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Dynamic light scattering study of the liquid ↔ glass transition for the $GdCl_3$-$3AlCl_3$ glass-forming mixture

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The dynamics of density and orientation fluctuations for a member of a family of inorganic glass-forming molten salts based on rare-earth halide–aluminum halide mixtures, namely, the $GdCl_3$-$3AlCl_3$, has been investigated in the supercooled state by means of dynamic light scattering. The temperature dependence of the structural relaxation time near the glass transition temperature was found to be rather strong, indicating the ''fragile'' character of this liquid. The microscopic origin of the structural relaxation has been rationalized by employing structural information that has been independently extracted from other spectroscopic techniques.

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I. INTRODUCTION

Understanding the microscopic origin of many effects observed in supercooled liquids while approaching the glass transition temperature T_g remains still a major challenge in condensed matter physics [1]. Among the not fully understood phenomena of supercooled liquids one can find: (i) the dramatic slowing down of dynamics for the α relaxation and the concomitant deviation of the temperature dependence for the corresponding relaxation time (or viscosity) from an Arrhenius behavior and (ii) the impact of spatially heterogeneous dynamics on various physical properties of glass-forming materials [2].

Due to the complex nature of the problem, theoretical efforts work out simplistic models that are anticipated to resemble some particular class of supercooled liquids. However, the generalization of their results to any type of glass-forming substance is a matter of strong debate [1]. Computer simulations are mainly oriented to the study of ideal systems that do not always capture all the important aspects of real glasses. On the other hand, experiments have been mostly focused on polymeric or organic molecular glass formers, while little attention has been paid to inorganic glass-forming materials and especially to nonoxide glasses. The lack of a consensus on the explanation of the observed phenomenology and its negative consequences on the formulation of a molecular theory for glass transition reveals the necessity for studying other classes of supercooled liquids.

Such a family of inorganic glasses, based on rare-earth halide–aluminum halide mixtures, i.e., RX_3-AlX_3 (R: Gd, La, Nd, Ho; X: Cl, Br) has been recently demonstrated [3]. The viscous, nonvolatile melts, being extremely hygroscopic, corrosive at high temperatures, and very difficult to prepare at high purity, are very important for developing industrial separation and extraction processes [4,5]. The structural properties of the glass-forming molten salts have been investigated by means of vibrational Raman spectroscopy varying both temperature (−196 to 400 °C) and RX_3 concentration and the glass-forming composition ranges have been determined [3]. In the case of the $GdCl_3$-$3AlCl_3$ glass and supercooled liquid, a Gd L_{III}-edge extended x-ray absorption fine structure (EXAFS) spectroscopic study has been undertaken, in order to further elucidate the short-range structural aspects concerning the first and second coordination sphere around Gd^{3+} ions and their temperature dependence [6]. In this paper, we present a dynamic light scattering study of the structural relaxation for the supercooled liquid $GdCl_3$-$3AlCl_3$, aiming at explaining further the glass transition properties of this material.

II. EXPERIMENTAL PROCEDURE

High-purity aluminum chloride (Fluka/Pure Inc. >99%) was prepared by repeated slow sublimations in pyrex tubes sealed *in vacuo*, using a suitable temperature gradient. $GdCl_3$ (Cerac Pure, 99.9%) was purified by dynamic sublimation ($\sim 10^{-7}$ mbar) at 800 °C and anhydrous pure crystals were obtained. All chemicals were very hygroscopic and their handling took place in a nitrogen-filled glove box with a water vapor content of less than 1 ppm. The cells used were made of fused silica tubes with dimensions 6.0 mm outside diameter, 4.0 mm inside diameter, and ~3.5 cm length. Before use, they were carefully cleaned, rinsed with hydrofluoric acid/water, flamed, and degassed by evacuating while hot. Calculated amounts of the component salts (total amount about 500 mg) with stoichiometry $GdCl_3/AlCl_3 = 1/3$ were transferred into the cells, which were then sealed under vacuum. The cells were slowly heated into a furnace in the temperature range 200–350 °C for a few hours. $GdCl_3$ was thus dissolved in liquid Al_2Cl_6 and clear/transparent solutions were obtained filling more than 2/3 of the cells' volume. Although the presence of the rare-earth chlorides lowers the vapor pressure of the aluminum chloride appreciably, the samples were not heated much above 400 °C due to possible tube explosion. This limitation determined also the maximum temperature at which spectra could be collected. The glasses were formed upon rapid cooling of the liquids (from ~280 °C) in water and remained stable at room temperature for months/years. More details about the sample preparation may be found elsewhere [3]. As the material under study is highly hygroscopic, the accurate determination of its glass transition temperature has not yet been possible, hence, a rather accurate estimation has been advanced by

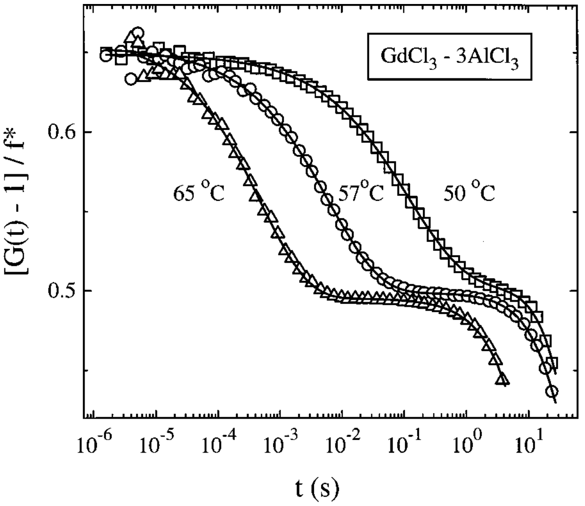

FIG. 1. Polarized intensity net correlation functions (open symbols) for GdCl$_3$-3AlCl$_3$ in the supercooled state. The continuous lines through the experimental data represent the best fits using Eq. (4).

means of the temperature dependence of the structural relaxation time, (see Sec. IV).

Correlation functions, $G(t)$, for GdCl$_3$-3AlCl$_3$ were measured at scattering angles 90° and 45° in the supercooled region 45–65 °C, with the upper-temperature limit being imposed by the unavoidable crystallization of the system upon further heating. The light source was an argon ion laser (Spectra Physics 2020) operating in single mode at 488 nm with a stabilized power of about 200 mW. The incident radiation was polarized vertically with respect to the scattering plane using a Glan polarizer. The scattered light was analyzed by a Glan-Thomson polarizer (Halle, Berlin) with an extinction coefficient better than 10^{-7}, allowing, thus, the detection of vertical (V) and horizontal (H) components and the measurement of the corresponding correlation functions, $G_{\mathrm{VV}}(t)$ and $G_{\mathrm{VH}}(t)$.

Polarized and depolarized (density and orientation) autocorrelation functions were measured on a broad time scale (almost nine decades, $10^{-6}-10^{3}$ s) with a full multiple taut digital correlator (ALV-5000/FAST) with 280 channels. Due to the care taken during the preparation procedure, the samples used in this study seem to be dust free and optically homogeneous, displaying thus only intrinsic scattered light. Hence, under the assumption of homodyne conditions, the desired normalized electric-field time correlation function $g(t)$ is related to the recorded $G(t)$ through the relation

$$G(t)=A[1+f^{*}|\alpha g(t)|^{2}], \tag{1}$$

where A describes the long delay-time behavior of $G(t)$ and f^{*} represents an instrumental factor obtained experimentally from measurements of the $G_{\mathrm{VV}}(t)$ from dilute PS/toluene solutions ($f^{*}=0.8$). The parameter α is a measure of the fraction of the total scattered light with correlation times longer than about 10^{-6} s. Figure 1 presents polarized intensity net correlation functions $[G(t)/A-1]/f^{*}$ at three different temperatures for GdCl$_3$-3AlCl$_3$.

III. DATA ANALYSIS

The information obtained by light scattering from an isotropic medium depends on the polarization of the incident in respect to the scattered light [7]. Fluctuations in dielectric constant, $\delta\varepsilon_{zz}(q,t)$, determine the electric-field correlation function $C_{\mathrm{VV}}(q,t)$ of the polarized scattered light. In a single-component system $\delta\varepsilon_{zz}(q,t)$ is proportional to the qth component of the number density fluctuations $\delta\rho(q,t)=\Sigma_j \exp[iqr_j(t)]$, with $r_j(t)$ being the position of the jth molecule

$$C_{\mathrm{VV}}(q,t)=\left(\frac{\partial\varepsilon}{\partial\rho}\right)^{2}\langle\delta\rho(q,t)\,\delta\rho(q,0)\rangle/\langle|\delta\rho(q,0)|^{2}\rangle. \tag{2}$$

In the depolarized geometry, scattered light is determined by the fluctuations in $\delta\varepsilon_{yz}(q,t)$ which arises from the fluctuations $\delta\alpha_{yz}(q,t)=\Sigma_j \alpha_{yz}^{j}(t)\exp[iqr_j(t)]$ in the molecular optical anisotropy $\alpha_{yz}(q,t)$, where α_{yz}^{j} is the yz component of the jth molecule. Then the corresponding normalized correlation function reads

$$C_{\mathrm{VH}}(q,t)=\langle\delta\alpha_{yz}(q,t)\,\delta\alpha_{yz}(q,0)\rangle/\langle|\delta a_{yz}(q,0)|^{2}\rangle. \tag{3}$$

As can be seen from Fig. 1, the experimental time correlation functions, found to be q independent in the time domain studied, present a two-step decay, a faster one, the structural relaxation or α process and a much slower relaxation whose nature will be discussed in the next section. This two-step relaxation pattern appears when both density and orientation fluctuations are considered. The structural relaxation (α process) is usually found to depart form the simple exponential relaxation. This nonexponential behavior has been mainly pursued within two limiting approaches, i.e., the *homogeneous* and the *heterogeneous* pictures.

The *homogeneous* approach dictates that nonexponentiallity is intrinsically embodied in the microscopic relaxation process. In that case, the stretched exponential or Kohlrausch-Williams-Watts (KWW) equation is a frequently adopted empirical scheme employed to describe structural relaxation. KWW is used as a three parameter, τ^{*}, β_{KWW} and A', fitting function.

$$g(t)=A'\exp[-(t/\tau^{*})^{\beta_{\mathrm{KWW}}}]. \tag{4}$$

The exponent β_{KWW} is a measure of the departure from the single exponential or Debye relaxation and has been correlated to the non-Arrhenius character of the α process [8]; τ^{*} is the structural relaxation time characterizing the process under study and A' the amplitude of $g(t)$.

On the other hand, within the *heterogeneous* approach, the nonexponential relaxation arises from a distribution of relaxation rates, each one assigned to a particular structural moiety that relaxes nearly exponentially. The convolution (mixing) of relaxation functions belonging to a diverse set of time scales results to the observed broad nonexponential decay to equilibrium. Formulating $g(t)$ under the guidelines of the *heterogeneous* scenario, the following expression is obtained:

$$g(t)=\int L(\log_{10}\tau)f(t,\tau)d\log_{10}\tau, \qquad (5)$$

where $f(t,\tau)=\exp(-t/\tau)$. Therefore, the field correlation function is the weighted sum, $L(\log_{10}\tau)$, of independent contributions, each one caused by an individual microdomain. The inverse Laplace transform (ILT) procedure to accomplish solution to Eq. (5) has been performed by employing the CONTIN code. The advantage following this approach is that no assumptions are made on any particular form of $L(\log_{10}\tau)$, except that $f(t,\tau)$ is simply exponential.

IV. RESULTS AND DISCUSSION

As can be seen from Fig. 1, the density autocorrelation functions, found to be q independent in the time domain studied, clearly display a two-step relaxation decay in the time window accessible by the photon correlation spectroscopy (PCS). The faster is attributed to the structural relaxation. The slower one is probably associated with the presence of long-range density fluctuations or ''cluster'' dynamics, also found in many molecular or macromolecular glass formers [9]. Due to the very slow relaxation dynamics of this slow mode, its quantitative analysis was not possible. The assignment to α relaxation and ''cluster'' dynamics and not to β and α relaxation for the faster and slower processes, respectively, has been based on the following reasons. First, fast β processes in supercooled liquids are always found in the ns to ps time scale, i.e., in the interval $10^{-9}-10^{-12}$ s, and therefore, are definitely out of the time window of our dynamic light scattering apparatus. Second, the strong temperature dependence observed for the faster of the two processes detected, is characteristic of the structural relaxation and not of the fast β process that has much smaller activation energy.

The corresponding electric-field time correlation functions $g(t)$ of the faster process were modeled by the Kohlrausch-Williams-Watts (KWW) equation. This three-parameter optimization procedure seems adequate for describing the experimental data (points), as evidenced from the solid lines representing Eq. (5), see Fig. 1. In order to improve the reliability of the fitting procedure for the α process we have included in the global fit the contribution of the slow process, shaped by an exponential decay. Therefore, there are two more fitting parameters (pre-exponential factor and time decay) for the second process. The reason for modeling the slow contribution with a single exponential is as follows. Since we do not have a complete picture of the slow dynamics, which would demand data recording for infeasible time, we have chosen to follow the common practice fitting this process with the simple exponential form so as to avoid over parametrization of the model. Indeed, in a recent study at high temperature for a molecular glass former, see Patkowski *et al.* in Ref. [9(b)], where the slow process was fast enough to be observed in the time window of PCS, it has been shown that ''cluster'' dynamics has indeed a single exponential character.

The stretching exponent for the α process was found almost unchanged, within experimental errors, for both scattering geometries, i.e., $\langle\beta_{\mathrm{KWW}}\rangle=0.52\pm0.02$. In Fig. 2, the β_{KWW} exponent obtained using the polarized intensity correlation functions is plotted as a function of temperature. It can be seen that there exists a small but discernible trend for a slight increase of the stretching exponent with temperature elevation. This finding conforms to the predictions of the coupling model [10]. Within the context of the latter, β_{KWW} relates to the cooperativity exponent n through the relation $\beta_{\mathrm{KWW}}=1-n$, and hence, β_{KWW} has to grow when cooperativity becomes less important, i.e, when the temperature increase weakens the intermolecular interactions. On the contrary, this particular behavior, i.e., the temperature dependence of the stretching exponent, would violate the time-temperature superposition principle, which is a basic outcome of the mode coupling theory [11].

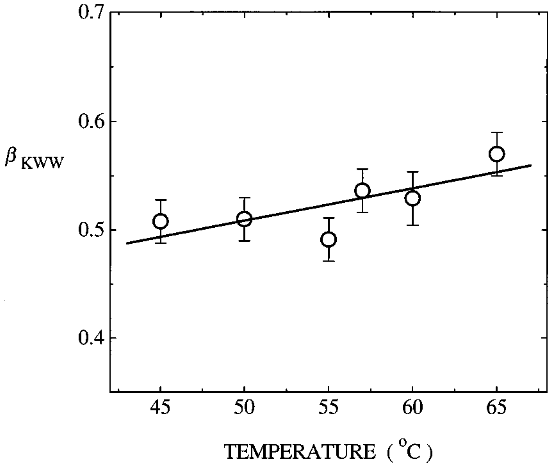

FIG. 2. Stretching exponent β_{KWW} as a function of temperature for $GdCl_3$-$3AlCl_3$. A small but detectable increase of the β_{KWW} values with temperature is also evident. The solid straight line represents the best linear fit.

We present here for comparison the $\langle\beta_{\mathrm{KWW}}\rangle$ values reported for the typical ''fragile,'' according to classification proposed by Angell [12], ionic molten nitrate salt CKN [$3KNO_3$-$2Ca(NO_3)_2$]: $\langle\beta_{\mathrm{KWW}}\rangle=0.47$ [13], the ''strong'' glass former As_2O_3: $\langle\beta_{\mathrm{KWW}}\rangle=0.82$ [14], and the ''intermediate'' halides $ZnCl_2$: $\langle\beta_{\mathrm{KWW}}\rangle=0.71$ and $ZnBr_2$: $\langle\beta_{\mathrm{KWW}}\rangle=0.68$ [15]. As it follows from the comparison, the present glass former is characterized by a value for the nonexponential parameter that is very close to the corresponding value for the nitrate glasses. Based upon the correlation between fragility and $\langle\beta_{\mathrm{KWW}}\rangle$, it is expected that the $GdCl_3$-$3AlCl_3$ system may be classified as a rather ''fragile'' liquid.

The issue of understanding the mechanisms underlying the non-Debye decay of the relaxation function has been tackled from the point of view of the relaxation-space dimensionality d [16]. The relaxation is anticipated to be a topological property of the space in which the relaxator is embedded. In particular, the experimentally measured values of β_{KWW}, in the early stages of the supercooled regime, may be related to d through the equation

$$\beta_{\mathrm{KWW}}(T_g)=\frac{d}{d+2}. \qquad (6)$$

It should be noted here that d has the meaning of the dimensionality of the configuration space in which the relaxing unit acts.

It is tempting now to try to relate the aforementioned idea with the results obtained in the present study. From Eq. (6) we see that low values of β_{KWW} correspond to low dimensionalities, i.e., $\beta_{\mathrm{KWW}}=1/3$ yields $d=1$. In other words, ''fragile'' systems should relax via certain channels that define a low-dimensional configuration space. Such a conjecture is indeed supported by recent molecular-dynamics simulations [17] on a glass-forming Lennard-Jones mixture where stringlike motions occur, manifesting cooperativity.

On the other hand, to rationalize larger values for the stretching exponent, (''strong'' glass-forming liquids), i.e., $\beta_{\mathrm{KWW}}=0.8$, the present model results to unrealistic large values of d, $(d\approx 8)$. This unrealistic situation stems from the fact that in ''strong'' network liquids, deterministic (Newtonian) rather than stochastic (Brownian) motion prevails, rendering the definition of the dimensionality d of the configuration space, in which the Brownian motion occurs, ill defined. In our case, the experimentally extracted values for the stretching exponents combined with Eq. (6) yield for the dimensionality the approximate value $d\approx 2$. This result would suggest that the configuration space, in which the molecular rearrangements—responsible for relaxation—occur, is effectively two dimensional. In order to obtain some insight for the relaxational mechanisms taking place on a molecular level, one has to invoke structural information provided separately by inelastic light scattering and by diffraction techniques. Commenting on the moderate but visible temperature dependence of the stretching exponent depicted in Fig. 2, we may conclude a possible dilation of the configuration space when passing from the strong (T close to T_g) to the moderate supercooled state (T close to T_m).

Following the alternative way to fit the experimental data, we may use the inverse Laplace transform analysis as was introduced in the previous section. The distributions $L(\log_{10}\tau)$ of the relaxation time for the density fluctuations are now directly obtained from the inversion of Eq. (5) and are illustrated in Fig. 3. The width of the distribution peaks is a measure of the departure from exponential relaxation; therefore, broad peaks reflect low values of β_{KWW} while narrow peaks are manifestations of nearly exponential decay. For comparison, we have added in Fig. 3 the ILT distributions for numerically calculated KWW functions with $\beta_{\mathrm{KWW}}=0.7$ (open squares) and $\beta_{\mathrm{KWW}}=0.5$ (open circles). In the first case, the distribution is evidently narrower than the experimental data while the ILT peak for $\beta_{\mathrm{KWW}}=0.5$ fits nicely to the experimental results. Finally, the position of the peak indicates the characteristic relaxation time-scale of the process under study, exhibiting similar temperature dependence as the relaxation times obtained by the KWW analysis.

Focusing now on the temperature dependence of the dynamics, we will try to discuss the fragility of the $GdCl_3$-$3AlCl_3$ in terms of structural information in the local and intermediate range order provided by other experimental techniques. Let us recall here that fragility has been introduced to account for the easiness of the structure degradation upon temperature changes. The fragility index may be obtained through the temperature dependence of the structural relaxation time as $m=d\log_{10}\langle\tau\rangle/d(T_g/T)|_{T=T_g}$. Transforming the τ^* values extracted from fitting with Eq. (4) to the mean relaxation time $\langle\tau\rangle=\tau^*\beta_{\mathrm{KWW}}^{-1}\Gamma(\beta_{\mathrm{KWW}}^{-1})$ (with Γ being the Gamma function) we find that they effectively coincide with the corresponding ones extracted from the ILT analysis. The relaxation times obtained from the maxima of the distribution peaks in ILT analysis are depicted in Fig. 4.

Having established the temperature dependence of the structural relaxation time and due to the lack of any calorimetric data for the systems studied, we may attempt a rough but helpful (for fragility plots) estimation of the glass transi-

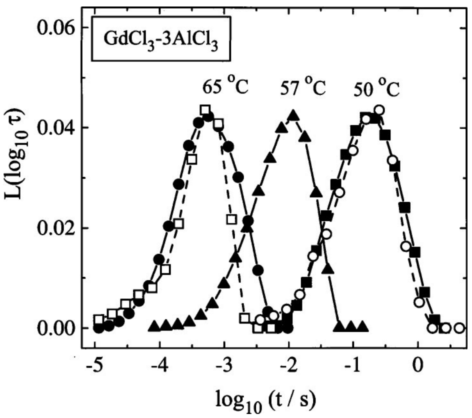

FIG. 3. Distribution of relaxation times $L(\log_{10}\tau)$ obtained by inverse Laplace transform (ILT) analysis [Eq. (5)] for the α-relaxation process in the experimental density autocorrelation function. For comparison, the ILT distributions for calculated KWW functions with $\beta_{\mathrm{KWW}}=0.7$ (open squares) and $\beta_{\mathrm{KWW}}=0.5$ (open circles) are also shown normalized to maximum peak height and scaled properly in the time axis so as to coincide with the experimental data.

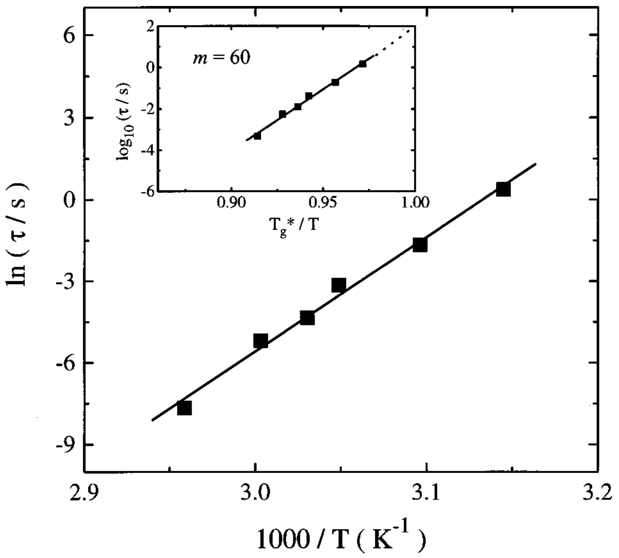

FIG. 4. Arrhenius plot of the temperature dependence for the α-relaxation time in $GdCl_3$-$3AlCl_3$. Inset: The same data have been scaled to the reduced temperature T_g/T. The dotted line is the extrapolation to the glass transition temperature.

tion temperature. This could be used to plot the relaxation time vs the reduced temperature T_g/T in order to estimate the fragility index m. It is a common opinion that the glass transition temperature T_g^*, for a supercooled liquid can be yielded as the temperature at which the relaxation time becomes of the order of 100 s. In our case, from an Arrhenius fit of the data of Fig. 4 we obtain $T_g^*(100\,\mathrm{s}) \approx 36\,^\circ\mathrm{C}$. Plotting the relaxation time in a modified Arrhenius or fragility plot (see inset in Fig. 4) one may directly obtain the fragility index m as the slope of the Arrhenius curve, therefore $m[\mathrm{GdCl_3\text{-}3AlCl_3}] \approx 60$. Reported values for some other glass formers are: $m[\mathrm{3KNO_3\text{-}2Ca(NO_3)_2}] \approx 92$ [13], $m[\mathrm{As_2O_3}] \approx 19$ [14], $m[\mathrm{ZnCl_2}] \approx 30$ [15], and $m[\mathrm{ZnBr_2}] \approx 45$ [15]. The comparison of the data obtained support, in general, the view that the $GdCl_3$-$3AlCl_3$ glass forming system has rather ionic bonding characteristics, that impart more structural and topological degrees of freedom than directional covalent bonding.

Let us now try to attempt a possible link between structure and dynamics. A Raman spectroscopic investigation of the $R$$Cl_3$-$AlCl_3$ systems has suggested that the main participating units of the glasses and the liquids are the $AlCl_4$ tetrahedra and occasionally the Al_2Cl_7 (two corner-shared tetrahedra), linked to the R ions in order to satisfy its preferential coordination [3]. For the system under study, the data indicate an eightfold coordination around Gd in $GdCl_3$-$3AlCl_3$ in both the glass and the $GdAl_3Cl_{12}$ crystal [3(a)]. Further, the Gd L_{III}-edge EXAFS study [4] corroborated the expectation that in $GdCl_3$-$3AlCl_3$ either in the crystalline or in the glassy state, the coordination environment of the Gd ion is the same, i.e., eight Cl form the first coordination shell and four Al are present as the next-nearest neighbors. The difference between crystal and glass was the longer Gd-Al distance, and hence, a probable increase of the Gd-Cl-Al angle in the latter. In the supercooled liquid at 60 °C, the Gd-Cl distance and coordination number remain unchanged, but a further rearrangement of the second-coordination shell (Al atoms) takes place; a temperature dependent increase in static disorder in the spatial disposition of $AlCl_4$ tetrahedra around Gd in the liquid was indicated, resulting to the absence of the second peak in the partial radial distribution function. The temperature increase seems to play a crucial role on the structural features of this liquid.

The foregoing information obtained through structure-probing techniques for the glass former under study may now be used as input for the interpretation of the dynamic properties in terms of structural modifications. To visualize this, a two-dimensional mapping of the possible structures for the glass (a) and supercooled liquid (b) is sketched in Fig. 5, assuming that the first- and second-coordination shells around the central Gd atom define the spatial extent in which the structural relaxation process takes place. EXAFS data have pointed out that the most drastic changes due to temperature rise are experienced by the Al atoms, which determine the next-nearest neighbors to Gd. One possible structural change should involve the enlargement of the Gd-Al distance and consequently, the widening of the Gd-Cl-Al angle. Naturally, other structural changes may also take place. Finally, it is reasonable to adopt the idea that these specific structural changes may account for the strong temperature dependence of the structural relaxation time for the $GdCl_3$-$3AlCl_3$ supercooled liquid, thus, offering a link between structure and dynamics.

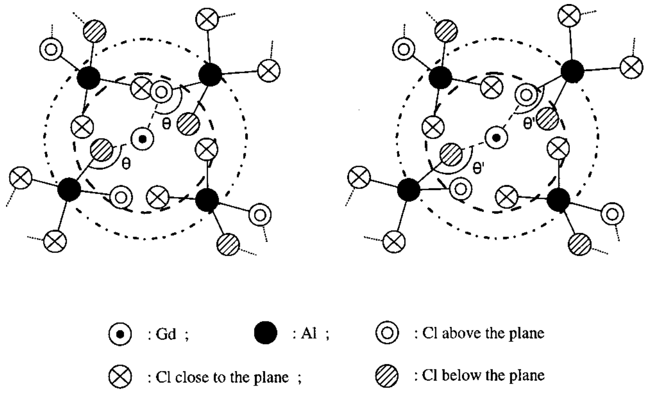

FIG. 5. Schematic representations of the local coordination environment around a Gd atom for glassy (a) and supercooled liquid (b) $GdCl_3$-$3AlCl_3$. The eight Cl atoms forming the first coordination polyhedron in the glass (represented in the two-dimensional picture as a dashed circle) are radially arranged around the central Gd atom with a mean distance ~2.8 Å. The Gd-Cl bonds are not sketched for simplicity. Four Al atoms are almost equidistant from the Gd atom in (a) at a distance ~3.85 Å (i.e., the radius of the dashed-dotted circle). The temperature rise causes, as described in the text, an increase of particular Gd-Cl-Al angles, from θ to $\theta' > \theta$, rendering, thus, the disposition of the Al atoms around Gd quite irregular in the supercooled liquid (b).

V. CONCLUSIONS

A dynamic light scattering investigation has been undertaken for the $GdCl_3$-$3AlCl_3$ member of the glass-forming family, RX_3-AlX_3 (R: Gd,La,Nd,Ho; X: Cl,Br). Density and orientation autocorrelation functions were found to decay highly nonexponentially. The temperature dependence of the characteristic time for the structural relaxation was found to be strong, classifying this material a ''fragile'' one. The origin of the nonexponential relaxation was discussed in the framework of specific models that relate the stretching exponent with the dimensionality of the space where the relaxators are supposed to act. Finally, the elucidation of the microscopic origin of the fragility that this system presents has been attempted, resorting to structural information provided by Raman spectroscopy and a temperature dependent EXAFS study. The strong temperature effect on the arrangement of the next-nearest neighbors sphere around Gd atoms, seems to be the determining factor of the structural relaxation in this glass former.

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