

Low-temperature specific heat of amorphous, orientational glass, and crystal phases of ethanol

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We have measured the specific heat between 0.5 and 20 K for three different solid phases of ethanol: the stable monoclinic crystal, the structural (amorphous) glass, and an orientationally disordered cubic crystalline phase (also named as orientational glass or "glassy crystal"). We have therefore extended previous experiments on ethanol down to temperatures low enough as to investigate the region typically dominated in glasses by two-level-systems excitations or tunneling states. It is found that the orientational glass (i.e., a disordered crystal) of ethanol exhibits the same linear-term coefficient in the specific heat, and hence the same density of tunneling states, than the true, structural glass (i.e., an amorphous solid). In addition, combining specific-heat measurements in both deuterated and hydrogenated ethanol has allowed us to study the isotopic effect on these universal glassy properties, as well as on the Debye coefficients.

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It is well known^{1,2} that glasses or amorphous solids exhibit *universal* thermal properties at low temperatures, which are in turn very different from those of crystalline solids. Below 1 K, the specific heat C_p of dielectric glasses is much larger and the thermal conductivity κ orders of magnitude lower than the corresponding values found in their crystalline counterparts. C_p depends approximately linearly ($C_p \propto T$) and κ almost quadratically ($\kappa \propto T^2$) on temperature. This is in clear contrast to the cubic dependences observed in crystals for both properties, well understood in terms of Debye's theory of lattice vibrations. Above 1 K, C_p still deviates strongly from the expected $C_{\text{Debye}} \propto T^3$ dependence, exhibiting a hump in C_p/T^3 which is directly related to the so-called *boson peak* observed by neutron or Raman vibrational spectroscopies. In the same temperature range the thermal conductivity exhibits an ubiquitous *plateau*. These and other "anomalous" low-temperature properties of amorphous solids² (at least for $T < 1$ K) were soon well accounted by the tunneling model,^{3,4} whose fundamental postulate was the general existence of small groups of atoms in amorphous solids which can tunnel between two configurations of very similar energy [two-level systems (TLS's)].

Although we have used above the terms "amorphous" and "glass" as synonymous, a subtle distinction between them can be made:⁵ An amorphous or noncrystalline solid is any solid lacking the long-range translational order characteristic of a crystal, whereas a glass is an amorphous solid exhibiting the glass-transition phenomenon, and is usually obtained by supercooling the liquid fast enough. Some theories or models⁶⁻⁸ have traditionally focused on the lack of translational periodicity in an amorphous solid (topological disorder) as the intrinsic source of all this "anomalous" behavior. On the other hand, other approaches⁹⁻¹¹ have considered more relevant the mere existence of sufficient configurational degrees of freedom, or some kind of elastic defects, etc., in the solid lattice (truly amorphous or not), hence being the *glassy* character of the material the essential ingredient. One natural method to address this issue has been the search for glassy behavior in crystalline solids with some kind of disorder, different from the translational one characteristic of

amorphous solids. Most of these experimental and theoretical efforts, aiming to elucidate the very nature of the disorder responsible for the low-temperature properties of glasses, have been devoted to alkali cyanide¹¹⁻¹⁴ and other mixed crystals.¹⁵ These mixed crystals are grown with a controlled amount of orientational disorder leading to an orientationally disordered state for appropriate concentrations, exhibiting low-temperature thermal properties very similar to those observed in structural (amorphous) glasses.^{11,13,15}

Nevertheless, another kind of "orientational glasses" exists that furthermore shows a glass transition from a homogeneous, vitreous (nonergodic) state to a liquidlike (ergodic) state. These "glassy crystals" are produced by quenching plastic crystals¹⁶ and exhibit orientational disorder of dynamic origin. In general, an orientational glass (OG) state can be reached by supercooling a high-symmetry crystalline phase where molecules are rotating (plastic crystal or rotator phase) and by-passing a lower symmetry crystalline phase, so that the rotational disorder of the plastic phase is quenched into an orientational disorder within a crystalline arrangement of the molecules. Three decades ago, Suga, Seki, and co-workers^{17,18} studied exhaustively the thermodynamic behavior of a number of pure low-molecular weight compounds, finding glass-transition phenomena in all of them typically around $T \sim 100$ K. In some cases, they corresponded to standard glass transitions from the (amorphous) structural glass to the supercooled liquid (they called them "glassy liquids"); in other cases, the transitions were from an orientationally disordered crystal (glassy crystals) to its rotationally disordered plastic crystalline phase. This dynamic transition from a non-ergodic state (the OG phase) to an ergodic one (the plastic crystal, which always has a small entropy of fusion and plays the role of the supercooled liquid) is therefore thermodynamically equivalent to the standard glass transition.

The most interesting case appeared to be ethanol, which could be prepared either as a stable crystal, as a structural (amorphous) glass, or as a glassy crystal (i.e., OG), depending upon temperatures and cooling rates below its melting

point at $T_m = 159$ K.¹⁸ Very strikingly, both kinds of glass transitions occur at the same temperature $T_g \approx 95$ K and with comparable jumps in specific heat. Ethanol therefore constitutes a unique model system to study even quantitatively the roles of translational and orientational disorder in the low-temperature properties of glasses and/or amorphous solids. More recent studies^{19–23} have shed light on the structural, dynamical and thermal properties of polymorphic ethanol. It was found that the OG phase exhibits a *boson peak* in the low-energy vibrational spectrum very similar to that of the amorphous glass, seen as peaks at ~ 2 meV in inelastic neutron-scattering spectra²² and broad maxima in C_p/T^3 at around 6 K,^{22,23} those of the structural glass always being slightly higher and occurring at slightly lower energies/temperatures than for the OG. On the contrary, the stable crystal showed the expected Debye behavior at low energies and temperatures.

However, the question remains whether these orientational glasses possess tunneling states or TLS (likely the most genuine fingerprint of glassy properties) to the same amount (and hence presumably of the same type) that structural, amorphous glasses. Both phases being attainable in pure ethanol, extending previous specific-heat measurements down to below 1 K will allow us to answer that important question. Furthermore, it could provide us with information concerning two different major views on the low-energy excitations in glasses. Namely, some views about the nature the boson peak attribute it, somehow, to modifications of the crystalline phonon spectra induced by the structural disorder in the amorphous network,⁸ and hence the TLS should be independent, localized excitations, with no direct relation with the vibrational states responsible for the boson peak, thermal properties above 1 K, etc. Other views such as the soft-potential model (SPM), (for a review, see Refs. 24,25) consider that both kinds of excitations originate from similar soft atomic potentials, either double-well ones (TLS) or single-well ones (soft vibrations responsible for the boson peak), which coexist at very low energies with ordinary acoustic phonons, and one should expect then a correlated presence of TLS and soft modes.

We have measured the heat capacity of the three solid phases of ethanol at low temperature (amorphous glass, orientational glass, and stable crystal) in a ³He cryostat, by using a quasiadiabatic calorimetric cell, identical to that previously used in experiments on glycerol.²⁶ Commercially available fully deuterated ethanol CD₃CD₂OD (M & G Chemicals, anhydrous 99%) was employed. The advantage of deuterated ethanol compared to hydrogenated one is a less stringent requirement of cooling rates to obtain the purely amorphous glass. We have followed the same experimental procedure used in earlier measurements of ethanol in a ⁴He cryostat,²³ by continuously monitoring the different ethanol phases through thermal and calorimetric measurements in the region ranging from above the melting point to below the glass transition temperature, either when cooling to prepare the glass or when heating to change its state. The liquid ethanol is placed inside a thin-walled copper can, and a gold wire is employed as heat switch to cool the experimental cell. The subtracted addenda contribution to the total mea-

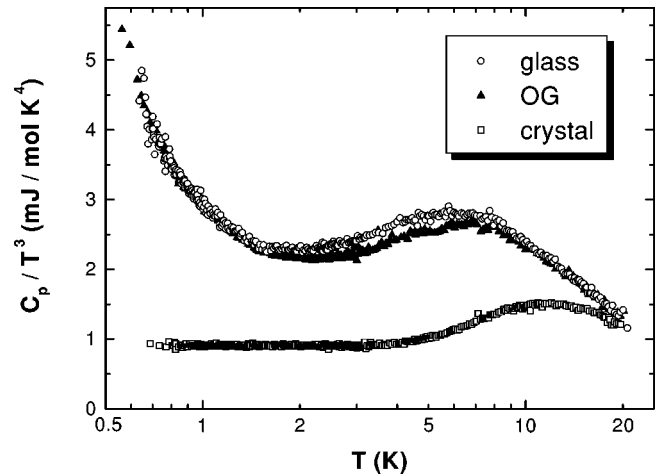


FIG. 1. Low-temperature specific heat C_p/T^3 of (amorphous) glass, orientational glass (OG), and stable (monoclinic) crystal phases of fully deuterated ethanol.

sured heat capacity at 4.2 (1 K) was about 6 (24%) for the glasses and about 16 (52%) for the crystal. In addition, we have also measured the specific heat of hydrogenated ethanol (CH₃CH₂OH, Merck, max. 0.02% H₂O) for both stable and orientationally disordered crystals, in order to study the isotopic effect. We were not able to obtain a 100% glass phase with hydrogenated ethanol in our ³He-cryostat experimental system, in contrast to the case of using deuterated ethanol, as evidenced by thermal monitoring during cooling and subsequent calorimetric characterization of the phase formed.²³

In Fig. 1, the specific heat of the three solid phases of fully deuterated ethanol is plotted as C_p/T^3 vs T in the whole measured temperature range. Data above 2 K agree reasonably well with those previously measured in different experimental setups.^{22,23} Below 2 K, a clear upturn for the two *glassy* phases is now observed, what is an indication of the presence of TLS excitations in both cases, and is in contrast to the typical Debye behavior observed in the stable crystal. Nevertheless, this can be studied more clearly by means of the usual C_p/T vs T^2 representation at the lowest temperatures, which is shown in Fig. 2(a). As can be seen there, amorphous and orientational glasses of ethanol exhibit a very similar linear term in the specific heat [the intercept at $T=0$ in Fig. 2(a)]. The usual method to obtain that linear term in the low-temperature specific heat of glasses has been making a linear fit $C_p = C_1 T + C_3 T^3$, where C_3 should be the Debye coefficient. This procedure has been questioned and discussed in more detail elsewhere,²⁷ where another simple method, partly based upon the SPM, was proposed instead to analyze quantitatively the specific heat of glasses below a few K. In short, it was suggested to fit specific-heat data in a C_p/T vs T^2 representation by using a quadratic polynomial $C_p = C_{\text{TLS}} T + C_D T^3 + C_{\text{sm}} T^5$ in the temperature range $0 < T < \frac{3}{2} T_{\text{min}}$, where the coefficients should correspond to the contributions of TLS, Debye lattice vibrations and quasiharmonic soft modes, respectively, and T_{min} is the temperature at which the minimum in C_p/T^3 occurs. The limit of the fit was chosen²⁷ from the SPM, as roughly the temperature where the simple $C_p = C_{\text{sm}} T^5$ SPM approximation^{24,25} starts

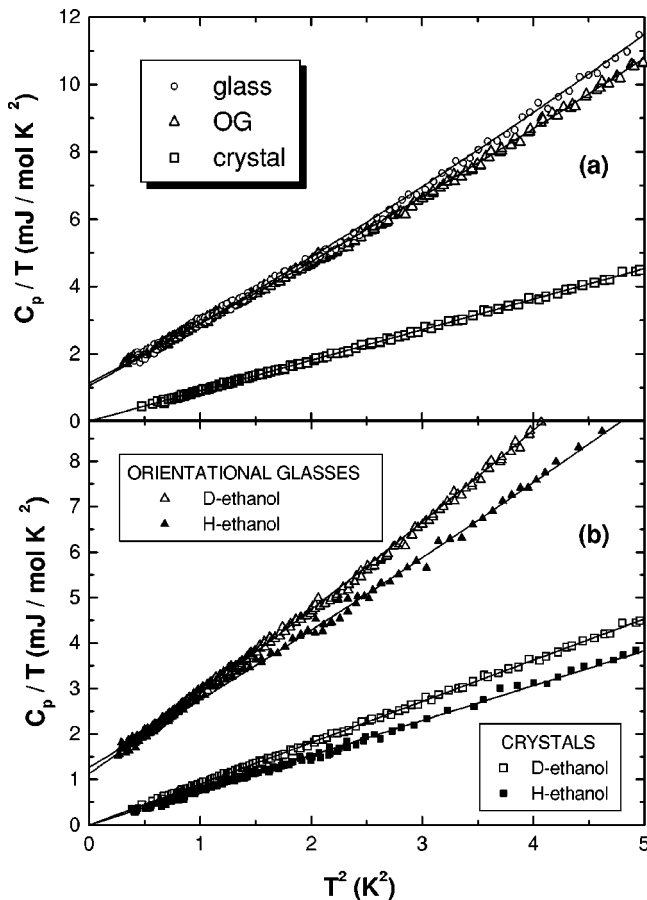


FIG. 2. Low-temperature specific heat C_p/T plotted versus T^2 for different solid phases of ethanol. Solid lines are least-squares fits to either a straight line passing through the origin (crystal) or a two-degree polynomial (glass and OG). See text for details of the fits. (a) Fully deuterated ethanol. (b) Comparison for both the stable and the orientationally disordered crystalline phases between fully deuterated (D) and normal, hydrogenated (H) ethanol.

deviating $\sim 5\%$ from the true $C_p(T)$ curve due to the boson peak feature. By using this method, $C_{\text{TLS}} = 1.05 \pm 0.05 \text{ mJ/mol K}^2$ is obtained for the amorphous glass and $C_{\text{TLS}} = 1.13 \pm 0.05 \text{ mJ/mol K}^2$ for the OG phase. From the cubic coefficients, we obtain Debye temperatures of $\Theta_D = 213 \pm 3 \text{ K}$ and $\Theta_D = 217 \pm 3 \text{ K}$, respectively. In any case, the main result of the present work is that the OG phase (a disordered crystal) of ethanol exhibits the same linear contribution to the specific heat as the conventional glass (an amorphous solid). Therefore, the density of TLS excitations is basically the same, within experimental error, independently on whether one has translational disorder or not. This finding also gives indirect support to SPM-like approaches, in the sense pointed out above that a similar boson-peak feature in both the amorphous and the orientational glass is correlated with a similar density of TLS. Moreover, a rigid amorphous network such as amorphous Si has been recently observed²⁸ not to have significant low-energy excitations. Hence the “glassy” character of a solid seems to be the fundamental ingredient to account for the universal low-temperature properties of noncrystalline materials, rather

than the topological or translational disorder of an amorphous solid.

In Fig. 2(b) we compare the specific heat below 2 K of fully deuterated (D) and fully hydrogenated (H) ethanol, both for stable crystal and OG phases. The former exhibit a clear Debye behavior with $\Theta_D = 268 \pm 2 \text{ K}$ for D ethanol and $\Theta_D = 284 \pm 2 \text{ K}$ for H ethanol. On the other hand, the quadratic fit defined above gives for the OG phase of H ethanol $C_{\text{TLS}} = 1.27 \pm 0.04 \text{ mJ/mol K}^2$, and $\Theta_D = 229 \pm 3 \text{ K}$.

If we assume that the elastic moduli are the same, the sound velocities are proportional to the inverse root of mass density, and hence $C_D \propto M^{3/2}$ and so $\Theta_D \propto M^{-1/2}$, where M is the molecular mass. The isotopic ratio is $(M_D/M_H)^{3/2} = 1.20$, which agrees very well with the corresponding isotopic ratios found for the Debye coefficient C_D between the crystals (1.18) and between the OG’s (1.19). Also, a similar value (1.16) is found^{23,27} from previous measurements at not so low temperatures for the amorphous glasses. Therefore, the mass difference seems to account naturally for the isotopic effect on the lattice-vibrational (Debye) contributions in every phase.

On the other hand, Theenhaus *et al.*²⁹ have recently studied the role of orientations and translation-rotation coupling in the microscopic dynamics of molecular liquids and glasses. They found a *boson peak* which originates from a localized and nonpropagating orientational mode coupled to translational, acoustic phonons. That “orientational peak” ω_{OP} exhibits an isotopic effect such as $\omega_{\text{OP}} \propto I^{-1/2}$, where I is the moment of inertia. Using ethanol-molecule bond lengths and angles obtained from neutron-scattering experiments,³⁰ one finds that full deuteration increases the moment of inertia as $I_D/I_H = 1.23$, so that ω_{OP} should decrease a factor 0.90. If we scale ω_{OP} with the temperature of the maximum in C_p/T^3 , we find isotopic ratios for the maxima of 6.0/6.1 for the structural glass and 6.4/6.8 for the OG, at least in qualitative agreement within experimental error. Concerning the TLS, we also observe that deuteration decreases the linear term C_{TLS} of the OG by a factor 0.89 ± 0.07 . These apparent correlations could be a signature of the *orientational* origin of the glassy low-temperature excitations, but their validity cannot be deduced only from these data. Further experiments employing partially deuterated ethanols could be very interesting to get more insight into the microscopic nature of TLS and boson-peak vibrational modes.

In summary, low-temperature specific heat measurements of ethanol have shown that *amorphicity* (lack of long-range translational order) is not an essential requisite for universal “glassy behavior,” since an orientationally disordered crystal exhibits—qualitative and quantitatively—very similar low-temperature specific heat (TLS and boson peak) to that of the structural (amorphous) glass of the same substance. Furthermore, the OG also presents a very similar “glass transition” (a dynamic transition between a nonergodic and an ergodic state). We have also studied the isotopic effect on the low-temperature specific heat of their different phases. In particular, the different Debye contributions, either for crystals or glasses, can be accounted simply by changes in the molecu-

lar masses, whereas the boson peak position and C_{TLS} decrease with increasing mass or moment of inertia of the ethanol molecule.

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- ¹R.C. Zeller and R.O. Pohl, Phys. Rev. B **4**, 2029 (1971).
²For a review, see *Amorphous Solids: Low Temperature Properties*, edited by W. A. Phillips (Springer, Berlin, 1981); W.A. Phillips, Rep. Prog. Phys. **50**, 1657 (1987).
³W.A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).
⁴P.W. Anderson, B.I. Halperin, and C.M. Varma, Philos. Mag. **25**, 1 (1972).
⁵S.R. Elliott, *Physics of Amorphous Materials*, 2nd ed. (Longman, Essex, 1990).
⁶R. Orbach, Science **231**, 814 (1986).
⁷A.J. Sievers and S. Takeno, Phys. Rev. B **39**, 3374 (1989).
⁸S.I. Simdyankin, S.N. Taraskin, M. Elenius, S.R. Elliott, and M. Dzugutov, cond-mat/0108336 v2 (unpublished), and references therein.
⁹A.V. Granato, Phys. Rev. Lett. **68**, 974 (1992); J. Phys. Chem. Solids **55**, 931 (1994).
¹⁰H. Tanaka, cond-mat/0106041 (unpublished), and references therein.
¹¹S.K. Watson, Phys. Rev. Lett. **75**, 1965 (1995).
¹²K. Knorr and A. Loidl, Phys. Rev. B **31**, 5387 (1985).
¹³J.J. De Yoreo, W. Knaak, M. Meissner, and R.O. Pohl, Phys. Rev. B **34**, 8828 (1986).
¹⁴E.R. Grannan, M. Randeria, and J.P. Sethna, Phys. Rev. B **41**, 7799 (1990).
¹⁵For a review, see R.O. Pohl, X. Liu, and E.J. Thompson, Rev. Mod. Phys. (to be published).
¹⁶*The Plastically Crystalline State (Orientationally-Disordered Crystals)*, edited by J.N. Sherwood (Wiley, New York, 1978).
¹⁷H. Suga and S. Seki, J. Non-Cryst. Solids **16**, 171 (1974).
¹⁸O. Haida, H. Suga, and S. Seki, J. Chem. Thermodyn. **9**, 1133 (1977).
¹⁹A. Srinivasan, F.J. Bermejo, A. de Andrés, J. Dawidowski, J. Zúniga, and A. Criado, Phys. Rev. B **53**, 8172 (1996).
²⁰R. Fayos, F.J. Bermejo, J. Dawidowski, H.E. Fischer, and M.A. González, Phys. Rev. Lett. **77**, 3823 (1996).
²¹F.J. Bermejo, A. Criado, R. Fayos, R. Fernández-Perea, H.E. Fischer, E. Suard, A. Gueylyah, and J. Zúniga, Phys. Rev. B **56**, 11 536 (1997).
²²M.A. Ramos, S. Vieira, F.J. Bermejo, J. Dawidowski, H.E. Fischer, H. Schober, M.A. González, C.K. Loong, and D.L. Price, Phys. Rev. Lett. **78**, 82 (1997).
²³C. Talón, M.A. Ramos, S. Vieira, G.J. Cuello, F.J. Bermejo, A. Criado, M.L. Senent, S.M. Bennington, H.E. Fischer, and H. Schober, Phys. Rev. B **58**, 745 (1998).
²⁴D.A. Parshin, Phys. Rev. B **49**, 9400 (1994).
²⁵M.A. Ramos and U. Buchenau, in *Tunneling Systems in Amorphous and Crystalline Solids*, edited by P. Esquinazi (Springer, Berlin, 1998), Chap. 9, pp. 527-569.
²⁶C. Talón, Q.W. Zou, M.A. Ramos, R. Villar, and S. Vieira, Phys. Rev. B **65**, 012203 (2002).
²⁷M.A. Ramos, C. Talón, and S. Vieira, J. Non-Cryst. Solids (to be published).
²⁸X. Liu, B.E. White, Jr., R.O. Pohl, E. Iwanizcko, K.M. Jones, A.H. Mahan, B.N. Nelson, R.S. Crandall, and S. Veprek, Phys. Rev. Lett. **78**, 4418 (1997).
²⁹T. Theenhaus, R. Schilling, A. Latz, and M. Letz, Phys. Rev. E **64**, 051505 (2001).
³⁰C.J. Benmore and Y.L. Loh, J. Chem. Phys. **112**, 5877 (2000).