Evidence for a supercooled plastic-crystal phase in solid ethanol

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The existence of an orientationally disordered cubic phase of solid ethanol is revealed by x-ray diffraction and Raman spectroscopic measurements. Such a phase, whose existence was postulated some time ago on the basis of specific-heat measurements, is produced by quenching below some 95 K a plastic crystal formed upon melting and subsequent annealing of the topologically disordered (glassy) solid. The relevance of the present findings for current discussions on glassy dynamics is analyzed in some detail.

Despite recent advances in our understanding of the microscopic mechanisms driving the dynamics of glasses at intermediate (above 1 K) temperatures,1 most studies regarding topologically disordered solids (i.e., real glassy materials) still encounter substantial difficulties when trying to go beyond descriptions of the data by means of phenomenological approaches. This contrasts with a more developed understanding regarding the dynamics of disordered crystals formed by either mixed2 or chemically homogeneous (plastic and glassy crystals3,4) materials, which in common with structural glasses exhibit some features considered as fingerprints of the glassy dynamics. Such developments are, however, restricted to materials which being disordered in some quantity (chemical composition, relative molecular orientations, etc.) still have an underlying crystal lattice, thus enabling the calculation of a number of physical properties (i.e., coupling between molecular translations and rotations, softening of elastic constants due to disorder, anomalous dielectric behavior, etc.) in terms of well-established techniques.5 The relevance of such findings for the understanding of real glasses was not explored in detail, perhaps due to the fact that most of the existing materials can either be converted into topologically or disordered-crystal states, exceptions to such a rule being rare (amorphous and hexagonal ice being an example which involves rather different routes of preparation which pose severe conditions when trying to compare the two in terms of transition temperatures).

The existence of some polymorphic phase in solid ethanol which could be prepared under mild thermal conditions was known to exist since the work of Haida et al.5 who observed calorimetric anomalies distinct from those associated with the glass transition (T_{g}=97 K), the melting of the stable crystal (T_{m}=169 K), or crystallization of the supercooled liquid into such a phase (T_{cr}=125 K). In fact, the presence of a well-defined exothermic anomaly at some 115 K was interpreted as the onset of a crystal phase (crystal II) which once grown exhibited a calorimetric transition into another crystalline phase (glassy crystal), showing small differences in heat capacity with those of the glass obtained by rapid cooling of the normal liquid, but evidencing a calorimetric entropy between that of the glass and the stable crystal. A NMR relaxation measurement reported later on6 showed that the dynamics of the real glass and that of the glassy crystal as sampled by the values of the second moment of the NMR shared some analogies, whereas inspection of the relative values of the relaxation times revealed some systematic differences between both.

Our aim here is to establish the nature of the crystal II and glassy crystal phases of this material. If, as expected, a supercooled plastic crystal (SPC) can be formed by freezing the rotational freedom of the plastic crystal (PC), it would then provide an excellent benchmark material where quantitative studies on the role of different degrees of freedom (positional and orientational) on the dynamics of the glass at intermediate temperatures could be carried in detail.

Spectroscopic grade ethanol was used without further purification, avoiding exposure to atmosphere to prevent capture of water vapour. The x-ray diffraction measurements were performed using a Stoe diffractometer, using the Cu Kα line λ=1.5418 Å, being the samples contained in glass...
capillaries cooled by an Oxford Instruments cryostream cooler. The Raman spectra were recorded on an X-Y Dilor spectrometer equipped with an enhanced photodiode array. Slit widths giving nominal resolutions of 1.8 and 3.7 cm$^{-1}$ were employed for crystal and glass spectra, respectively. Excitation was achieved by an Ar$^+$ source lasing at 514 nm and delivering some 10 mW to the sample which was contained within 5 mm quartz tubes. These were kept within a Oxford Instruments flux cryostat used to keep temperatures between 10 K and ambient. The scattered light was collected on the Stokes side at right angles.

Sample preparation regarding the normal glass and stable (monoclinic) crystal phases is straightforward since it only involves a quench below $T_g=97$ K at a rate not slower than 6 K min$^{-1}$ (glass) and a subsequent annealing at some 130 K for at least a half hour (crystal). As regards the preparation of the supercooled-plastic-crystal phase, our own experience has shown that this involves a quench below $\approx 100$ K for at least a half hour (normal glass at 80 K, supercooled liquids 10 $\rho=958.2$ kg m$^{-3}$). The value for the lattice constant mentioned above becomes very close to that of 5.377(4) Å corresponding to the $a$ dimension of the monoclinic cell. On the other hand, the close location of the (110) reflection with the wave vector characteristic of the peak maximum in the glass phase provides a clear example of the physical meaning of the first diffraction peak in glasses, an issue which was the focus of some recent controversies. In fact, comparison of diffractograms of glass and cubic crystal clearly suggests that only the width of such a peak should bear a clear physical significance in a glass.

Because of the small number of observed Bragg reflections, further details regarding the structure of such a cubic phase could only be derived from additional independent measurements. Between these, a comparison of the Raman spectra of the solid within its three (cubic, monoclinic, and glass) phases was chosen and the most relevant results are displayed in Fig. 2. The immediate consequence of such a comparison regards the existence of a strong static disorder in the cubic phase as demonstrated by the absence of well-resolved phonon peaks below some 40 meV. That such a disorder is of static (orientational) nature is further ratified by the absence of any thermal anomaly for this phase below our actual $T=80$ K, which should be present if substantial rotational motions were still present. It seems then clear that the cubic phase represents a SPC or glassy crystal phase, where the large rotational motions present above 97 K have frozen into a strongly orientationally disordered phase. In fact, spectra measured during annealing time show in addition to the peaks shown in the SPC phase an additional strong diffuse background. The amount and kind of disorder (i.e., statistical or through some preferential direction) cannot be inferred from the available data, although the similitude between the...
orientations as it is known to occur in the glass phase of the existence of remarkable correlations between molecular with the maximum of $S$. The coincidence of the position of the intense Bragg reflection ~\(~Z \)R~\)corresponds to the same one explored by calorimetric measurements where the maxima of the SPC sample is located at some 6.5 K whereas that for the glass appears at \(~\approx\)4.5 K.

In consequence, and with the above provisos in mind, it seems clear that the cubic SPC phase of ethanol here studied corresponds to the same one explored by calorimetric means. This being the case, the difference in specific heats at $T_g$ discussed by Johari and others upon melting the glass and that arising from the SPC-plastic crystal transition can be rationalized on a more quantitative basis. In fact, comparison of the jumps in $C_p$ at the glass transition and rotational arrest points $T_g = T_a = 97$ K of 35 and 23 J K$^{-1}$ mol$^{-1}$ evidences that some 66% of the jump upon melting the glass can be accounted by the onset of rapid molecular rotations. Such a percentage becomes even larger (75%) for the jump in entropy, and goes to some 63% for the configurational entropy.

In conclusion, the existence of a orientationally disordered phase in a system considered since many decades ago as one of the clearest examples of a glass-forming liquid has been demonstrated. From the present data as well as from that already available, the SPC solid can be rightly considered as a phase with an intermediate kind of disorder between the ground state (monoclinic crystal) and the glass. In this respect, its detailed study will open up the possibility of separating the effects of positional and orientational disorder on different magnitudes usually considered in studies on glassy dynamics.

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5 O. Haida, H. Suga, and S. Seki, J. Chem. Thermodyn. 9, 1133