Relaxation dynamics in orientational glasses

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The multipolar relaxation dynamics observed in dipolar and quadrupolar glasses are reviewed. Special attention is given to the distribution of the relaxation times and to the temperature dependence of the mean relaxation rates. Experimental evidence is provided that orientational glasses can be described in terms of 'strong glasses' that are characterized by a low density of configurational states in the potential energy surface. It is suggested that this behavior results from the natural separation of timescales of reorientational and diffusive processes in these crystals.

1. Introduction

Orientational glasses (OG) are crystalline materials that transform from a high-temperature crystalline phase into a low-temperature glassy state (for a recent review see ref. [1]). Analogous to spin glasses (SG) (for a review see ref. [2]), randomly substituted impurity ions (or molecules) that carry a moment are located on a topologically ordered lattice. These moments have orientational degrees of freedom and they interact with one another. The dominant exchange interaction can be of electrostatic dipolar, quadrupolar or octupolar or of elastic quadrupolar nature. In the latter case the interaction is mediated via lattice strains. Due to site disorder and anisotropic interactions, the orientational disorder is cooperatively frozen-in. In the spin-glass problem site disorder of the spins and the Rudermann/Kittel/Kasuya/Yoshida (RKKY) interaction, which changes sign with distance, yield a frustrated ground state [2].

The use of the term 'glass-state' suggests some similarity with canonical glasses such as vitreous silica. Indeed, orientational glasses exhibit relaxation dynamics similar to those observed in canonical glasses. In addition, the low-temperature thermodynamic, elastic and dielectric properties are characteristic of amorphous systems. The advantage of OG is that they can be modelled in terms of a Hamiltonian. Prerequisites of model Hamiltonians are random fields (RF) which can be thought to be introduced by the substitutional impurity atoms, or random bonds (RB). In the RB systems, frustrated ground states appear when the variance of the interaction ΔJ is larger than the average interaction J.

Schematic x,T-phase diagrams of $A_{1-x}B_x$ mixed crystals are shown in figs. 1(a) and (b). A characteristic phase diagram of solid solutions of a constituent B, which is characterized by a multipolar moment, with a non-polar constituent A, is given in fig. 1(a): KCl:KOH [3], para-ortho hydrogen mixtures [4], KBr:KCN [5], Ar:N_2 [6], Kr:CH_4 [7], $KTaO_3$:Li [8] are the most prominent examples. At high temperatures, the mixed crystals and the pure molecular compounds exhibit a high-symmetry crystalline phase that is stabilized by a fast reorientational motion of the moments. With decreasing temperatures, the crystals with a high concentration of the constituent B undergo transitions into orientationally ordered phases. However, below a critical concentration, x_c, long-range orientational order is

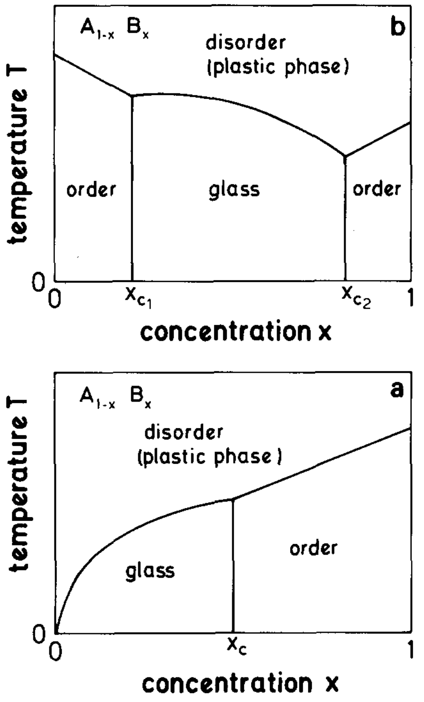

Fig. 1. (a) Schematic $x-T$ phase diagrams of A : B mixed crystals. B denotes an orientationally ordered compound. A denotes a constituent without multipolar moments. (b) Schematic $x-T$ phase diagram of two orientationally ordered compounds.

suppressed and the crystals freeze into a disordered glassy state. Figure 1(b) shows mixtures of two orientationally ordered compounds A and B that exhibit a disordered low-temperature state. Well known examples are mixtures of ferroelectric and antiferroelectric compounds such as rubidium ammonium dihydrogen phosphate (RADP) [9] and mixtures of elastically ordered KCN and NaCN [10]. In RADP, a frustrated ground state is believed to occur via the competing electric interactions. In NaCN : KCN, it seems plausible that random fields suppress long-range elastic order [11]: random strains are introduced by the volume difference of the impurity atoms that cause quenched elastic relaxations of the neighboring ions.

Here we focus especially on the relaxation dynamics in OG at the glass transition and compare the results to what is observed in canonical glasses and in polymers. These systems exhibit a primary (α-type) relaxation that shows a broad and asymmetric distribution of relaxation times when plotted versus the logarithm of the measuring frequency, f. The shape can be described in terms of a Kohlrausch–Williams–Watts (KWW) expression that corresponds to a stretched exponential behavior in the time domain. The temperature dependence of the mean relaxation times often shows clear deviations from an Arrhenius behavior and usually is parameterized in terms of the phenomenological Vogel–Fulcher (VF) law. Secondary (β-type) relaxation processes in canonical glasses exhibit a broad distribution of relaxation times which often can be fitted with a Cole–Cole ansatz. The mean relaxation times of the β-relaxation follow a purely thermally activated behavior.

In what follows, we discuss the relaxation dynamics in dipolar and quadrupolar glasses, i.e. in systems where the topological disorder is quenched far above the glass transition. Orientational glasses exhibit a natural separation of the timescales for reorientation and for translation. It is interesting to compare the results in orientational glasses with what is observed in canonical glasses where these timescales are of the same order of magnitude and to search for similarities and for systematic differences. In addition, we tried to obtain a microscopic understanding of primary and secondary relaxation processes.

2. Dipolar glasses

Dipolar glasses are characterized by only one orientational degree of freedom. Thus, we expect only one relaxation mode, i.e. only the primary relaxation.

2.1. *Dipoles in a non-polar host*

2.1.1. *KCl : OH*

The pioneering work in KCl : OH of Känzig et al. [3] was the first investigation of a system exhibiting an orientational glass transition. However, the authors interpreted their data in terms of a smeared-out ferroelectric phase transition. In 1965, Brout [12] gave an interpretation in terms of a glass-like state reminiscent to what was observed in dilute magnetic systems like Cu : Mn. Later, detailed experimental reports were given by Knop and Känzig [13] on KBr : OH and by Anderson and co-workers [14]. The published data provide some evidence for a broadening of the relaxation time distribution growing from about one decade at 2 K to three decades at 0.3 K. A Gaussian distribution of relaxation times provided a satisfactory fit to the data. A detailed analysis of the data in terms of a distribution of relaxation times and of a temperature dependence of the mean relaxation times is hampered by the increasing importance of tunneling phenomena at low temperatures. It seems that quantum fluctuations suppress the glass transition [15].

2.1.2. *KI : NH$_4$I*

It has been shown by Fehst et al. [16] that the NH$_4$ ion in the rocksalt modification of NH$_4$I exhibits a large permanent dipole moment. In solid solutions of KI : NH$_4$I, the rocksalt structure is stabilized down to the lowest temperatures and the dipolar moments undergo a cooperative freezing process devoid of long-range order. Figure 2 (taken from ref. [16]) shows the temperature dependence of the dielectric loss in $(KI)_{1-x}(NH_4I)_x$ for concentrations $x = 0.14$ and $x = 0.43$. The insets indicate an extremely broad distribution of relaxation times and strong deviations from an Arrhenius behavior, which again reveal the increasing importance of tunneling phenomena with decreasing temperatures.

2.2. *Off-center systems*

2.2.1. *KTaO$_3$: Li (KTL)*

Pure potassium tantalate has a cubic perovskite structure that is known to have little stability against polar distortions. However, KTaO$_3$ does not become ferroelectric but exhibits a dielectric constant that reaches almost 4000 at 4 K. Li substitutes for K and has twelve nearest oxygen neighbors. Due to its small ionic radius, Li takes an off-center position and thus carries a dipole moment. At sufficiently low doping levels, the Li ions freeze in into a glassy state [8].

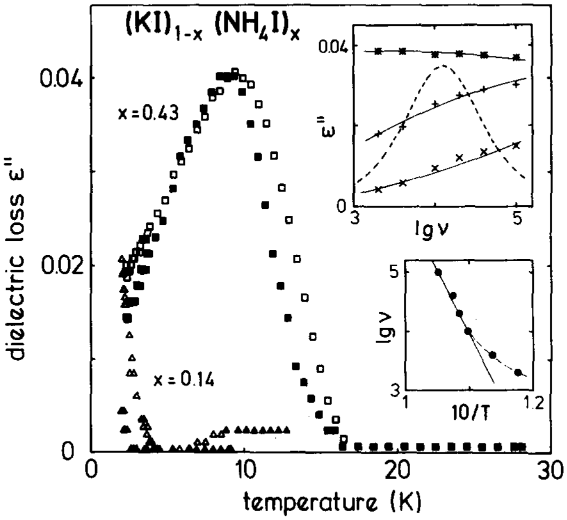

Fig. 2. Temperature dependence of the dieletric loss in solid solutions of KI : NH$_4$I measured at 4 kHz (full symbols) and 100 kHz (open symbols). The upper inset shows the frequency dependence of the dielectric loss for $x = 0.43$. The dashed line is calculated using a Debye relaxator model. In the lower inset the T-dependence of the mean relaxation time is plotted versus the inverse temperature. Figure taken from ref. [16].

In KTL the the frequency dependence of the impurity relaxation mode can be modelled using a Gaussian distribution of energy barriers. The mean relaxation rate follows a Vogel–Fulcher behavior with a VF-temperature $T_{VF} = 6$ K and a most probable height of the energy barriers of the order of $E_B = 1400$ K at the freezing temperature [8].

2.3. *Proton glasses*

2.3.1. *RADP*

At room temperature the hydrogen-bonded phosphates (MH$_2$PO$_4$) form a class of isostructural crystals. When M is an alkali ion, the low-temperature state is ferroelectric. However, the ammonium compounds exhibit a paraelectric-to-ferroelectric phase transition. Mixtures of ferroelectric and antiferroelectric compounds show a broad regime in which the long-range electric order is suppressed owing to frustration effects, and these systems were treated as dipolar analogs to spin glasses [9].

Considerable efforts have been undertaken to study the dipolar relaxation in an extremely broad range of frequencies: in $Rb_{0.65}(NH_4)_{0.35}H_pO_4$, the temperature dependence of the mean relaxation time was studied over 17 orders of magnitude in frequency, including dielectric spectroscopy, Brillouin and Raman scattering and measurements of the saturation of the electric polarization [17]. A fit to the phenomenological Vogel–Fulcher law yielded $T_{VF} = 9$ K and a hindering barrier $E_B = 268$ K. The distribution of relaxation times can be modelled using a Gaussian distribution of relaxation times.

2.3.2. Mixed betaine compounds

The structural and the dielectric properties of a number of addition compounds of α-amino acids with inorganic components have been investigated in detail [18]. These compounds consist of an amino acid and an inorganic component. Most of them undergo a paraelectric-to-ferroelectric phase transition. The best known representative of this group is triglycine sulfate. Betaine phosphite (BPI) is another ferroelectric representative with an ordering temperature of 216 K. From the protonated samples, only betaine phosphate (BP) undergoes an antiferroelectric transition at 86 K. The first experimental evidence for a glassy low-temperature state in solid solutions of BP and BPI was reported by Santos et al. [19].

Figure 3 shows the dielectric loss versus the logarithm of frequency as measured in $(BP)_{0.4}$ $(BPI)_{0.6}$ (the figure is taken from ref. [20]). Figure 3 reveals an increasing width of the loss peaks with decreasing temperatures. The asymmetric line shapes can be described using a KWW fit (solid lines). The mean relaxation times follow almost an ideal Arrhenius behavior with a hindering barrier $E_B = 252$ K.

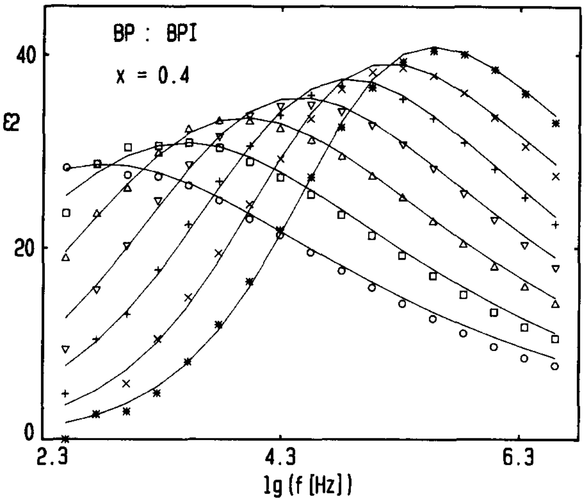

Fig. 3. Dielectric loss versus the logarithm of the measuring frequency in the mixed betain compound $(BP)_{0.4}(BPI)_{0.6}$ for different temperatures ranging from 14 K to 21 K: ○, 14 K; □, 15 K; △, 16.1 K; ▽, 17.2 K; +18.2 K; ×, 19.3 K; *, 20.3 K. The solid lines are calculated using a asymmetric distribution of relaxation times. Figure taken from ref. [20].

3. Quadrupolar glasses

3.1. KBr : KCN and NaCN : KCN

The pure cyanides KCN and NaCN exhibit a NaCl-type structure at high temperatures. This high-symmetry phase is stabilized by a fast reorientational motion of the CN molecules between symmetry equivalent orientations. At 168 K (288 K) KCN (NaCN) undergoes a first-order phase transition to an orthorhombic structure in which the CN ions are aligned along the former cubic ⟨110⟩ axis. This phase transition into an elastically ordered phase is driven by a strong coupling of the CN reorientations to transverse acoustic phonons. The CN molecule also carries a small dipole moment. Thus, below 83 K (172 K) KCN (NaCN) exhibits antiferroelectric order in which the CN ions are ordered with respect to head and tail.

In KBr : KCN the phase transitions are suppressed below a critical concentration (fig. 1(a)) and the orientational disorder is collectively frozen-in. NaCN : KCN mixtures can be described by phase diagrams of type 1(b), in which the elastic (and electric) order is suppressed at intermediate concentrations. From the pure compounds, it becomes clear that the CN molecule is characterized by a strong elastic quadrupolar moment and by a weaker electric dipole moment. In the relaxation dynamics at the glass transition, we thus expect two relaxation modes. Volkmann et al. [21] presented data on the elastic and the dielectric dispersion in KBr : KCN which covered a common frequency range of six decades. Their results

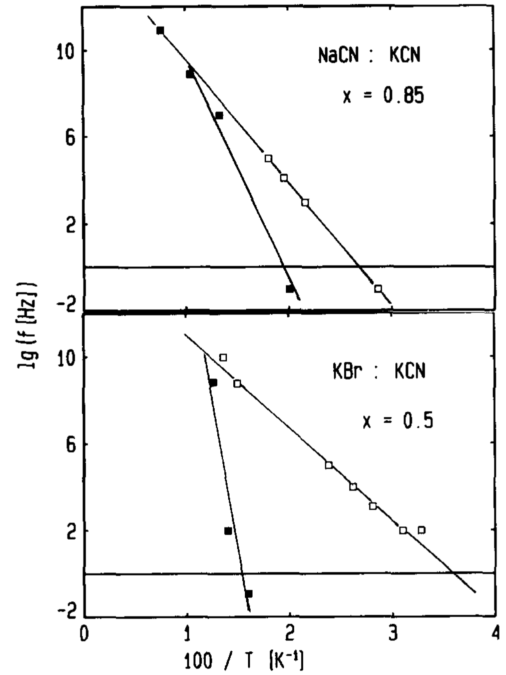

Fig. 4. Mean relaxation rates in $(KBr)_{0.5}(KBr)_{0.5}$ and in $(NaCN)_{0.15}(KCN)_{0.85}$ plotted versus the inverse temperature: quadrupolar relaxation (full symbols); dipolar relaxation: (empty symbols). For references see text.

demonstrated unambiguously that dipolar and quadrupolar freezing is fully decoupled.

Figure 4 reveals the temperatures of the cusp maxima of the imaginary parts of the quadrupolar and dipolar susceptibilities in $(KBr)_{1-x}(KCN)_x$ for $x = 0.5$ and for $(NaCN)_{1-n}(KCN)_x$ for $x = 0.85$ (quadrupolar susceptibilities: neutron scattering studies: THz [22]; Brillouin measurements; GHz [23,24]; ultrasonic results; 10 MHz [25] and torsion pendulum experiments 0.1 H [26]; dipolar susceptibilities: dielectric results: 100 Hz–1 GHz [21]; 100 Hz–100 kHz [10]; 1 GHz–10 GHz [27]; torsion pendulum experiments: 0.1 Hz [26]). The temperature dependence of both relaxation rates can roughly be described by an Arrhenius law. Significant deviations appear for the quadrupolar freezing. The hindering barriers for the quadrupolar relaxation are unphysically high (KBr : KCN: $E_B = 6000$ K; NaCN : KCN : $E_B = 2400$ K). The quadrupolar relaxation in the cyanide glasses has been described by Walton [24] in terms of a hierarchically constrained relaxation. The T-dependence of the dipolar relaxation rates can be described by an Arrhenius law with energy barriers that are of the order of 1000 K. These results reveal a striking similarity with the relaxation dynamics in canonical glasses: the quadrupolar relaxation that can be viewed as the freezing-in of local shear distortions corresponds to the α-relaxation, while the dipolar reorientations that probe the energy barriers as set up by the quadrupolar interaction energies can be viewed as secondary processes.

4. Conclusion

The main features of the relaxation processes of orientational glasses have been discussed. We find that primary relaxation modes exhibit an almost symmetric distribution of relaxation times and show only very weak deviations from a purely thermally activated behavior. If the data are parameterized in terms of a modified Vogel–Fulcher law $f = f_0 \exp[D \cdot T_{VF}/(T - T_{VF})]$, the parameter D, which gives the ratio of the mean hindering barrier E_B to the Vogel–Fulcher temperature T_{VF}, for orientational glasses is significantly larger than 20. Thus, according to a classification scheme of strong and fragile glasses [28], OG belong to the class of strong glasses. Accordingly, specific heat anomalies at the glass transition are totally absent [1]. Strong glasses are characterized by a low density of configurational states of the potential energy surface [28]. It seems that the quenched disorder of OG is responsible for their 'strong' character.

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