Quantitative Assessment of the Effects of Orientational and Positional Disorder on Glassy Dynamics

M. A. Ramos and S. Vieira
Laboratorio de Bajas Temperaturas, Departamento de Física de la Materia Condensada, Facultad de Ciencias, C-III, Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain

F. J. Bermejo and J. Dawidowski
Instituto de Estructura de la Materia, Consejo Superior de Investigaciones Científicas, Serrano 123, E-28006 Madrid, Spain

H. E. Fischer, H. Schober, and M. A. González
Institut Laue-Langevin, B.P. 156, F-38042 Grenoble Cedex 9, France

C. K. Loong and D. L. Price
Argonne National Laboratory, Argonne, Illinois 60439

(Received 6 May 1996)

The microscopic dynamics of several phases of solid ethanol are studied under the same thermodynamic conditions by inelastic neutron scattering. It is found that the vibrational density of states of the orientational glass phase, where the molecules are arranged on an ordered lattice but with disordered orientations, is very similar to that of the structural glass phase, where the molecules are disordered both in position and orientation. Low-temperature specific heat measurements on the same phases strongly support the neutron measurements. We therefore find that positional disorder, even in a stoichiometrically homogeneous system such as ethanol, is not essential for the manifestation of glasslike behavior to an extent comparable with that exhibited by the structural glass. [S0031-9007(96)02079-0]

PACS numbers: 63.50.+x, 65.40.+g

The quest for a simple microscopic model which retains sufficient detail to explain the principal phenomena of so-called "glassy behavior" (e.g., in the context of low-temperature thermal [1] or elastic [2] properties) has recently been the focus of increased research activity [3]. In fact, a number of physical models have been developed which exhibit typical "glassy anomalies" but which do not contain the structural disorder characteristic of a true glass or amorphous solid. These models encompass a variety of conceptually simple systems which vary from a finite temperature Frenkel-Kontorova chain [4] to mean-field descriptions devoid of multiple free-energy barriers [5] and ordered periodic objects such as a long-range array of Josephson junctions [6]. As far as condensed matter systems are concerned, an outstanding question is the extent to which the loss of periodicity, going from an ideal crystal to a true structural glass, affects the microscopic dynamics and gives rise to the whole variety of phenomena characteristic of glasses, such as the appearance of complex relaxational behavior and low-energy two-level systems (TLS) [7]. A natural way of addressing this question would be to study a single system which can be produced in two different phases showing glassy behavior at the same temperature, one phase retaining molecular periodicity, and the other not. This is the subject of the present paper.

A class of condensed matter systems which can exhibit the characteristics of glassy dynamics is that of crystals where only the positional order is preserved while the relative orientations of the (nonspherical) particles at lattice sites show either rotational or orientational disorder [8,9], the former referring to rotating molecules (a rotator-phase crystal) and the latter to molecules being fixed but randomly oriented (an orientational glass). Because of the presence of an underlying lattice, such orientationally disordered crystals offer the possibility of a fully analytical treatment for a number of static and dynamical properties also considered as being characteristic of the glassy state, such as the softening of the elastic constants due to orientational disorder, the frequency dependence of the sound velocity and the well-known anomalies in the dielectric behavior seen in most glasses [10,11].

However, most materials which can be prepared easily as orientationally disordered crystals cannot be produced in amorphous form [9]. In addition, the best-studied examples of the former, such as complex organics [12] or the stoichiometrically mixed orientational glasses [13,14], exhibit in some respects [15] a behavior disparate with that shown by canonical (i.e., structural) glasses [1,16]. These two factors have, to some extent, separated the study of glassy dynamics into two camps: structural glasses and orientational glasses. As a result, some significant advances arising from microscopic studies on orientationally disordered crystals (e.g., the origin of excess modes in the vibrational density of states $Z(E)$ [11]) have been considered

0031-9007/96/78(1)/82(4)$10.00

to have limited relevance for the understanding of similar phenomena in amorphous matter [17].

The purpose of this work is to present, by means of a case study of ethanol, some results which should help to bridge the gap between studies of orientational glasses and structural glasses. Ethanol appears to be unique in that it can be prepared as a stable orientationally ordered crystal, a rotator-phase (RP) crystal, an orientational glass (OG), and a structural glass, all from the liquid state with relative ease [18] and *in situ* using the same sample subjected to mild variations in temperature and thermal history. Most importantly, the OG and structural glass phases can be studied in the same temperature range ($T < 95$ K).

The structural glass is formed by quenching the liquid at a rate greater than about 6 K/min ($T_g \approx 97$ K), and the RP crystal (metastable) is formed through a subsequent anneal at a temperature between about 105 and 110 K for several hours. The OG phase can then be obtained simply by cooling the RP crystal below the transition temperature $T_g^{\mathrm{OG}} \approx 97$ K. Finally, the stable crystal can be formed either through slow cooling from the liquid ($T_m = 159$ K) or by annealing the RP phase at a temperature above 125 K. The structure of the stable crystal has been determined by Jönsson to be monoclinic [19].

Based on preliminary x-ray diffraction work, as well as recent neutron diffraction measurements [20], the structures of the OG and RP phases are known to be those of bcc crystals with lattice constants of $a_{\mathrm{og}} = 5.28$ Å ($T \approx 30$ K) and $a_{\mathrm{rp}} = 5.32$ Å ($T \approx 105$ K). In both cases the molecules sit at lattice positions, in the RP crystal executing nearly spherical rotations and in the OG being frozen in apparently random orientations [20].

To investigate in more detail the close similarity between the generalized frequency distributions of ethanol in its amorphous and orientationally disordered crystal forms, already illustrated by previous Raman studies [18], a set of measurements of the dynamic structure factors by cold neutron time-of-flight (TOF) spectroscopy was carried out. In both cases, the spectrum of the stable crystal was taken as a base line to which the glassy anomalies could be referred.

Figure 1(a) shows a set of TOF spectra averaged over all detector angles ($Q_{\max} \approx 2$ Å^{-1}) for a fully deuterated sample of ethanol in its OG, amorphous and stable crystal phases (all at $T = 30$ K), using the IN6 spectrometer at the Institut Laue-Langevin. The fully deuterated sample was chosen since its substantial coherent cross section made it possible to ascertain the phase of the sample by plotting the total intensity versus wave number, displayed in the inset of Fig. 1(a).

The comparison between the three spectra of Fig. 1(a) constitutes the clearest indication, to the authors' knowledge, of the close relationship between the dynamics of an orientationally disordered crystal with that of a state attained by the removal of its underlying lattice (i.e., amorphous). Although it was already known, from previous studies of low-temperature thermal properties (e.g., Ref. [14]), that the vibrational densities of states of an orientational glass and a structural glass should be similar, this is the first time that such a similarity has been demonstrated quantitatively for a single system at the same temperature. As can be seen, the main discrepancy between the glass and OG spectra is the small difference in height of the inelastic feature located at about 2 meV, customarily called the "boson" peak in the glass literature [17]. In fact, the glass and OG spectra become basically indistinguishable above 3 meV, while their convergence to the stable crystal's spectrum near 6 meV sets an upper limit to the frequency range of their excess "glassy" modes. This frequency range corresponds roughly to the "plateau region" [1] in the thermal conductivity of glassy materials.

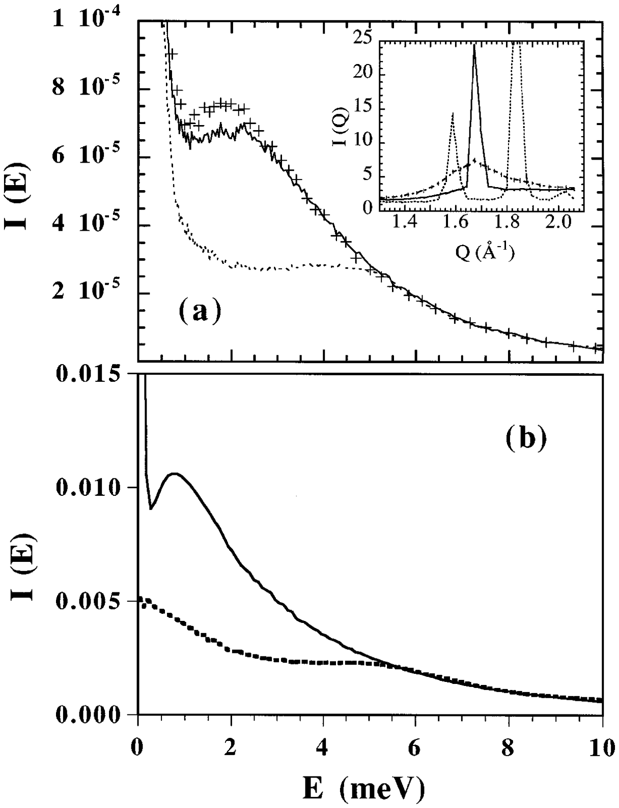

FIG. 1. (a) A comparison of TOF spectra for deuterated ethanol within the frequency range characteristic of the boson peak for the stable crystal (dots), OG (solid), and structural glass (crosses), all at $T = 30$ K. The inset shows the *in situ* TOF diffraction results, which confirm production of (i) the stable crystal (dots) showing the two peaks which index in terms of envelopes over $(110, 002, 11\bar{1})$ and $(10\bar{2}, 012, 111, 020)$ grouped reflections, (ii) the OG phase (solid line) showing the (110) reflection, and (iii) the glass phase (vertical bars). Notice that both the stable crystal and OG peaks are resolution limited due to the grouping of detector banks for improved counting statistics. (b) TOF spectra for the RP crystal (solid line) and the stable crystal (dots) at 105 K.

Figure 1(b) compares TOF spectra at 105 K for the RP phase and the stable crystal (produced by annealing the RP at 125 K), which clearly shows that, apart from a noticeable downshift in the boson peak frequency of the RP phase, the extent of glassy modes (i.e., relative to the spectrum of the stable crystal) in the RP crystal is comparable with that of the OG phase.

To probe the extent to which the close similarity of the glass and OG spectra translates into thermodynamic properties, several sets of specific heat C_p measurements at temperatures within the interval $2 \leq T \leq 30$ K were carried out using a calorimetric cell described elsewhere [21]. This experimental setup has been designed to prepare *in situ* the different phases and to conduct low-temperature C_p measurements of molecular solids which are liquid at ambient temperature [22].

Some results for the measured specific heats C_p of fully hydrogenated ethanol in its stable crystal, OG and glass phases are shown in Fig. 2(a) plotted as $C_p(T)/T^3$. The data for the stable crystal show (as expected) far smaller values than those for the glass (a bit less than half), and the broad maximum at some 14 K arises mainly from the first intense maximum (due mostly to molecular rotations) appearing in the stable crystal TOF spectrum at about 6 meV. The glass and OG crystal curves are remarkably similar, the differences being a shift of some 1.5 K in the temperature corresponding to their maxima (denoted as $T_{\max}$), a few percent decrease in the height of that peak (denoted as P_c) and, possibly, a small difference in the onset of the quasilinear contribution ascribed to tunneling between two-level systems. We find that $T_{\max}$ and P_c scale as $P_c \propto T_{\max}^{-1.52}$, an exponent not far from that of -1.6 recently found from the analysis of a large number of materials [23]. Following the scaling of Liu *et al.* [24], the inset of Fig. 2(a) shows a graph of $[C_p(T)/T^3]/P_c$ versus $T/T_{\max}$, where it is seen that the data for the glass and OG crystal superimpose for temperatures above $T/T_{\max} = 0.6$. In contrast, and following similar findings regarding different forms of vitreous silica of various densities [24] upon scaling, the curve for the ordered crystal shows a far narrower shape.

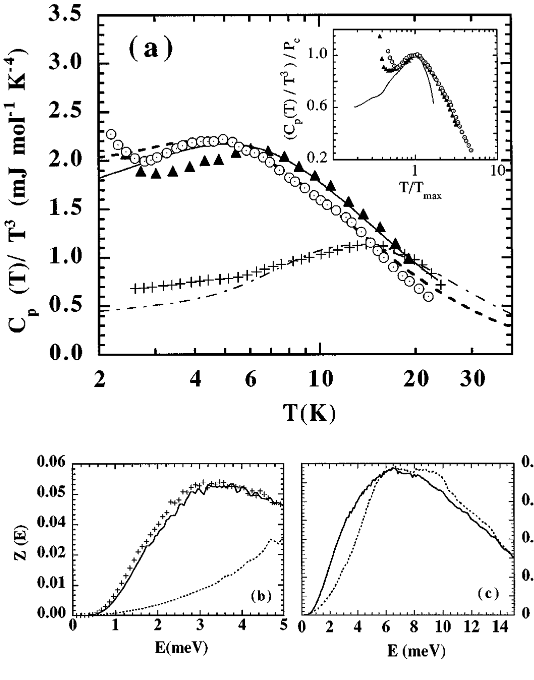

FIG. 2. (a) Measured specific heats of hydrogenated ethanol for the stable crystal (crosses), OG (triangles), and structural glass (circles), displayed as $C_p(T)/T^3$. The smooth lines show the specific heat calculated within the harmonic approximation from the $Z(E)$ generalized vibrational frequency distributions obtained from TOF measurements. Inset: A scaling of the specific heat curves as described in the text. (b) The low-frequency region of the $Z(E)$ curves for the glass (crosses), OG (solid), and stable crystal (dots). (c) A comparison of the $Z(E)$ curves for the RP (solid) and stable crystal (dots) measured at 125 K.

A calculation of the specific heats was attempted using data for the vibrational frequency distributions measured by neutron TOF on several instruments, allowing the measurement of $Z(E)$ up to energies corresponding to the maximum temperature considered. Whereas accurate low-frequency data (down to 0.35 meV) were derived from the measurements on IN6, data extending up to 35 meV were measured using the HRMECS spectrometer at IPNS (ANL) at the two incident energies of 10 meV and 40 meV, which enabled us to derive useful information on the down-scattering side of the spectrum. The results for the specific heat calculated on the basis of the harmonic approximation are shown in Fig. 2(a) and give a rather good agreement with the measured $C_p(T)/T^3$ data. The calculated curves, which correspond to spectra measured at a single temperature (i.e., anharmonic effects are neglected) follow the trend shown by the calorimetric data down to about 3 K, where resolution effects start to be important. The present measurements are also in rather good agreement with estimates for the densities of states derived from our previous Raman data [18].

Additional specific heat (C_p) data [21] for ethanol show that a freezing of the rotational motions (RP → OG) leads to a drop in C_p which is almost 90% of that involved in the liquid → glass transition (wherein both rotational and translational movements freeze out), attesting to the large amount of energy in the molecular rotations of the RP phase. It is therefore not too surprising that the two transition temperatures (T_g and T_g^{OG}) are the same within our precision of measurement. It is, however, somewhat curious that neither of these two temperatures changes significantly upon complete deuteration of the ethanol molecule (showing only an increase of about 2 K), since one could expect deuteration to change significantly the moment of inertia of the molecule.

In conclusion, we have shown, through measurements of the microscopic dynamics of the orientational glass and structural glass phases of a single system (ethanol) at the same temperature, that the loss of the positional order of the molecules perturbs only slightly the amount of excess glassy vibrational modes already present in the orientational glass. In addition, the evidence of glassy behavior in the rotator-phase crystal and the presence of a freezing transition into the orientational glass phase, apart from constituting a physical realization of some rigid-needle models which show glassy behavior [25], opens up the possibility of investigating whether the RP → OG transition is a purely dynamic phenomenon; if so, then it might be explained within some mode-coupling approach of the kind used to investigate solid-solid transitions [26]. Towards this aim, we are planning to carry out high-pressure measurements of the dynamics of the phases and phase transitions in ethanol.

This work was supported in part by DGICYT Grant (Spain) No. PB92-0114-C03-01, and EU Grant No. INTAS 93-32-30. M. García-Hernández and F. Mompeán gave us invaluable assistance regarding initial measurements carried out at ANL. The work at ANL was supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract No. W-31-109-ENG-38. Technical assistance by A. Buendía and help with the software by J. G. Rodrigo for the low-temperature work is gratefully acknowledged.

[1] R. C. Zeller and R. O. Pohl, Phys. Rev. B **4**, 2029 (1971).

[2] B. E. White, Jr., and R. O. Pohl, Z. Phys. B **100**, 401 (1996).

[3] See, for instance, E. R. Grannan, M. Randeria, and J. P. Sethna, Phys. Rev. B **41**, 7784 (1990); **41**, 7799 (1990), and references therein.

[4] A. L. Shumway and J. P. Sethna, Phys. Rev. Lett. **67**, 995 (1991).

[5] F. Ritort, Phys. Rev. Lett. **75**, 1190 (1995); see also B. J. Kim, G. S. Jeon, and M. Y. Choi, Phys. Rev. Lett. **76**, 4648 (1996).

[6] P. Chandra, M. V. Feigelman, and L. B. Ioffe, Phys. Rev. Lett. **76**, 4805 (1996).

[7] For recent attempts to develop a dynamical model for stretched exponential relaxation in solids, see, for instance, D. L. Huber, Phys. Rev. E **53**, 6544 (1996); C. G. van de Walle, Phys. Rev. B **53**, 11 292 (1996).

[8] R. M. Lynden-Bell and K. H. Michel, Rev. Mod. Phys. **66**, 721 (1994).

[9] *The Plastically Crystalline State (Orientationally-Disordered Crystals)*, edited by J. N. Sherwood (Wiley, New York, 1978).

[10] A. Loidl and R. Böhmer in *Disorder Effects on Relaxational Processes*, edited by R. Richert and A. Blumen (Springer-Verlag, Berlin, 1994), p. 659.

[11] J. P. Sethna, E. Grannan, and M. Randeria, Physica (Amsterdam) **169B**, 316 (1991), and references therein.

[12] M. Descamps, M. Bée, P. Derollez, J. F. Willart, and L. Carpentier, in *Quasielastic Neutron Scattering*, edited by J. Colmenero *et al.* (World Scientific, Singapore, 1994), p. 107.

[13] K. Binder and J. Reger, Adv. Phys. **41**, 547 (1992).

[14] J. J. DeYoreo, W. Knaak, M. Meissner, and R. O. Pohl, Phys. Rev. B **34**, 8828 (1986).

[15] See, for instance, Fig. 2.6 in R. Böhmer and C. A. Angell in Ref. [10], p. 11.

[16] R. B. Stephens, Phys. Rev. B **8**, 2896 (1973).

[17] F. J. Bermejo, A. Criado, and J. L. Martinez, Phys. Lett. A **195**, 236 (1994).

[18] A. Srinivasan, F. J. Bermejo, A. de Andrés, J. Dawidowski, J. Zúñiga, and A. Criado, Phys. Rev. B **53**, 8172 (1996), and references therein.

[19] P. G. Jönsson, Acta Crystallogr. Sect. B **32**, 232 (1976).

[20] R. Fayos, F. J. Bermejo, J. Dawidowski, H. E. Fischer, and M. A. González, Phys. Rev. Lett. **77**, 3823 (1996). They report a study by neutron diffraction on the microscopic structure of the liquid, glass, RP crystal, OG crystal, and stable crystal phases of the material. The structures of the RP and OG cubic phases are shown to exhibit a remarkably short range for the orientational (intermolecular) correlations.

[21] M. A. Ramos, Q. W. Zou, S. Vieira, and F. J. Bermejo, Proceedings of the XXI International Conference on Low Temperature Physics, Prague, 1996, Czech. J. Phys. **46**, Suppl S4, 2235 (1996).

[22] Preliminary low-temperature specific heat data are given by M. A. Ramos and S. Vieira in *Nanostructured and Non-Crystalline Materials*, edited by M. A. Vazquez *et al.* (World Scientific, Singapore, 1995), p. 212; see also M. A. Ramos, Q. W. Zhou, J. A. Moreno, and S. Vieira in Proceedings of the Workshop on Non-equilibrium phenomena in Supercooled liquids, Glasses and Amorphous Materials (World Scientific, Singapore, to be published).

[23] X. Liu and H. von Löhneysen, Europhys. Lett. **33**, 617 (1996).

[24] X. Liu, H. von Löhneysen, G. Weiss, and J. Arndt, Z. Phys. B **99**, 49 (1995).

[25] C. Renner, H. Löwen, and J. L. Barrat, Phys. Rev. E **52**, 5091 (1995).

[26] E. R. Duering, R. Schilling, and H. P. Wittmann, Z. Phys. B **100**, 409 (1996).