I. INTRODUCTION

Organic compounds are commonly known for showing the phenomenon of polymorphism, i.e., they may exist in structurally different crystalline phases. For example, in the case of the compound ROY, at least seven polymorphs have been identified. Under the given conditions, only a single phase can be thermodynamically stable whereas the others are all metastable. Finding the routes to obtain and capture such metastable phases has thus become an important issue in materials science.

Many liquids can be supercooled leading to a strong increase of their transport coefficients like viscosity or diffusion coefficient. At temperatures around the glass transition temperature $T_g$, the crystallization process of the deeply supercooled liquid is typically diffusion controlled and therefore avoided on laboratory time scales. Then the liquid is in a metastable state. Considering the chemical potential $\mu(T)$ of the highly supercooled liquid as a function of temperature, usually a large gap opens with respect to the potential $\mu(T)$ of the thermodynamically stable crystalline phase (cf. Fig. 1). A metastable crystalline phase with its potential $\mu_m(T)$, if present, will appear within this gap. In other words, by increasing the temperature of the highly viscous liquid and thus again facilitating diffusion the usually occurring phase transition does not necessarily have to end up with the thermodynamic equilibrium phase but may yield metastable phases. Thus, strongly supercooling a liquid opens the possibility for searching unknown metastable phases of molecular systems.

A prominent example is liquid ethanol, which transforms into a metastable crystal if it is kept close to $T_g = 97$ K, i.e., well below the melting point $T_m = 159$ K. Regarding its orientational degrees of freedom, this crystal exhibits “glassy” dynamics, i.e., highly cooperative molecular rotation above the corresponding $T_g$. Upon heating, the glassy crystal phase of ethanol transforms into the orientationally ordered and thermodynamically stable phase, which melts at $T_m$.

Studying the regime of a supercooled liquid or even the glass ($T < T_g$) with respect to possible phase transitions is also an important issue in understanding how to stabilize glasses against crystallization. For some applications, for example, pharmaceuticals, the glassy state is advantageous over the crystalline state, and it is important to avoid crystallization or at least to minimize the rate of crystal growth. In a recent application, Ediger and co-workers have investigated the diffusion coefficient $D$ of the supercooled liquid indomethacin ($T_g = 315$ K). The authors have found that the temperature dependence of the diffusion is significantly weaker than that of viscosity, and that it is indeed $D(T)$, which controls the transformation into the three identified crystaline polymorphs of indomethacin.

In the present contribution, the polymorphism of the compound quinaldine (2-methyl quinoline, 2mq, see Fig. 3) is examined. Quinaldine is a liquid at room temperature, which can easily be supercooled below its melting temperature $T_m \approx 264–270$ K as demonstrated by Capaccioli et al. Like in other glass-forming liquids, the structural relaxation becomes very slow upon cooling, i.e., the reorientational correlation time of a molecule rises from $10^{-12}$ s at the melting point to $100$ s at the glass temperature $T_g$. Since the quinaldine molecule is polar, this behavior is well verifiable by means of dielectric spectroscopy, and we have determined the glass transition temperature to be $T_g \approx 180$ K. We demonstrate that
two phase transitions can be monitored with the help of
dielectric spectroscopy, x-ray diffractometry (XRD) and
differential scanning calorimetry (DSC) upon heating the highly
supercooled liquid. Here, we benefit from the fact that all the
three phases of quinaldine are dielectrically active and thus al-
low to probe the dynamics in each phase as well as both phase
transitions. Moreover, as quinaldine is a rigid molecule of low
symmetry, any dynamics has to involve the total molecule.
This is likely to result in some kind of cooperative dynamics
in the range of

\[ T_g \] and glass transition temperatures \( T_g \) are indicated.

The interpolation of the so-called excess wing (EW), ap-
pearing on the high-frequency flank of the \( \alpha \)-relaxation peak as a kind of power-law, was obtained by including the step
response of the Cole-Davidson function (CD function)

\[ \phi_{CD}(t) = \frac{\Gamma(y, \frac{\tau_a}{\tau_{CD}}) - \Gamma(y)}{\Gamma(y)} \] (4)

together with the Williams-Watts approach\(^{17}\)

\[ \phi(t) = [C \phi_{CD}(t) + (1 - C)] \phi_{\alpha}(t) \] (5)

with C being a measure for the amplitude of the EW. The
time constants of both contributions are set equal \( \tau_g = \tau_{CD} \) so that only the high-frequency power-law with the exponent
\( \gamma \) of the Cole-Davidson contribution remains visible.\(^{18}\)

The second observed quinaldine phase (2mq2) exhibits
a relaxation peak, which has again the spectral shape of a
structural relaxation peak rather than the shape of a secondary
process. Since its low-frequency flank, however, has an expon-
ent slightly smaller than 1 we used the normalized Havriliak-
Negami susceptibility function as fit function,

\[ \tilde{\chi}_{HN}(\omega) = \frac{1}{[1 + (i \omega \tau^\beta)]^\alpha} \] (6)

The third phase (2mq3) shows a broad relaxation peak, which is best interpolated by the distribution of correlation
times usually applied for secondary relaxations in glasses.\(^{19}\)

Explicitly,

\[ G_\beta(\ln \tau) = N_\beta(a, b) \frac{1}{b(\frac{a}{\tau_\beta})^\alpha + (\frac{a}{\tau_\beta})^\alpha - ab} \] (7)

with the normalization factor

\[ N_\beta(a, b) = \frac{a(1 + b)}{\pi} b^{\alpha + \beta} \sin \left( \frac{\pi b}{1 + b} \right) \] (8)

The parameter \( a \) causes a symmetric broadening of the
distribution while \( b \) only affects its short time flank. Therefore
\( b \) can also be called “asymmetry parameter.” After Laplace
transforming \( G_\beta(\ln \tau) \) into frequency domain, the resulting
susceptibility peak is broadened symmetrically by \( a \), which is also the exponent of the power-law approached asymptoti-
cally by the peak’s low frequency flank. The exponent of the
power-law asymptote of the high-frequency flank is given by
the product \( ab \).
For all phases, a power-law accounts additively for the dc conductivity contribution
\[ \chi_{\text{DC}}''(\omega) = \Lambda \omega^{-1.2 - -0.8}. \]

C. Differential scanning calorimetry

For the DSC measurements, we used a Netzsch DSC 200. Its temperature scale was calibrated within the range of interest with the help of the first order phase transitions of six reference samples (cyclohexane, chloroform, mercury, carbon tetrachloride, water, benzene). The DSC-signal intensity was not calibrated; yet, any conclusions can be drawn in a qualitative way. Throughout the DSC studies within this work, temperature has either been kept constant (isothermal measurement) or heating/cooling rates of 20 K/min (ramp experiments) were applied. Any temperature scan shown below was compiled of a cooling stage from room temperature to 120 K, an isothermal stage lasting 10 min and a heating run back to room temperature. If additional stages were applied in order to induce phase transitions, it will be explained explicitly.

D. X-ray structure analysis

The x-ray diffraction (XRD) experiments were carried out using Cu-K\(\alpha\)1 radiation and a curved position sensitive detector (INEL CPS120) and a furnace (MRI) as sample environment. The sample was kept on a temperate stage in a thermally isolating vacuum. Using this setup, it was possible to gain diffractograms on short time scales in order to obtain several snapshots of the phase transition processes in the sample. In order to gain higher signal qualities for characterizing the neat crystalline phases, the data accumulation time could be increased and adapted to the experimental situation.

III. RESULTS

A. Dielectric spectra

1. Supercooled liquid (2mq1)

Typical dielectric susceptibility spectra of the supercooled quinaldine’s liquid phase (2mq1, \(T > T_g\)) are shown in Fig. 2. In addition to a main (\(\alpha\)-) relaxation peak, an EW is observed on the high-frequency flank of the relaxation peak. Since no secondary \(\beta\)-relaxation peak can be resolved, the system can be categorized as type-A glass former.\(^\text{15}\) Both spectral features shift to lower frequencies with decreasing temperature without any significant spectral changes.

In order to fit the full spectra, including the EW, the relaxation function is made up of a convolution of the generalized Kohlrausch/Cole-Davidson function (\(\alpha\)-process, Eq. (1)) with a CD function with width parameter \(\gamma\) (Eq. (4)) applying the Williams-Watts ansatz (Eq. (5)); the CD function accounts for the EW, which follows a power-law behavior (\(\epsilon''_{\text{EW}}(\nu) \propto \nu^{-\beta}\)). The decomposition of the spectra is indicated in Fig. 2. The high-frequency shape parameter of the \(\alpha\)-peak is found to be temperature independent with \(\beta = 0.71\), and also the exponent of the EW \(\gamma = 0.30\) can be kept constant at all measured temperatures. The parameters \(\alpha\) (low-frequency shape parameter) and \(C\) (amplitude of the EW) vary weakly with temperature (cf. inset Fig. 3). In other words, frequency-temperature superposition (FTS) holds in good approximation for the full spectra. This is verified once again with the help of the corresponding master curve shown in Fig. 3 where the normalized susceptibility is plotted versus \(\omega_0 \tau_\alpha\). No significant changes in the spectral shape of both main relaxation and EW are observed. The spectral shape is in almost perfect agreement with that reported by Capaccioli et al.,\(^\text{14}\) as demonstrated in Fig. 2. A small discrepancy in amplitude (factor 1.1) and frequency position (factor 1.4) exists, which is barely recognized on logarithmic scale and probably due to a tiny mismatch in temperature calibration.

The extracted relaxation times \(\tau_\alpha\) (cf. Eq. (3)) are shown in Fig. 4(a) (squares). Their non-Arrhenius temperature

![Graph](https://example.com/graph.png)

FIG. 2. Dielectric spectra of supercooled liquid quinaldine (2mq1), open symbols: this work, connected dots: data taken from Ref. 14). Continuous lines: fits including relaxation peak and EW (Eqs. (1)–(5)). Dashed lines: decomposed fit of the spectrum at 185 K. The shape parameters \(\beta\) and \(\gamma\) have been kept fixed for all temperatures (numbers); the shape parameter \(\alpha\) and the EW amplitude \(C\) vary weakly (inset in Fig. 3).

![Graph](https://example.com/graph2.png)

FIG. 3. Susceptibility spectra (182 K–215 K) of supercooled liquid quinaldine normalized by the relaxation strength \(\Delta \epsilon\) and plotted versus \(\omega_0 \tau_\alpha\) (continuous lines). For comparison: main relaxation of the second phase 2mq2 (at 215 K, dashed line). Inset: temperature dependence of the fit parameters \(\alpha\) and \(C\) (cf. Eqs. (1), (4), and (5)).
of 2mq2 (triangles) and 2mq3 (crosses) are fitted by Arrhenius laws. The corresponding values of $T_g$ (defined by $\tau(T_g) = 100$ s) are indicated. Larger open symbols: time constants as obtained by DSC. (b) Testing the Curie law: product $T\Delta \varepsilon$ versus temperature for each phase.

dependence being typical of supercooled liquids, indicating cooperative molecular dynamics, can be interpolated by a Vogel-Fulcher-Tammann (VFT) law, explicitly

$$\tau = \tau_0 \exp \left( \frac{B}{T - T_0} \right). \quad (10)$$

We define the glass transition temperature as $T_g = T(\tau_g = 100$ s), which is determined as $T_{g1} = 180$ K (cf. Fig. 4(a)). In order to compare the effective dipole moments $\mu_{\text{eff}}$ participating in the relaxation processes of the different quinaldine phases, we analyze the relaxation strengths (see also Eq. (2)) via the Curie law

$$\Delta \varepsilon = \frac{N\mu_{\text{eff}}^2}{3k_B T} \quad (11)$$

with $N$ being the number density of dipoles. In Fig. 4(b), the product $T\Delta \varepsilon$ for phase 2mq1 is plotted versus temperature and compared to that of the other phases (cf. below). In agreement with Eq. (11), a constant value is obtained all over the analyzed temperature range.

2. Second phase (2mq2)

When the supercooled liquid of quinaldine is kept at temperatures above, say, 200 K, the dielectric spectra become time dependent, cf. Fig. 5. Here the sample was kept at $T = 210$ K. The time interval between two shown data sweeps was about 35 min. With advancing time, the amplitude of the $\alpha$-relaxation of the liquid decreases monotonically, while the dc-conductivity contribution at low frequencies is lowered similarly. At intermediate frequencies a second, weaker relaxation peak is revealed. Its amplitude increases monotonically with time (arrows in Fig. 5(a)). Finally, the dielectric response becomes again temperature independent, and the transformation was completed after 6 h. Since the amplitude of the relaxation peak in the dielectric susceptibility is proportional to the density of rotationally mobile dipoles (cf. Eq. (11)), the strong decrease of the signal in the frequency range of the main relaxation of the liquid indicates the disappearance of the liquid phase. We conclude that the sample is performing a phase transition to another phase (2mq2) with different rotational degrees of freedom, which results in a new relaxation peak at lower frequencies.

FIG. 4. (a) Time constants $\tau$ of the three dielectrically active phases of quinaldine; $\tau$ of 2mq1 (liquid, squares) are interpolated by a VFT law (Eq. (10)); $\tau$ of 2mq2 (triangles) and 2mq3 (crosses) are fitted by Arrhenius laws. The corresponding values of $T_g$ (defined by $\tau(T_g) = 100$ s) are indicated. Larger open symbols: time constants as obtained by DSC. (b) Testing the Curie law: product $T\Delta \varepsilon$ versus temperature for each phase.

FIG. 5. (a) Monitoring dielectric spectra (symbols) at $T = 210$ K over 6 h demonstrating the phase transition from the liquid (2mq1) to a second phase (2mq2); arrows: progress of time. Lines: fits made up of the sum of the contributions of 2mq1 relaxation (Eqs. (1), (4) and (5)), of 2mq2 relaxation (Eq. (6)) and of conductivity contribution (Eq. (9)). (b) Transition times $\tau_{\alpha}$ (open diamonds) compared to the structural relaxation times $\tau_\alpha$ of 2mq1 (full squares). Inset: decrease of the property $T\Delta \varepsilon(t)$ of the liquid phase 2mq1 during transition to phase 2mq2 versus time at different temperatures (squares). Lines: fits according to the Avrami law (Eq. (12)).
In Fig. 5(a), the overall susceptibility curves at different times are compared and interpolated by the sum of three spectral contributions: the 2mq1 relaxation described by Eqs. (1), (4), and (5), the 2mq2 relaxation (Havriliak-Negami, Eq. (6)), and the conductivity contribution given by Eq. (9). During fitting, all time constants and spectral shape parameters were kept constant. Only the relaxation strength parameter $\Delta \varepsilon$ of both phases and the conductivity parameters were adjusted. For the sake of clarity, only every sixth susceptibility scan is shown in Fig. 5(a). In order to access the phase transition kinetics, the time dependence of the relaxation strength of the liquid’s spectral contribution shall be quantified. In the inset of Fig. 5(b) the obtained decay curves $T \Delta \varepsilon(t)$ are interpolated with the Avrami law

$$T \Delta \varepsilon(t) = T \Delta \varepsilon (t = 0) \exp \left[ -\left( \frac{t}{\tau_{tr}} \right)^n \right],$$

which is often used to describe crystallization kinetics. Any induction period is neglected since the preparation time of each experiment is short compared to the transformation process, which itself set in already during the first frequency scans. Here $T \Delta \varepsilon(t)$ is assumed to be proportional to the fraction of untransformed liquid. The resulting exponents $n$ show some variation: $n(200 K) = 2.2$, $n(210 K) = 2.6$ and $n(215 K) = 2.9$. Dantuluri et al. have found values of the same range for the crystallization kinetics of supercooled celecoxib. In Fig. 5(b), the obtained transformation times $\tau_{tr}$ (open diamonds) are compared to the structural relaxation times $\tau_\alpha$ (full squares) of the liquid phase 2mq1 (cf. Fig. 4(a)). Obviously, $\tau_{tr}$ shows a temperature dependence different from that of the structural relaxation, following the relation $\tau_{tr} \propto \tau_\alpha^{-0.44}$. According to Ref. 22, the Avrami transition time $\tau_{tr}$ is connected with the linear crystallization velocity $u$ via

$$u \propto \tau_{tr}^{-\frac{1}{n}} \propto \left( \frac{\tau_\alpha}{\tau_\alpha^{0.44}} \right)^{-\frac{1}{n}} = \tau_\alpha^{-0.72},$$

assuming a time and cluster-size independent rate of thermal nucleation at constant temperature. The last equality was obtained after inserting the average exponent of the three Avrami interpolations $(n) = 2.57$ (see text above). Since a decoupling of the diffusion coefficient $D$ from viscosity $\eta$, explicitly

$$D \propto \eta^{-\xi} \propto \tau_\alpha^{-\xi}$$

is well established, diffusion controlled crystal growth is expected to lead to $u \propto D \propto \tau_\alpha^{-\xi}$. This has been confirmed by Sun et al. for the crystallization of different (supercooled) liquids ($\xi = 0.7$–0.8). As we find a similar exponent, we assume that the phase transition from 2mq1 to 2mq2 is controlled by diffusion, too.

The dielectric spectra of the phase 2mq2 at different temperatures can be monitored as demonstrated in Fig. 6. In order to account for the low-frequency exponent of the relaxation peak, which is smaller than one, interpolations have been done by applying the Havriliak-Negami function (Eq. (6)). The dc conductivity contribution has been included in the fitting procedure by adding a power law according to Eq. (9). At low temperatures, the susceptibility deviates from the Havriliak-Negami shape due to an emerging high-frequency contribution reminding of an EW. Since this feature is not resolved well in the whole temperature range, it has been excluded from the fits. At higher temperatures, the conductivity contribution deviates from a simple power law behavior. Here the fitting range was limited to frequencies one decade below the minimum position. As shown in Fig. 6, a small increase of the low-frequency exponent $\beta$ of the relaxation peak is observed. This is reflected once again by the increase of $\alpha$ (low frequency exponent) with a constant product $\alpha \beta$ (high-frequency exponent, cf. inset of Fig. 6). The resulting time constants $\tau_{HN}$ are included in Fig. 4(a). In contrast to the supercooled liquid, $\tau_{HN}$ of 2mq2 seems to show an Arrhenius temperature behavior yielding an activation energy $E_a/k_B = 24 \ 100 \ K$. Considering the exponential prefactor $\tau_0 = 7.10 \times 10^{-53}$ s of the Arrhenius fit, which is not a physically reasonable value for a single particle attempt time, we expect the $\tau(T)$ curve to flatten at higher temperatures. Since the permittivity curves are presented on logarithmic scale, it shall be pointed out that the second phase’s relaxation strength is strikingly smaller than the one of the liquid. In Fig. 4(b) the product $T \Delta \varepsilon$ is plotted in order to be compared with the findings for the liquid (2mq1). We find again a temperature independent value with $T \Delta \varepsilon (2mq2) \approx 0.06 \ T \Delta \varepsilon (2mq1)$.

3. Third phase (2mq3)

Similar to the above described transformation of the supercooled liquid, the dielectric spectra of 2mq2 become time dependent at high temperatures, say, $T = 210 \ K$–230 K. The phase transformation evolves on a slower time scale compared to that from phase 2mq1 to 2mq2, therefore, slightly higher temperatures are considered. The transformation leading to the third phase (2mq3) at $T = 218 \ K$ is displayed in Fig. 7. The time interval between two shown spectra is now about 158 min. The complete transformation took 130 h. In contrast to the transformation shown in Fig. 5, the appearing relaxation peak of phase 2mq3 is situated at slightly higher frequencies, compared to the diminishing peak of phase 2mq2.
The spectra of phase 2mq3 at different temperatures are shown in Fig. 8. Here the best interpolations of the quite broad peaks can be obtained with the help of a distribution of correlation times \(G_\rho(\ln \tau)\) (Eq. (7); constant \(b = 0.36\), typically applied to interpolate a secondary relaxation process in molecular glasses.\(^{19}\) The resulting time constants \(\tau_\beta\) show approximate Arrhenius behavior with a mean activation energy \(E_a/k_B = 19\, 100\) K (cf. Fig. 4(a)). For a thermally activated process governed by a distribution of activation energies, the width of the relaxation peak is expected to diminish until the peak assumes Debye shape at infinite temperature, since here the temperature dependent \(G_\rho(\ln \tau)\) becomes a \(\delta\)-distribution. The time constant then approaches the attempt time \(\tau_0\) of the Arrhenius law. As shown in the inset of Fig. 8, the reciprocal width parameter \(1/a\) does not vanish at infinite but rather at a finite temperature. This may be explained\(^{15}\) by writing the Eyring expression for each correlation time of the distribution

\[
\tau = \tau_0 \exp \left( \frac{-\Delta S_a}{k_B} \right) \exp \left( \frac{E_a}{k_B T} \right)
\]

\(\tau_0\) being the activation enthalpy and \(\Delta S_a\) the activation entropy. Introducing now the so-called Meyer-Neldel rule,\(^{24}\) which assumes a linear relationship between entropy and enthalpy, explicitly

\[
\Delta S_a = \frac{E_a}{T_\delta},
\]

leads to the expression

\[
\tau = \tau_0 \exp \left[ \frac{E_a}{k_B} \left( \frac{1}{T} - \frac{1}{T_\delta} \right) \right],
\]

which explains the limit \(\tau_\beta(T) = \tau_0/\exp\left(-E_a/k_B T\right)\) to be reached at \(T = T_\delta\). The width of the relaxation peak, and thus the property \(1/a\), follows the temperature dependence\(^{19}\)

\[
\frac{1}{a} \propto \frac{1}{T} - \frac{1}{T_\delta}
\]

and consequently vanishes when \(T_\delta\) is reached. We find for 2mq3 \(T_\delta = 235\) K, being actually quite a low value, and \(\tau_\beta(T = T_\delta) = \tau_0 = 10^{-9}\) s, which is at least somewhat closer to a physically reasonable value for a single molecule attempt time (cf. inset of Fig. 8).

B. Differential scanning calorimetry

The transitions observed by dielectric spectroscopy were investigated further with DSC. DSC heating scans applying a heating rate \(Q = 20\) K/min of the supercooled quinaldine (2mq1) in the temperature range from 120 K to room temperature revealed an endothermal step with an onset at 183 K (“glass step,” see Fig. 9, topmost line). Additionally, an exothermal peak was observed at 235 K followed by an endothermal peak at 255 K. Finally, at 266 K the endothermal melting peak was found in accordance with the literature \((T_m \approx 264–270\) K). Tentatively, we attribute the two peaks observed in the DSC scan below the regular melting point to phase transitions to the phases 2mq2 and 2mq3, respectively.

The relaxation times probed by DSC can be compared with those from dielectric spectroscopy after calculating the
The endothermal peaks at higher
only a very weak step in the same temperature region remains.

As expected, the exothermal peak is missing now,
and reheating to room temperature results in the central trace
30 min. Afterwards, a cooling to 120 K, 10 min of waiting,
from 2mq1 to 2mq2 starts and will be completed in less than
is interrupted at, e.g.,

\[ \frac{\partial \ln \tau}{\partial T} = \frac{k_B B}{(1 - \frac{T}{T_g})^2} \]  

holds in the case of a VFT temperature dependence (Eq. (10)),
and \( \Delta H_{\text{eff}} \equiv E_a = \text{const.} \) for the case of an Arrhenius temperature dependence. The extracted DSC time constants for all three phases (see below) are plotted in Fig. 4(a) as open symbols and show fair accordance with the dielectric time constants.

In order to further clarify the nature of the phase transition, in the next step the heating scan starting below \( T_g \)
is interrupted at, e.g., \( T = 218 \) K. Now the phase transition from 2mq1 to 2mq2 starts and will be completed in less than 30 min. Afterwards, a cooling to 120 K, 10 min of waiting, and reheating to room temperature results in the central trace in Fig. 9. As expected, the exothermal peak is missing now, only a very weak step in the same temperature region remains. The endothermal peaks at higher \( T \) are found at the same positions as in the former measurement. This proves that the central curve in Fig. 9 results from probing the 2mq2 phase of quinaldine. At \( T = 195 \) K, a weak step is found in the DSC signal (cf. inset) which we interpret, similar to the glass transition of the liquid, as an indication of a “freezing” of motional degrees of freedom within phase 2mq2. Calculating the corresponding calorimetric time constant according to Eq. (19) leads to the result included in Fig. 4(a).

The experiment can be repeated with 2mq2 by introducing an additional isothermal stage at, for instance, \( T = 255 \) K. After subsequent cooling, waiting, and heating again to room temperature, the lowermost line in Fig. 9 is obtained. The missing of the first endothermal peak is proof of the second phase transition from QN2 to QN3 to have already proceeded during the isothermal stage. We now find a weak DSC-step at \( T = 191 \) K (cf. inset), which is situated about 4 K below the step in 2mq2 and in accordance with the dielectric findings (cf. Fig. 4(a)).

C. X-ray diffraction

XRD experiments provide a straightforward way to identify the observed quinaldine phases. The experiment is started with cooling the liquid below \( T_g = 180 \) K. Afterwards, the sample temperature was increased in 5 K steps. After each increment, XRD data were accumulated isothermally for ca. 15–20 minutes. In Fig. 10(a), the amorphous “halo” of the supercooled liquid (2mq1) is shown (“\( t = 0 \)”). After increasing the temperature up to 205 K, the sample was kept for 1 h while several diffractograms were recorded. The last one is shown in Fig. 10(a) (“\( t = 1 \) h”). As can clearly be seen, Bragg reflexes from some crystalline phase, most probably 2mq2, have emerged on top of the diffractogram of the liquid. After 2 h, the amorphous contribution has decreased further (“\( t = 2 \) h”). Since this last signal did not seem to evolve anymore even after further temperature increments up to 215 K, the sample was cooled again to 200 K in order to conserve the present phase of the sample. Here another diffractogram was accumulated for 15 h (Fig. 10(a), “\( t = 17 \) h”). There is no recognizable change but an improved S/N ratio due to longer accumulation time.

Subsequently, the same strategy as described above was repeated with the present crystalline sample at higher temperatures. At 220 K–225 K, the signal becomes time dependent again: new peaks appear and old peaks start to shrink or even vanish, respectively. This is interpreted as the phase transition from 2mq2 to 2mq3. After keeping the sample at 225 K for ca. 6 h and at 230 K for another hour, no more change in the signal could be observed. The sample was then cooled again to 200 K, where another diffractogram was accumulated for 15 h. Figure 10(b) shows the comparison of the measurements with long accumulation times of both, significantly different, crystalline phases of quinaldine.

Due to the isolation vacuum in the chamber where the sample is situated during the measurement, it was not pos-
sible to watch the melting process, i.e., the phase transition from 2mq3 to 2mq1. Instead, the 2mq3 signal disappears in the range of 240–250 K until the sublimation of the sample is terminated.

D. 3-methyl quinoline

At this point, it shall be mentioned that the findings presented above for quinaldine (2-methyl quinoline) are not at all unique for the quinoline family. Quite similar phenomena are observed for 3-methyl quinoline (molecule cf. Fig. 12(b)), and a corresponding analysis of their dielectric spectra shall be presented briefly here. Figure 11 shows a compilation of dielectric susceptibility data of three phases found for 3-methyl quinoline. The liquid phase (3mq1, open symbols) can be supercooled like 2mq1 and its susceptibility data is again interpolated by the same response function (thin lines on top of the open symbols) given by Eqs. (1)–(5). Here, the shape parameters $\beta = 0.70$ and $\gamma = 0.30$ were kept fixed and $\alpha$ and $C$ showed only small changes with temperature. All in all, the dielectric spectra of the supercooled liquid are very similar to those of quinaldine, i.e., FTS holds and indications of an EW are observed.

The supercooled phase 3mq1 performs a phase transition to phase 3mq2 (Fig. 11, full symbols) when the sample is kept at temperatures higher than, say, 200 K. The full-symbol curve for $T = 204$ K shows the relaxation peaks of both 3mq1 and 3mq2 with reduced amplitudes since the phase transition is presumably not completed. At higher temperatures only the 3mq2 relaxation remains visible and can be interpolated by the Havriliak-Negami model function (Eq. (6)) with $\alpha = 0.73$ and $\beta = 0.49$ kept constrained. After a temperature excursion to $T > 240$ K, a third phase, 3mq3, appears (Fig. 11(b), lines). The susceptibility of phase 3mq3 consists of two broad peaks, which merge with increasing temperature and cannot be decomposed easily. In order to determine some time constant and relaxation strength, the fitting range was limited to the larger low-frequency relaxation peak. Interpolations were obtained by applying the $G_\beta(\ln \tau)$ distribution (cf. Eqs. (7) and (8)) with an additional conductivity contribution (Eq. (9)). The asymmetry parameter was fixed to $b = 0.36$.

FIG. 11. Susceptibility data of the three phases of 3-methyl quinoline, namely, 3mq1 (liquid, open symbols in (a)), 3mq2 (full symbols in (a) and (b)), and 3mq3 (lines in (b)) as indicated. Temperature was incremented in 2 K-steps (3mq1), 5 K-steps additionally to $T = 204$ K (3mq2), and 4 K-steps (3mq3). Lines on top of open symbols in (a): fits including relaxation peak and EW of 3mq1 (Eqs. (1)–(5), $\beta = 0.7$, $\gamma = 0.3$).

FIG. 12. Comparison of the dynamics in phases 3mq1 (full squares), 3mq2 (full triangles), and 3mq3 (full stars); and 2mq1 (open squares), 2mq2 (open triangles), and 2mq3 (asterisks), respectively. (a) Time constants with Arrhenius fits (3mq2, 3mq3) and VFT fit (3mq1). $T_g$ as indicated by dashed lines. (b) Testing the Curie law: product $T \Delta \varepsilon$ versus temperature for each phase.
Figure 12(a) summarizes the time constants found for all 3-methyl quinoline phases. The structural relaxation time of the liquid (3mq1) was fitted by a VFT law yielding a $T_g = 186$ K, which is 6 K higher than for the liquid 2-methyl quinoline phase. The $\tau$ of 3mq2 ($E_d/k_B = 21 400$ K) and 3mq3 ($E_d/k_B = 22 000$ K), respectively, were fitted by an Arrhenius law. Again they are shifted to somewhat higher temperatures compared to those of 2-methyl quinoline. In Fig. 12(b), the products $T\Delta \varepsilon$ for all phases are plotted versus temperature. Both liquids, 2mq1 and 3mq1, yield the same constant value. This is not surprising since both molecules are almost identical (Figs. 3 and 12(b)) and, thus, have almost the same molecular dipole moment. The relaxation strengths for 3mq2 and 3mq3 are, within a factor of two, the same as for 2mq2 and 2mq3. The continuous increase of the relaxation strength of 3mq3 can be explained with the merging of two susceptibility peaks of comparable amplitude.

IV. DISCUSSION/CONCLUSIONS

Deeply supercooled liquid quinaldine transforms via an intermediate metastable crystalline polymorph (2mq2) into a structurally distinct and, presumably, thermodynamically stable phase (2mq3). The time scale of the phase transition can be controlled by choosing temperature properly. In addition to the liquid, the two crystalline phases are dielectrically active, i.e., molecular dynamics is present in all phases, the nature of which, however, is not easily identified. As the molecule is rigid and of low symmetry, motion always involves reorientation of the entire molecule and one expects cooperative dynamics for each crystalline phase. Very similar phase behavior is observed for the isomer 3-methyl quinoline.

The dynamics in phase 2mq2 exhibits Arrhenius temperature dependence with an exponential pre-factor, which is beyond any physically reasonable value for a single particle motion. In other words, at higher temperatures, due to the fast transformation into phase 2mq3, actually not accessible experimentally, the $\tau(T)$ curve is expected to bend over, exhibiting some decreasing apparent activation energy. Thus, one can speculate whether phase 2mq2 in analogy to the case of ethanol is a plastic crystal in which still cooperative dynamics occurs. However, inspecting the significantly lower apparent dipole moment with respect to that of the liquid (cf. Fig. 4(b)), the geometry of the motion has to be significantly reduced, i.e., the degree of spatial hindrance is highly increased. This conclusion holds, provided that the corresponding Kirkwood factors included in $\mu_{eff}$, reflecting static correlations among the dipoles, are not significantly different. As the molecule is sterically flat, one expects a reorientation around an axis perpendicular to the molecular plane. Yet, a full rotation around this axis is not possible as this cannot explain the strong reduction of the effective dipole moment. In contrast, in the case of ethanol being a non-rigid molecule, the glassy crystal exhibits isotropic reorientational dynamics. Its dielectric spectra are virtually indistinguishable in shape and amplitude; only the time constant slows down in the glassy crystalline with respect to the liquid phase. Although the spectral shape in phase 2mq2 is distinct from that in the supercooled liquid (cf. Fig. 3), it changes only weakly with temperature (cf. Fig. 6), a behavior typical of cooperative dynamics. In addition, one may speculate that a similar high-frequency wing is found in the dielectric spectra of phase 2mq2 like in phase 2mq1 (cf. Fig. 6). In conclusion, we argue that phase 2mq2 is a glassy crystal with an in-plane cooperative dynamics.

The molecular motion in phase 2mq3 exhibits even smaller relaxation strength and for a given temperature its motion is faster than in the case of 2mq2. The spectra exhibit features, which are well known from secondary relaxation processes in molecular glasses. In this case, the spectral width increases with lowering temperature and the time constant follows an approximate Arrhenius behavior. This behavior is usually explained by assuming a distribution of activation energies. Although in phase 2mq3, indeed, the spectra broaden linearly with the reciprocal temperature, however, no proper Arrhenius behavior is observed. The motion in phase 2mq3 is still expected to show some extent of cooperativity, but the spatial hindrance of the dynamics has to be rather large since the relaxation strength is significantly smaller than that in phase 2mq2. A particularity of phase 2mq3 is the transformation enthalpy from phase 2mq2 to 2mq3 appearing to be positive (cf. Fig. 9), i.e., an endothermic phase transition is involved. Here we note that the DSC results are difficult to be fully reproduced; they are highly dependent on the temperature/time protocol.

Clearly, XRD identifies two crystalline phases. In accordance with the dielectric and DSC experiments, we attribute the diffractogram at $T \leq 215$ K to phase 2mq2 and the one at $220$ K $\leq T \leq 230$ K to phase 2mq3, as is shown in Fig. 10(b). The number of Bragg reflexes in phase 2mq2 is not significantly smaller than in phase 2mq3. Thus, we cannot say that the symmetry of the crystal is higher in phase 2mq2, a behavior often found in orientationally disordered crystals like ethanol, cyanoadamantane28, 29 or caffeine.30, 31 XRD as well as dielectric spectroscopy and DSC experiments indicate both phase transitions to be monotropic in quinaldine, since no reversal can be observed after having cooled down the corresponding new phase.

Concluding, the two crystalline phases of quinaldine show cooperative dynamics, the nature of which cannot be fully assessed, however. Currently, NMR as well as high resolution XRD studies are under way to further dwell on identifying the motional mechanism involved. Finally, we note that the family of methyl quinoline derivatives show a rich phenomenology of different dielectrically active phases and may become a playground for investigating a variety of metastable phases.

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