) also, a secondary relaxation with such a low $\langle \Delta H_\beta \rangle$ was found in the structural glass as well as in the so-called glacial phase [60]. The strengths of both secondary relaxations in ethanol follow a Curie law with $\Delta\varepsilon_\beta T \approx 16$ K (cf. figure 8) to a good approximation.

Inspecting $W(T)$ for both glassy phases (figure 8) we find that we can approximately

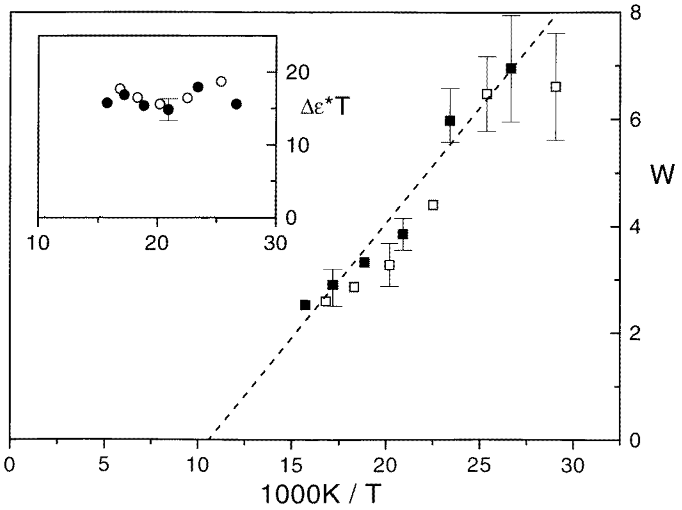

Figure 8. The temperature dependence of the parameters (relaxation strength $\Delta\varepsilon$: circles; width w: squares) describing the secondary relaxation (open symbols: glassy crystal; filled symbols: structural glass). The dashed line is a fit to equation (8).

describe the data with

$$W(T) = \frac{\sigma}{R\ln(10)}\left(\frac{1}{T} - \frac{1}{T_\delta}\right) \tag{8}$$

and $T_\delta > 0$, a behaviour also observed for the β-relaxation in simple organic liquids [61, 56, 62]. This finding differs from $W \propto T^{-1}$, the prediction of the model of a simple thermally activated process, and can be explained by a slight temperature dependence of the barrier height distribution [62], but also by introducing a distribution of activation entropies $g(\Delta S_\beta)$ with $\Delta S_\beta \propto \Delta H_\beta$, a kind of Meyer–Neldel rule [63, 64]. For details, see [56, 61]; here we just want to stress that besides the correct description of the experimentally found $W(T)$ it also leads to physically reasonable attempt frequencies of the order of 10^{11} Hz. For ethanol, $W(T)$ is similar in the two glassy phases, leading to $\sigma = 7 \pm 1.5$ kJ mol^{-1} and $T_\delta = 130 \pm 40$ K. The width of the activation enthalpy distribution σ is typical of the β-process, but T_δ is lower than the commonly observed $T_\delta \approx 2.4T_g$ [56].

Summing up, we found a secondary relaxation in both glassy phases of ethanol. The two processes show nearly the same temperature dependences of their parameter widths W, strengths $\Delta\varepsilon_\beta$ and peak frequencies ν_P, and thus we emphasize that this process is not influenced by the development of the crystal lattice of crystal II. The comparison of the secondary relaxation with the β-relaxation observed in many structural glasses and polymers showed some similarities. However, we have to state that the observed process is faster than the β-process, as the mean activation enthalpy $\langle\Delta H_\beta\rangle$ is found to be significantly smaller than $24RT_g$.

4. Discussion

Studying the dielectric loss of ethanol in the plastic crystal and the supercooled liquid, we found that the relaxation strength $\Delta\varepsilon_\alpha$ as well as the lineshape of the main relaxation is essentially the same for the two phases. Before drawing any conclusion, we want to discuss possible physical origins of the main relaxation peak in primary alcohols.

We recall that in the fluid regime of ethanol, different experimental techniques lead to different correlation times and width parameters (see the preceding section), and also the observed activation energy E_a for high temperatures found with dielectric spectroscopy (17.5 kJ mol^{-1}) is different from the value of 12.5 ± 2 kJ mol^{-1} found with many other techniques, for example viscosity measurements. The latter suggests that dielectric spectroscopy does not probe the structural relaxation. On the other hand, the results from viscosity and dielectric spectroscopy show the same correlation between the activation energy in the fluid regime and the molecular weight for the series of primary alcohols [20]: although the activation energies from methanol to octanol change by more than a factor of two, the ratio E_a^{DK}/E_a^{η} remains constant at 1.42 ± 0.05. Interestingly, the DC conductivity, a transport coefficient connected with translational diffusion, scales with the viscosity [20, 21] in this temperature regime. These facts suggest that the two methods, dielectric spectroscopy and viscosity measurement, probe different aspects of the same phenomenon. Translational and rotational motion seem to be coupled, but no longer via a linear relation for the time constants such as the Stokes–Einstein–Debye equation.

Although these somewhat puzzling findings have long been known of, their explanation is still controversial. Discussing data obtained by dielectric spectroscopy for liquid ethanol, Hassion and Cole [65] speculate that '... *the principal dispersion is attributed to reorientation of a molecule's OH moment by breaking of its intermolecular hydrogen bond* ...'. This is in contrast to considerations of Floriano and Angell [66, 67], who state that for the related case of *n*-propanol: '... *slowly relaxing hydrogen-bonded molecular clusters dominate the dielectric susceptibility* ...'.

In contrast to the case for high temperatures, where the transport coefficients in many primary alcohols behave as if thermally activated, but are not proportional to each other, one finds that at lower temperatures all transport coefficients show the same temperature dependence [21]. In this temperature range the structural relaxation seems to determine the temperature dependence of the main relaxation as seen with dielectric spectroscopy. However, in the case of 1-propanol, Hansen *et al* [47] and Kudlik *et al* [25] attributed the strong Debye-type relaxation process to *distinct –OH group effects*. All in all we have to conclude that the origin of the main relaxation peak in primary alcohols is not well understood. However, taking into account the strong permanent dipole moment situated in the OH group of the molecule, it becomes obvious that the reorientation of this molecular subunit dominates the susceptibility spectrum of ethanol.

From the fact that neither the relaxation strength nor the lineshape for ethanol change significantly during the transformation from the supercooled liquid to the plastic crystal, we conclude that the motional mechanism of the reorientation of the molecules remained essentially unchanged. As the reorientational motion in the supercooled liquid state is associated with an isotropic reorientation of the molecule in the sense that in the course of time all molecular orientations are presumed to occur with the same probability, we conclude that this also holds for the plastically crystalline state of ethanol. Furthermore, we exclude the possibility of reorientation of clusters or multimers as a more or less rigid unit in the plastically crystalline phase as well as in the supercooled liquid, because such motions are not compatible with a crystalline lattice.

Bearing in mind the structural difference of the two phases studied, the high degree of similarity for $\varepsilon''(\nu)$ seems to be surprising. Can one rationalize our observation? The most fundamental observable connected with structure is the density $\rho(T)$, differing by 3% at most for the two glassy states at around T_g [8]. Taking into account the fact that the density of the liquid changes by more than 20% from room temperature to T_g [50], this difference appears not to be very large. Moreover, on the basis of an analysis of the static structure factor, Fayos *et al* [17] state that the structures on short length scales become very similar for the different phases of ethanol. Thus, the local environment of the molecules does not seem to differ much between crystal II and the supercooled liquid, supporting the proposal of a high degree of similarity from a dynamical point of view.

In addition to the above-discussed similarity of the two glass transitions studied, one important difference was found: the supercooled liquid is, in the terminology of Angell, a more fragile glass former than the plastic crystal. Following Angell, this can be rationalized in terms of the energy landscape [68], namely the potential energy as a function of the particle coordinates. Whether a system is strong or fragile will in this picture mainly depend on the density of accessible states (i.e. minima in the hypersurface). The more densely these states are packed, the more fragile the system should be. Applying this picture to ethanol, the density of accessible configurations in the supercooled liquid should be higher than for the less fragile plastically crystalline phase, which can indeed be rationalized, as in the latter phase fewer configurations per molecule are possible, due to the fact that in crystal II the molecules are fixed to a lattice.

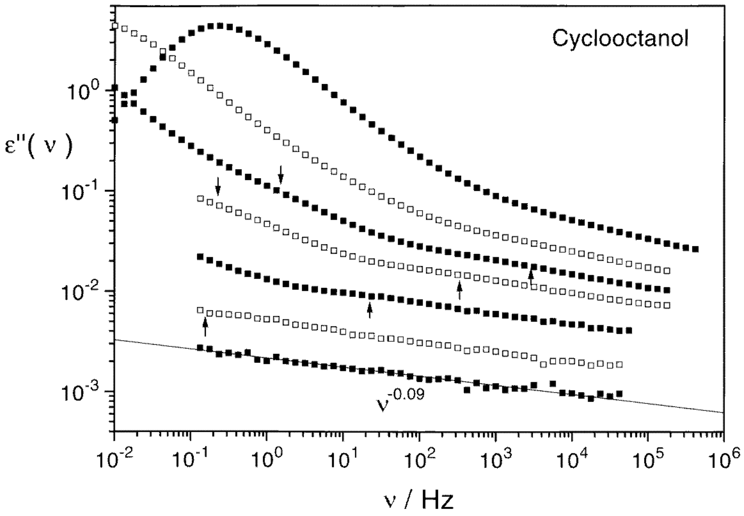

Figure 9. The imaginary part $\varepsilon''(\nu)$ of the dielectric susceptibility of cyclooctanol in the glassy crystalline phase (100 K, 124 K, 142 K, 154 K, 160 K, 166 K, 175 K). The arrows indicate the positions of the additional processes (after [6]) at the given temperature. At 100 K, where both additional processes are slower than 10^5 s, a power-law behaviour $\nu^{-\gamma}$ with $\gamma = 0.09$ is found.

Finally, another interesting feature of the glass transition as monitored with dielectric spectroscopy is the high-frequency wing that is observed in many structural glasses with no or weak secondary relaxation and also in both disordered phases of ethanol. Here the question arises of whether the high-frequency wing is a general feature of the dielectric loss of plastic crystals also. In the past there have only been a few studies examining the lineshape of dielectric spectra of supercooled plastic crystals in detail. In our opinion, cyclooctanol is the substance that has been studied in the greatest detail, but the results are controversial. Leslie-Pelecky and Birge [69] stated that cyclooctanol shows a main relaxation with a spectral shape indistinguishable from that exhibited by a supercooled liquid including the high-frequency wing, as both data sets fall on the same master plot. In contrast, Brand *et al* [6] show that besides the main relaxation there exist two additional processes, leading to the situation that the exact spectral shape of the main relaxation process at high frequencies is difficult to analyse. Their experimental evidence for the latter scenario is convincing, but additional results obtained by our group on the same substance indicate that at 100 K, where both additional processes are slower than 10^5 s and therefore have shifted out of our frequency window, as for many structural glasses, a power law $\varepsilon''(\nu) \propto \nu^{-\gamma}$ with $\gamma = 0.09$ is still detected, as demonstrated in figure 9. This spectral feature can be interpreted as the remainder of the high-frequency wing in the glass, as is seen for several glass formers, for example for glycerol [44], remarkably with a very similar exponent γ.

For the plastic crystal o-carborane, the situation is clear, as no significant deviations from the CD function at high frequencies are found [70].

Concluding, we have to state that as regards the high-frequency wing in plastic crystals no general picture can be developed yet, as the number of systems for which the lineshape has been studied in detail is still small. Further experiments are necessary.

5. Summary

Summing up this study of the dielectric loss in the plastic crystalline phase and the supercooled liquid of ethanol we can make the following statement.

The dynamic susceptibilities of the two phases, namely the supercooled liquid and the plastic crystal, are very similar, as regards both the main and secondary relaxation, even including the high-frequency wing of the main relaxation. We conclude that the reorientational motions of the ethanol molecules in the supercooled liquid and crystal II are essentially the same, being isotropic. The possibility of the reorientation of clusters or multimers as a more or less rigid unit can be ruled out for the deeply supercooled liquid. For the plastic crystal ($m = 40$), the glass transition is, in the terminology of Angell, less fragile than for the liquid phase ($m = 60$). As regards the secondary relaxation observed, it still has to be clarified whether it belongs to some kind of intramolecular motion or exhibits features typical for the β-relaxation in structural glass formers. After having shown the similarity of the dynamics for the two disordered phases, we think that the plastically crystalline state is a good starting point for theoretical approaches to the glass transition phenomenon.

Acknowledgment

The authors would like to thank H E Fischer from the ILL in Grenoble for helpful discussions and for supplying preprints.

Note added in proof. Very recently, Miller and co-workers [71] have also measured $\hat{\varepsilon}(\omega)$ for ethanol, obtaining results which are very similar to ours.

References

[1] Haida O, Suga H and Seki S 1977 *J. Chem. Thermodyn.* **9** 1133
[2] Aihara A, Kitazawa C and Nohara A 1970 *Bull. Chem. Soc. Japan* **43** 3750
[3] Brot C and Darmon I 1970 *J. Chem. Phys.* **53** 2271
[4] Amoureux J P, Noyel G, Foulon M, Bée M and Jorat L 1984 *Mol. Phys.* **52** 161

[5] Krüger J K, Schreiber J, Jiménez R, Bohn K-P, Smutný F, Kubát M, Petzelt J, Hrabovská-Bradshaw J, Kamba S and Legrand J F 1994 *J. Phys.: Condens. Matter* **6** 6947

[6] Brand R, Lunkenheimer P and Loidl A 1997 *Phys. Rev.* B **56** R5713

[7] Eguchi T, Soda G and Chihara H 1980 *Mol. Phys.* **40** 681

[8] Srinivasan A, Bermejo F J, de Andrés A, Dawidowski J, Zúñiga J and Criado A 1996 *Phys. Rev.* B **53** 8172

[9] Jönsson P-G 1976 *Acta Crystallogr.* B **32** 232

[10] Szwarc H 1986 *Thermochim. Acta* **109** 91

[11] Adachi K, Suga H and Seki S 1968 *Bull. Chem. Soc. Japan* **41** 1073

[12] Renner C, Löwen H and Barrat J L 1995 *Phys. Rev.* E **52** 5091

[13] Ramos M A, Zou Q-W, Vieira S and Bermejo F J 1996 *Czech. J. Phys.* **46** 2235

[14] Vieira S, Ramos M A, Zou Q W and Talón C 1997 *Phase Transitions* **64** 87

[15] Talón C, Ramos M A, Vieira S, Cuello G J, Bermejo F J, Criado A, Senet M L, Bennington S M, Fischer H E and Schober H 1998 *Phys. Rev.* B **58** 745

[16] Ramos M A, Vieira S, Bermejo F J, Dawidowski J, Fischer H E, Schober H, Gonzáles M A, Loong C K and Price D L 1997 *Phys. Rev. Lett.* **78** 82

[17] Fayos R, Bermejo F J, Dawidowski J, Fischer H E and Gonzáles M A 1996 *Phys. Rev. Lett.* **77** 3823

[18] Bermejo F J, Criado A, Fayos R, Fernández-Perea R, Fischer H E, Suard E, Guelylah A and Zúñiga J 1997 *Phys. Rev.* B **56** 11 536

[19] Hugo M, Schlüter K and Würflinger A 1992 *Z. Phys. Chem., NF* **175** 235

[20] Stickel F-J 1995 *PhD Thesis* Johannes Gutenberg Universität, Mainz

[21] Stickel F, Fischer E and Richert R 1996 *J. Chem. Phys.* **104** 2043

[22] Barthel J, Bachhuber K and Hetzenauer H 1990 *Chem. Phys. Lett.* **165** 369

[23] Mandal H, Frood D G, Saleh M A, Morgan B K and Walker S 1989 *Chem. Phys.* **134** 441

[24] Puranik S M, Kumbharkhane A C and Mehrotra S C 1993 *Indian J. Phys.* B **67** 9

[25] Kudlik A, Tschirwitz C, Benkhof S, Blochowicz T and Rössler E 1997 *Europhys. Lett.* **40** 649

[26] Fischer H E 1997 private communication

[27] Böttcher C J F and Bordewijk P 1978 *Theory of Electric Polarization* vol II (Amsterdam: Elsevier)

[28] Davidson D W and Cole R H 1950 *J. Chem. Phys.* **18** 1417

[29] Davidson D W and Cole R H 1951 *J. Chem. Phys.* **19** 1484

[30] Emery J, Gasse S, Pethrick E A and Phillips D W 1978 *Adv. Mol. Relax. Interact. Process.* **12** 47

[31] *CRC Handbook of Chemistry and Physics* 1997 (Boca Raton, FL: Chemical Rubber Company Press)

[32] Andrade E 1934 *Phil. Mag.* **17** 698

[33] Mitsukuri S and Tonomura T 1929 *Proc. Chem. Soc. Japan* **5** 23

[34] Carpenter M R, Davies D B and Matheson A 1967 *J. Chem. Phys.* **46** 2451

[35] Versmold H 1974 *Ber. Bunsenges. Phys. Chem.* **78** 1318

[36] Krüger G J and Weiss R 1970 *Z. Naturf.* a **25** 777

[37] Jannelli M P, Magazú S, Migliardo P, Aliotta F and Tettamanti E 1996 *J. Phys.: Condens. Matter* **8** 8157

[38] Versmold H and Yoon C 1972 *Ber. Bunsenges. Phys. Chem.* **76** 1165

[39] Fung B M and McGaughy T W 1976 *J. Chem. Phys.* **65** 2970

[40] Haida O, Suga H and Seki S 1977 *Bull. Chem. Soc. Japan* **50** 802

[41] Fujimori H, Mizukami M and Oguni M 1996 *J. Non-Cryst. Solids* **204** 38

[42] Mizukami M, Fujimori H and Oguni M 1997 *Prog. Theor. Phys. Suppl.* **126** 79

[43] Dixon P K, Wu L, Nagel S R, Williams B D and Carini J P 1990 *Phys. Rev. Lett.* **65** 1108

[44] Blochowicz T, Kudlik A, Benkhof S, Senker J and Rössler E 1998 *J. Phys. Chem.* submitted

[45] Götze W 1991 *Liquids, Freezing and the Glass Transition* (Amsterdam: North-Holland)

[46] Jonscher A 1983 *Dielectric Relaxation in Solids* (London: Chelsea Dielectric)

[47] Hansen C, Stickel F, Berger T, Richert R and Fischer E 1997 *J. Chem. Phys.* **107** 1086

[48] Kim B and Mazenko G F 1992 *Phys. Rev.* A **45** 2393

[49] Kirkwood J G 1939 *J. Chem. Phys.* **7** 911

[50] Sun T F, Schouten J A, Trappeniers N J and Biswas S N 1988 *J. Chem. Thermodyn.* **20** 1089

[51] Chamberlain J, Afsar M N, Davies G J, Hasted J B and Zafar M S 1974 *IEEE Trans. Microwave Theory Tech.* **22** 1028

[52] Johari G P and Goldstein M 1970 *J. Chem. Phys.* **53** 2372

[53] Johari G P and Goldstein M 1971 *J. Chem. Phys.* **55** 4245

[54] Wu L 1991 *Phys. Rev.* B **43** 9906

[55] Murthy S, Shobhanadri J and Gangasharan 1994 *J. Chem. Phys.* **100** 4601

[56] Kudlik A, Tschirwitz C, Blochowicz T, Benkhof S and Rössler E 1997 *J. Non-Cryst. Solids* at press

[57] Böhmer R 1989 *J. Chem. Phys.* **91** 3111

[58] Birge N, Jeong Y, Nagel S, Bhattacharya S and Susman S 1984 *Phys. Rev.* B **30** 2306

[59] Fujimori H and Oguni M 1995 *Solid State Commun.* **94** 157

[60] Dvinskikh S, Benini G, Senker J, Vogel M, Wiedersich J, Kudlik A and Rössler E 1998 *J. Phys. Chem.* submitted

[61] Kudlik A 1997 *PhD Thesis* University of Bayreuth

[62] Wu L and Nagel S 1992 *Phys. Rev.* B **46** 11 198

[63] Meyer W and Neldel H 1937 *Z. Tech. Phys.* **12** 588

[64] Dyre J 1986 *J. Phys. C: Solid State Phys.* **19** 5655

[65] Hassion F X and Cole R H 1953 *J. Chem. Phys.* **23** 1756

[66] Angell C A 1991 *Hydrogen-Bonded Liquids* (Dordrecht: Kluwer) p 59

[67] Floriano M A and Angell C A 1989 *J. Chem. Phys.* **91** 2537

[68] Angell C A 1997 *Complex Behaviour of Glassy Systems (Springer Lecture Notes in Physics 492)* ed C Perez-Vincente (Berlin: Springer) p 1

[69] Leslie-Pelecky D L and Birge N O 1994 *Phys. Rev. Lett.* **72** 1232

[70] Lunkenheimer P 1998 private communication

[71] Miller M, Jimenez-Ruiz M, Bermejo F and Birge N 1998 *Phys. Rev.* B **57** 13 977