Structural changes across the glass-transition in a glassy-crystal

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1. Introduction

Some substances formed by globular-shaped molecules display a mesophase between the fully disordered liquid and the completely ordered crystalline phase, in which molecules reveal a hindered rotation about the molecular centres of mass, which form a crystal lattice usually showing high space-group symmetry [1]. This phase is usually referred to as a plastic crystal, rotator- or rotationally-disordered crystal phase. In some cases, such a phase can be supercooled by rapid cooling, preventing complete orientational ordering and an orientational-glass (OG) state exhibiting static orientational disorder is achieved. Previous experience shows that such a phase shares many common features with canonical glasses.

The fragility index provides a measure of the temperature dependence of typical dynamical properties of glass-forming materials such as the relaxation time τ, associated to viscous flow. Such a quantity portrays *strong* glasses (*e.g.*, most covalent glasses) as those showing Arrhenius temperature dependence of τ, while *fragile* glasses are those departing from such behavior. Most materials forming plastic phases are rather strong glass formers. Here we focus on 1,2-difluoro-1,1,2,2-tetrachloroethane (also called Freon112), which strongly departs from this behavior.

Freon112 has two molecular conformations, trans and gauche, as shown in Fig. 1. The trans conformer is the most stable at high temperatures. When the liquid is cooled, a transition to a plastic crystal with a BCC structure takes place and further cooling leads to an OG state [2,3]. Specific heat measurements showed three thermal effects, which were ascribed to the OG transition ($T_g = 90$ K), a secondary glass-transition ($T_{gII} = 60$ K) and the freezing of the trans–gauche conformational disorder ($T_{gc} = 130$ K) [2]. The most astonishing feature of this compound is its

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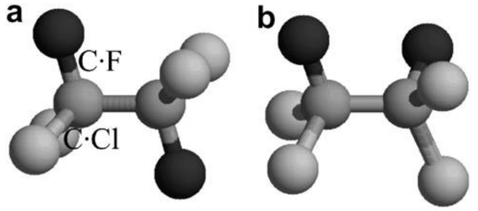

Fig. 1. Trans (a) and gauche (b) conformers of Freon112.

dynamical behavior, characterizing Freon112 as the most fragile OG known so far [3,4]. Furthermore, a recent dielectric study revealed a complex behavior, with the presence of an unusually strong secondary relaxation merging with the main relaxation at about 130 K [3].

2. Experimental

Freon112 with a minimum purity of 99% was used without further purification. In order to monitor structural changes across the thermal transitions, neutron diffraction experiments were performed at the Institute Laue–Langevin (ILL) using the D1b and D4c diffractometers. Data from D4c collected up to 23 Å^{-1} allow us to obtain information about changes of the intra- and inter-molecular structure of this compound across the calorimetric transitions, while spectra obtained with D1b, using a smaller momentum transfer ($Q_{\max} = 3.3$ Å^{-1}), were used to determine the evolution of the crystal lattice parameter with temperature.

3. Results and discussion

Fig. 2 shows the three main structural features, in order to investigate their correlation and the relationship to the dynamics of the system. In Fig. 2(a), we provide the relative temperature variation of intramolecular distances within the crystalline BCC phase, namely the distances of a carbon atom from the F or Cl atoms directly bonded to it (distances C · Cl and C · F in Fig. 1). The same figure depicts the variation of the relevant bond angles (Cl–C–Cl and Cl–C–F). Both sets of results suggest the onset of a prominent change in molecular structure at about 130 K, which has a particularly strong influence on the Cl–C–F bond angle.

Fig. 2(b) shows a set of radial distribution functions $g(r)$ for temperatures comprising the OG, plastic crystal and liquid states. This graph reveals rather drastic changes in short-range order that take place across the successive thermal transitions. In particular, notice the variations of the main peak as well as the leading shoulder at about 6–7 Å and the strong change of the position of the peak at about 9 Å with temperature (inset). These findings unveil drastic rearrangements in the molecular structure as well as in molecular packing within the crystal or liquid phases as well as a density effect. Because of the underlying BCC lattice structure, the latter type of changes can be followed quite accurately from alterations in the position of the main Bragg peaks. The result is shown in Fig. 2(c) where the temperature dependence of the atomic number density is plotted for the BCC phase and the liquid phase. As expected, the strongest variation takes place within the region of the primary calorimetric glass-transition (ca. 90 K). A weaker feature at 130 K, only seen when depicting the density of the BCC phase relative to that fitted at temperatures above 145 K is revealed by the inset of Fig. 2(c).

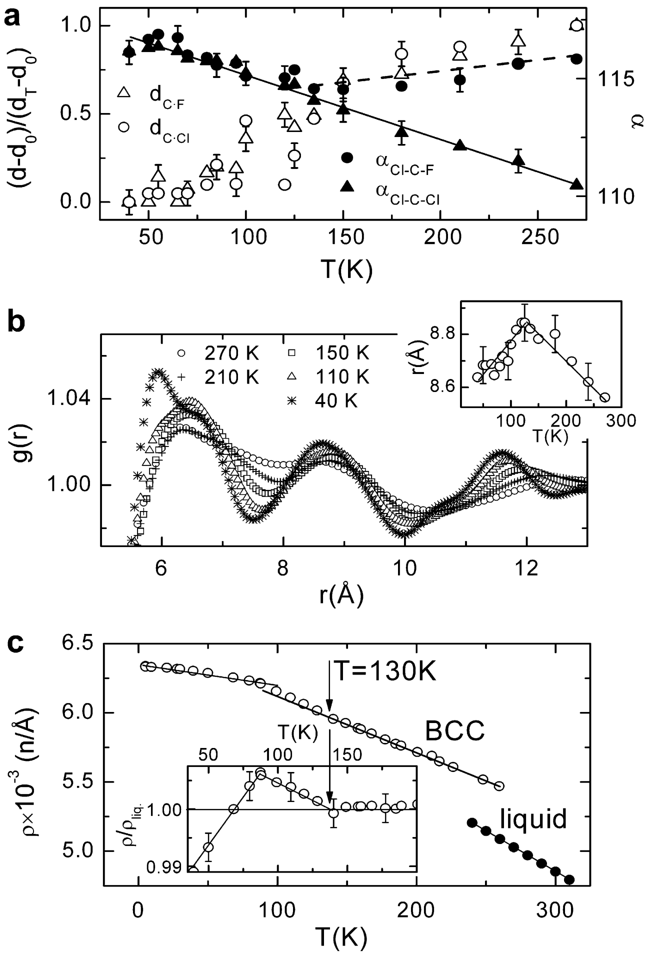

Fig. 2. (a) Molecular structure changes in Freon112: Reduced C · F (open triangles) and C · Cl distances (open circles), defined in Fig. 1 (d_0 and d_T denote the distances at 40 and 275 K, respectively), and the Cl–C–F (filled circles) and Cl–C–Cl angles (filled triangles) as a function of temperature. (b) Radial distribution function $g(r)$ for some representative temperatures. The inset shows the temperature variation of the second peak position. (c) Temperature variation of density for the BCC phase, together with that of the liquid. The inset shows the density of the BCC phase related to that for temperatures above 145 K. All lines are shown to guide the eyes.

4. Conclusions

The presented preliminary analysis of the diffraction data evidences the presence of rather large molecular rearrangements that take place across the thermal transitions in this material. To assess the magnitude of such changes, a direct comparison can be made with results from other materials forming plastic and OG-phases such as ethanol [5]. Data on the diffraction patterns as well as a quantitative analysis of the radial distributions for ethanol show much weaker changes than those reported here. In fact, most of such changes concern an enhancement of orientational correlations upon crossing the phase boundary from the plastic crystal to the OG phase from above, while changes associated with molecular structure were far more subtle. The observed relatively strong anomalies at about 130 K in Freon112 indicate a phase-transition like change of the molecular conformation at about 130 K, a notion that is of high relevance for the explanation of the unusual dynamic behavior of this material [3], and deserves further investigation.

In summary, structural studies on Freon112 indicate a strong interplay between internal and external molecular dynamics. Notice that the two conformers of Freon112 do give rise to rather different molecular potential energy surfaces and as such, they provide the material with an intrinsic source of competing interactions. The role of such built-in frustration in the unusual dynamic properties of the material is at present being studied in greater detail [3].

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