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# Low-temperature specific heat of structural and orientational glasses of simple alcohols

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## Abstract

In this work, we review, extend and discuss low-temperature specific-heat experiments, that we have conducted on different molecular (hydrogen-bonded) solids both in crystalline and glassy (either amorphous or orientationally disordered) phases. In particular, we have measured the low-temperature specific heat  $C_p$  for a set of simple, well known alcohols: glycerol, propanol and ethanol. For glycerol, we have prepared and measured  $C_p$  of both glass and crystal phases down to 0.5 K. The same has been done for propanol, in this case comparing the strikingly different values observed for the two chemical isomers, 1-propanol and 2-propanol. Moreover, ethanol exhibits a very interesting polymorphism presenting three different solid phases at low temperature: a fully ordered (monoclinic) crystal, an orientationally disordered (cubic) crystal or 'orientational glass' and the ordinary structural (amorphous) glass. By measuring and comparing the low-temperature specific heat of the three phases, in the *boson peak* range 2–10 K as well as in the tunnelling-state range below 1 K, we provide a quantitative confirmation that 'glassy behaviour', either concerning low-temperature properties or the glass-transition phenomenon itself, is not directly related to the lack of long-range crystalline order occurring in amorphous solids.

## 1. Introduction

The universal properties exhibited by glasses at low temperatures or frequencies [1, 2] continue to be one of the major unsolved and debated issues of condensed matter physics, together with the proper phenomenon of the glass transition and the concept of glassy state. It is well known [2–4] that glasses or amorphous solids have physical properties (thermal, vibrational,

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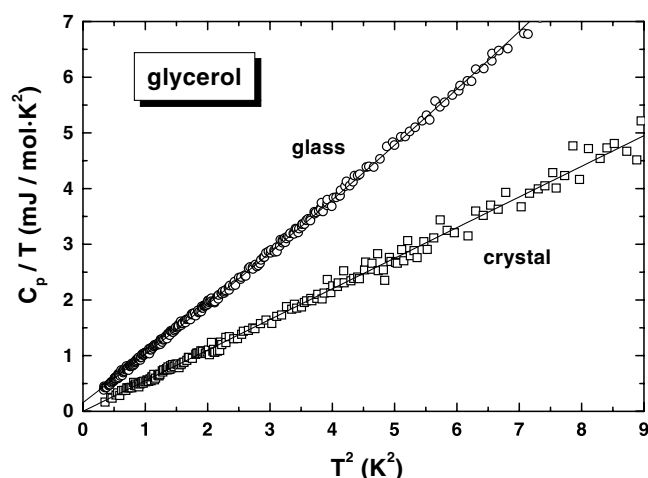
dielectric or acoustic) very different from those of crystalline solids, especially at low energies. Moreover, these properties are very similar among all different types of glassy material, hence the name ‘universal’ [5]. For instance, at temperatures typically  $T < 1$  K, the specific heat  $C_p$  depends approximately linear ( $C_p \propto T$ ) and the thermal conductivity  $\kappa$  almost quadratically ( $\kappa \propto T^2$ ) on temperature [1, 2], in contrast to  $\propto T^3$  dependences observed in crystals for both properties, which are well understood in terms of Debye’s theory. At  $T > 1$  K,  $C_p$  still deviates from the expected  $C_{\text{Debye}} \propto T^3$  dependence, presenting a broad maximum in  $C_p/T^3$ , in the same temperature range where the thermal conductivity exhibits a universal *plateau* [1, 2]. It is now accepted that this universal feature is related to a difference or excess in the vibrational density of states  $g(\nu)$  over the crystalline Debye behaviour, leading to a ubiquitous maximum in  $g(\nu)/\nu^2$  at frequencies  $\nu \sim 1$  THz which is known as the *boson peak*, a dominant feature in the vibrational spectra of glasses very thoroughly observed and studied [6] by Raman and inelastic neutron scattering. Nevertheless, the specific nature of these low-frequency vibrations is still a matter of intense debate.

The above-mentioned low-temperature properties of amorphous solids [2] for  $T < 1$  K were soon successfully accounted for by the tunnelling model (TM) [7, 8], which postulated the ubiquitous existence of atoms or small groups of atoms in amorphous solids which can tunnel between two configurations of very similar energy. Nonetheless, the also rich universal behaviour of glasses above 1 K (the broad maximum in  $C_p/T^3$ , the corresponding boson peak in vibrational spectra or the above-mentioned plateau in the thermal conductivity) still remained unexplained. In short, one may distinguish two types of current approach to addressing these issues: some assume the coexistence at low enough frequencies of Debye-like sound waves with *excess* vibrational excitations to be responsible for the boson peak, whereas others consider that disorder in glasses makes that distinction unsuitable in the whole frequency range of the boson peak region, which would be dominated by hybrid modes. Among the former approaches, the phenomenological soft-potential model (SPM), which can be regarded as an extension of the TM, is one of the best accepted and most often considered. The SPM [9, 10] postulates the coexistence in glasses of acoustic phonons (crystalline-like, extended lattice vibrations) with quasilocalized low-frequency (*soft*) modes. For a more detailed description of the SPM, the reader is referred to the reviews of [11, 12].

To gain understanding in this subject, we have conducted a series of measurements [13–17] of specific heat at low temperatures for a special family of glasses, simple alcohols such as ethanol [13–15], propanol [16] and glycerol [17], which have low glass transition temperatures  $T_g$  (they are liquid at room temperature) and a molecular, hydrogen-bonded network. In this work, we complete and compile these experimental data, and make use of a simple but systematic method to analyse those low-temperature specific-heat data, that allows a more meaningful comparison and discussion of the results. For the cases of glycerol and propanol, we are able to compare elastic data and calorimetric data. In all substances, the specific heat of the corresponding crystalline phase is also presented as a useful reference.

## 2. Experimental details

In order to perform specific-heat measurements at low temperature on different solid alcohols, we have employed an experimental set-up especially designed [14] for samples which are liquid at room temperature and that allows us to prepare *in situ* different solid phases. The calorimetric cell consists in a quasiadiabatic, vacuum-tight sample can of copper, suspended by nylon threads from the inner flange of the cryostat. A calibrated germanium thermometer (Cryo Cal, MCR-50) suited to low-temperature runs, a standard silicon diode (LakeShore D-471) for the measurements at temperatures around 100 K and an electrical heater were attached



**Figure 1.** Low-temperature specific heat of glass (circles) and crystal (squares) phases of glycerol in a  $C_p/T$  versus  $T^2$  plot. Solid lines are least-squares fits, as explained in the text.

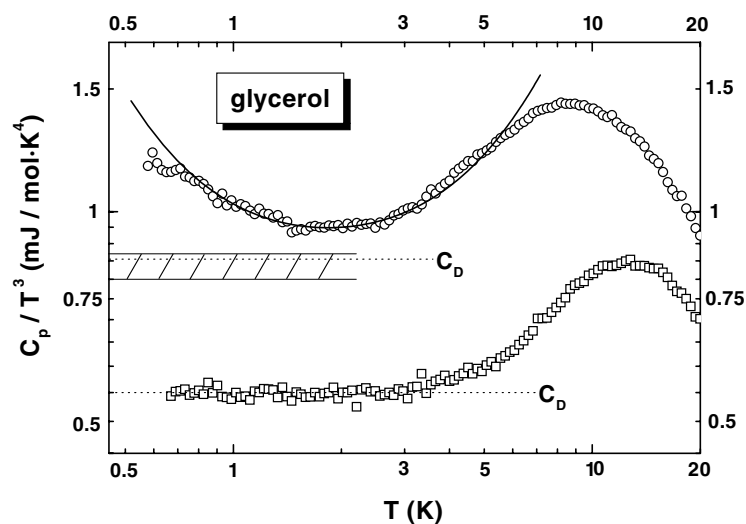
to the thin-walled copper can. To facilitate the rapid attainment of thermal equilibrium *inside* the can, a thin copper mesh was fitted inside the sample holder. A simple mechanical heat switch was used to cool the experimental cell. This consisted in a thin gold wire glued to the copper can. After completely filling this container with the liquid alcohol (typically  $2 \text{ cm}^3$ ), the sample holder is mechanically sealed. Firstly, experiments were conducted in a  $^4\text{He}$  cryostat, reaching temperatures down to  $\sim 1.7 \text{ K}$ . In a second set of experiments, we used a very similar calorimetric cell within a  $^3\text{He}$  cryostat, so that we were able to measure the specific heat to about  $0.5 \text{ K}$ . For all the substances studied, commercially available pure products were used, without further purification.

### 3. Results and discussion

#### 3.1. Glycerol

Glycerol is probably the most widely studied glass-forming liquid. Its high viscosity at a melting point around room temperature ( $T_m = 291 \text{ K}$ ), as well as its very low rate of crystallization, provides a very convenient temperature range where the supercooled liquid (SCL) can be studied. Below the glass transition at  $T_g \simeq 185 \text{ K}$ , the frozen-in liquid becomes a glass with a relatively weak, hydrogen-bonded network structure. Nevertheless, glycerol can also be obtained in an orthorhombic crystalline state [18], with four  $\text{C}_3\text{H}_5(\text{OH})_3$  molecules per unit cell, building up a structure of infinite hydrogen-bonded chains [19].

In figure 1, the specific heat of both glassy and crystalline glycerol below  $3 \text{ K}$  is displayed in a typical  $C_p/T$  versus  $T^2$  plot. The crystal phase exhibits the expected Debye behaviour  $C_p = C_D T^3$  (a straight line passing through zero), whereas the glass phase presents at least a (*quasi*-) linear contribution (the intercept at  $T = 0$  with the ordinate axis), that is ascribed to the above-mentioned tunnelling states or two-level systems (TLSs) [2, 7, 8]. Traditionally, a least-squares linear fit  $C_p = C_1 T + C_3 T^3$  has been used to determine the specific-heat coefficients and hence the density of tunnelling states and the Debye-like cubic contribution. Without exception, this direct method has provided [20] *calorimetric* cubic coefficients clearly exceeding the *elastic* ones obtained from Debye's theory in those cases where sound-velocity



**Figure 2.** Specific heat  $C_p/T^3$  of glass (circles) and crystal (squares) phases of glycerol for the whole measured temperature range in a log–log scale. The solid curve shows the quadratic fit to glass data as explained in the text. Dotted lines show the corresponding Debye contributions  $C_D$  to the specific heat measured calorimetrically. The dashed region limited by horizontal lines indicates the Debye contribution estimated for the glass from elastic data.

measurements are available, i.e.,  $C_3 > C_D$ . As a consequence, the applicability of Debye's theory and the idea of well defined, extended sound waves within the amorphous lattice is questioned.

However, as figure 2 emphasizes, there is an additional source of specific heat arising from the low-frequency vibrations responsible for the boson peak and the maximum in  $C_p/T^3$ . This contribution should not be completely negligible below, say, 2 K, and therefore interferes with the above-mentioned linear fits. Furthermore,  $C_1$  and especially  $C_3$  will depend on the chosen range for that linear fit. To overcome these difficulties and analyse specific-heat data consistently, we proposed [21] an alternative method partially based upon the SPM [11, 12]. As said above, the central idea of the SPM is the coexistence at low frequencies of ordinary sound waves and additional *quasi-resonant* modes, either anharmonic ones describable by double-well potentials (TLSs) or quasiharmonic ones by single-well potentials (*soft* modes). The latter vibrations would be responsible for the maximum in  $C_p/T^3$ —the boson peak—and are predicted to contribute as  $C_p \propto T^5$  at low enough temperatures [11, 12].

It seems widely accepted that sound waves, tunnelling states and some other resonant or quasilocalized vibrational modes exist in glasses. The disputed question is up to which frequency one can make a clear distinction among these excitations and treat them separately, or, in other words, up to which temperature if any Debye's theory can be applied to separate an elastic contribution to the specific heat from other additional ones due to tunnelling states or soft modes. In our opinion, this limiting temperature should lie somewhere between  $T_{\min}$  and  $T_{\max}$ , the temperatures at which the minimum and the maximum in  $C_p/T^3$  occur, respectively. More specifically, we suggest [21] identifying such a limit with the temperature at which the SPM prediction  $C_p \propto T^5$  starts deviating by  $\sim 5\%$  from the true  $C_p(T)$  curve due to the boson peak feature, which roughly takes place at  $T = \frac{3}{2}T_{\min}$ . Therefore, we have fitted all our specific-heat data for glassy phases in a  $C_p/T$  versus  $T^2$  representation by using a quadratic

**Table 1.** Measured data and fit parameters obtained for several studied glassy alcohols (see the text).

	H-ethanol		D-ethanol		1-propanol glass	2-propanol glass	Glycerol glass
	Glass	OG	Glass	OG			
$P_{\text{mol}}$ (g mol <sup>-1</sup> )	46.1		52.1		60.1	60.1	92.1
$T_g$ (K)	95	95	95	95	98	115	185
$T_{\text{min}}$ (K)	2.3	2.6	2.1	2.3	1.8	1.6	2.0
$T_{\text{max}}$ (K)	6.1	6.8	6.0	6.4	6.7	5.0	8.7
$(C_p/T^3)_{\text{max}}$ (mJ mol <sup>-1</sup> K <sup>-4</sup> )	2.4	2.2	2.8	2.6	2.7	3.6	1.4
$C_{\text{TLS}}$ (mJ mol <sup>-1</sup> K <sup>-2</sup> )	1.2	1.27	1.05	1.13	0.424	0.516	0.157
$C_D$ (mJ mol <sup>-1</sup> K <sup>-4</sup> )	1.55	1.45	1.80	1.72	1.77	2.54	0.855
$C_{\text{sm}}$ (mJ mol <sup>-1</sup> K <sup>-6</sup> )	0.0432	0.0288	0.0572	0.0419	0.0367	0.0845	0.0139

**Table 2.** Melting temperatures and fitted Debye parameters for the crystalline phases of the studied solid alcohols.

	H-ethanol	D-ethanol	1-propanol	2-propanol	Glycerol
$T_m$ (K)	159	159	148	185	291
$C_D$ (J mol <sup>-1</sup> K <sup>-4</sup> )	0.766	0.906	1.10	1.55	0.550
$\theta_D$ (K)	284	268	277	247	367

polynomial

$$C_p = C_{\text{TLS}}T + C_D T^3 + C_{\text{sm}} T^5 \quad (1)$$

in the temperature range  $0 < T < \frac{3}{2}T_{\text{min}}$ , where the coefficients should correspond to the contributions of TLSs, Debye lattice vibrations and quasiharmonic soft modes, respectively. For the crystalline phases, only the cubic term was considered. These fits are shown by solid lines in figures 1, 3 and 7, and the corresponding coefficients compiled in table 1 (glasses) and table 2 (crystals).

Thus, the key question is whether the proposed method of analysis is consistent and hence provides a cubic coefficient with the expected value (i.e., the *true* elastic or Debye contribution) or the hypothesis is not valid and one just gets a coefficient devoid of physical meaning, as seemed to be the case [2]. We recall that Debye's theory predicts in the limit of very low temperatures a specific heat given by  $C_p = C_D T^3$ , with

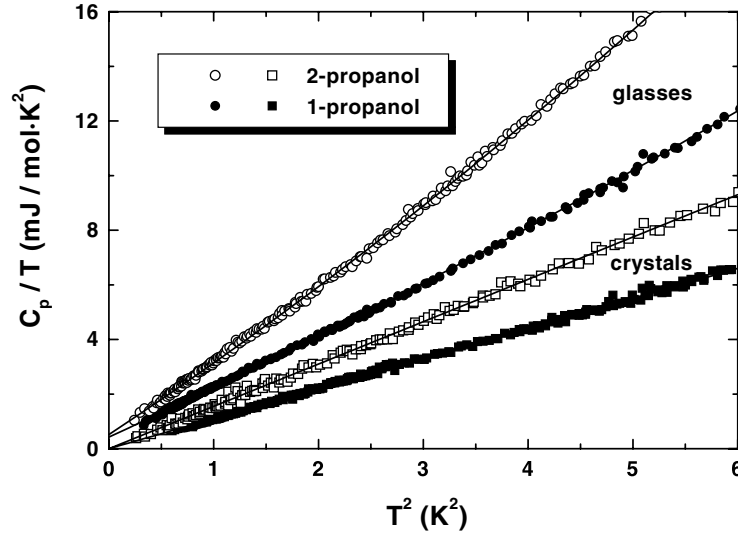
$$C_D = \frac{2\pi^2}{5} \left( \frac{k_B^4}{\hbar^3 \rho v_D^3} \right), \quad (2)$$

where  $v_D$  is the average Debye sound velocity defined by

$$\frac{3}{v_D^3} = \frac{1}{v_L^3} + \frac{2}{v_T^3} \quad (3)$$

$v_L$  and  $v_T$  being the longitudinal and transverse sound velocities, respectively.

A practical problem in studying this issue is the lack of elastic data at low enough temperatures for these glassy alcohols, since they are liquid at room temperatures, and one needs measurements of longitudinal and transverse sound velocities, and of mass density, well below  $T_g$  in order to get the true low-temperature Debye coefficient. At least for glycerol, a combination of available data allows us to estimate such a coefficient as follows.

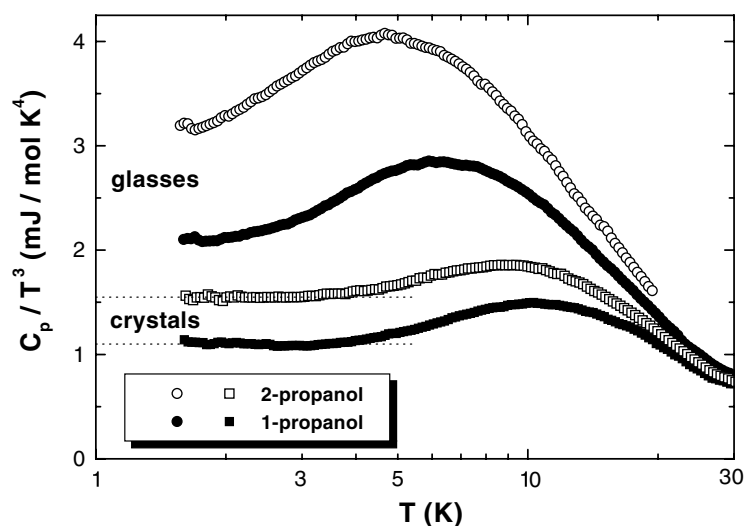


**Figure 3.** Low-temperature specific heat of glass (circles) and crystal (squares) phases of both 1-propanol (full symbols) and 2-propanol (open symbols), in a  $C_p/T$  versus  $T^2$  plot. Solid lines are least-squares fits, as explained in the text.

Equation (3) has been often simplified throughout the literature by assuming that the ratio  $v_L/v_T$  is more or less constant in glasses [22] whenever transverse data were not available. This method unavoidably introduces significant error, since transverse sound velocity is the dominant factor in the Debye coefficient (see equations (2), (3)). Indeed, Brillouin measurements of *longitudinal* sound velocity in glycerol down to very low temperatures were performed by Vacher and Pelous [23], but *transverse* sound velocity has only been measured [24] at relatively high temperatures, in the SCL state. However, Krüger *et al* [25] have recently proposed a general Cauchy-like relation for isotropic solids such as glasses or polymers, and shown that is very well fulfilled in all studied cases. They showed that the ideal Cauchy relation  $c_{11} = 3c_{44}$  between longitudinal modulus  $c_{11}$  and shear modulus  $c_{44}$  should be replaced by a generalized Cauchy relation including an additive term, and finally the longitudinal and transverse sound velocities are directly related *at any temperature* (or even at any ageing time for polymers) by

$$v_L^2(T) = A + 3v_T^2(T) \quad (4)$$

where  $A$  is a material parameter *independent* of temperature. Therefore, if both  $v_L$  and  $v_T$  are known at some temperature, equation (4) allows one to obtain properly the zero-temperature Debye sound velocity  $v_D$  even if only longitudinal sound velocity can be measured at low temperatures, as is often the case. From ultrasonic data after Piccirelli and Litovitz [24] between  $+26$  and  $-42$  °C, we obtain  $A = (3.0 \pm 0.2) \times 10^6 \text{ m s}^{-1}$ . Taking the zero-temperature extrapolated data for longitudinal sound velocity [23]  $v_L = 3710 \text{ m s}^{-1}$  and for mass density [26]  $\rho = (1.42 \pm 0.01) \text{ g cm}^{-3}$ , equations (2) and (3) give  $C_D = (0.835 \pm 0.035) \text{ mJ mol}^{-1} \text{ K}^{-4}$ , which is indicated in figure 2 by the shaded region. As can be observed, the Debye coefficient obtained from calorimetric data,  $C_D = 0.855 \text{ mJ mol}^{-1} \text{ K}^{-4}$ , agrees with that evaluated from elastic data within experimental error.



**Figure 4.** Specific heat  $C_p/T^3$  of glass (circles) and crystal (squares) phases of both 1-propanol (full symbols) and 2-propanol (open symbols), measured in a  $^4\text{He}$  cryostat. Dotted lines show the corresponding Debye contributions to the specific heat obtained calorimetrically for the crystalline phases.

### 3.2. Propanol

We have also investigated the behaviour of the simplest monoalcohols, ethanol and propanol, which can be readily obtained in both crystalline and glassy phases (methanol has a strong tendency to crystallization). Propanol is the smallest one which already presents two different stereoisomers, 1- and 2-propanol, hence allowing us to comparatively study the effect of rearrangements of the hydrogen-bonded lattice on the low-temperature properties of glasses and crystals.

The specific heat at low temperatures of both 1- and 2-propanol glasses and crystals, measured in a  $^3\text{He}$  cryostat, is shown in figure 3. These measurements extend earlier ones [16] performed in a  $^4\text{He}$  cryostat ranging from 1.7 to 30 K, that we reproduce in figure 4. Both propanol glasses exhibit the usual ‘glassy behaviour’, with a broad maximum in  $C_p/T^3$  below 10 K (see figure 4) and a linear contribution to the specific heat at lower temperatures (see figure 3). We have used the same fitting procedure as described above for glycerol, whose results are displayed by solid lines in figure 3 and collected in tables 1 and 2.

It is noteworthy that 2-propanol possesses a much larger specific heat than 1-propanol (and than any other glassy alcohol measured). The main reason however for this difference is based on the significantly larger *Debye* contribution in 2-propanol, which is supported by the fact that this difference between both propanol isomers also occurs in their crystalline states (see figure 4). In other words, the ratio of the linear slopes for glasses is very similar to that for crystals:  $C_D$  of 2-propanol is 43.5% higher than that of 1-propanol for glasses and 41% for crystals. Notwithstanding this, the glass phase of 2-propanol also has a non-negligible excess of TLS and *soft* modes compared to 1-propanol. In conclusion, the influence of the position of the hydroxyl ion ( $\text{OH}^-$ ) on the elastic constants of the hydrogen-bonded structural network, and hence on the low-temperature properties, seems to be very relevant independently of whether the lattice is crystalline or amorphous. Very recent neutron-diffraction experiments on propanol [27] have confirmed that the crystalline structures of the two isomers of propanol



are significantly different, since they even present a different crystalline symmetry: monoclinic for 1-propanol and triclinic for 2-propanol.

Unfortunately, there are to our knowledge no published acoustic data on glassy propanol in order to check here whether the obtained calorimetric Debye coefficients agree with elastic ones, as we showed above with glycerol. Therefore, we plan to conduct right-angle Brillouin measurements at low temperatures to determine both longitudinal and transverse sound velocities. Preliminary results at liquid nitrogen temperatures give  $v_L = 2950 \text{ m s}^{-1}$ ,  $v_T = 1470 \text{ m s}^{-1}$  for 1-propanol and  $v_L = 2760 \text{ m s}^{-1}$ ,  $v_T = 1360 \text{ m s}^{-1}$  for 2-propanol. If we use these data, together with the corresponding densities estimated in [27], we obtain  $C_D = 1.7$  and  $2.3 \text{ mJ mol}^{-1} \text{ K}^{-4}$  for 1- and 2-propanol, respectively, in reasonable agreement (see table 1) with the fitted data from specific-heat measurements. Nevertheless, elastic data at liquid helium temperatures are needed to make a more accurate comparison.

### 3.3. Ethanol

Three decades ago, Suga, Seki and co-workers in Osaka [28, 29] studied exhaustively the thermodynamic behaviour of many molecular substances, finding glass-transition phenomena in all of them. In some cases, they observed when heating standard glass transitions from the (amorphous) structural glass to the SCL (they called them *glassy liquids*); in other cases, the transitions were from an orientationally disordered crystal (*glassy crystals* or, as we will name them hereafter, ‘orientational glasses’ (OGs)) to its rotationally disordered plastic crystalline phase. The latter are therefore dynamic transitions from a non-ergodic state (the OG phase) to an ergodic one (the plastic crystal), that are thermodynamically equivalent to standard glass transitions.

Among all the substances studied by the Osaka group, the most interesting one is undoubtedly ethanol, which can be prepared either as a stable crystal, as a structural (amorphous) glass or as an OG obtained by quenching a plastic-crystal phase, depending upon temperatures and cooling rates below its melting point at  $T_m = 159 \text{ K}$  [29]. X-ray diffraction experiments [30] have shown that the stable crystal exhibits a monoclinic structure (as 1-propanol), the plastic crystal (and hence the OG) has a body-centred cubic (bcc) structure and the structural glass exhibits an amorphous pattern reminiscent of that of the OG phase but very broadened. Strikingly, both the standard transition glass  $\leftrightarrow$  SCL and the dynamic transition OG  $\leftrightarrow$  plastic crystal are found to occur at the same temperature  $T_g \simeq 95 \text{ K}$  and have comparable discontinuities in specific heat [14, 29]. Ethanol therefore constitutes a unique model system to assess the roles of translational and orientational disorder in the low-temperature properties of glasses. In addition, fully deuterated ethanol was found [13, 14] to present the same rich polymorphism, even with the same values of  $T_g$  and  $T_m$ , and hence has been studied too.

The procedure followed to prepare, measure and characterize the different solid phases of ethanol (either normal H-ethanol or fully deuterated D-ethanol) can be understood through the schematic phase diagram shown in figure 5. More technical details are given in [14]. We start with liquid ethanol in thermal equilibrium slightly above its melting point. Then, the calorimetric cell containing the ethanol is supercooled (1) faster than  $-20 \text{ K min}^{-1}$  down to below  $95 \text{ K}$ , so that any kind of crystallization is avoided and the SCL enters the glass state. After conducting the specific-heat measurements on the glass phase at low temperatures, ethanol is heated up to liquid-nitrogen temperatures and then its specific heat is measured, using the continuous method, in the glass-transition range to characterize the phase previously obtained and measured (see figure 2 of [14]). By further heating the SCL, a first-order phase transition into the plastic crystal (2) irreversibly occurs around  $105\text{--}110 \text{ K}$ . By now cooling

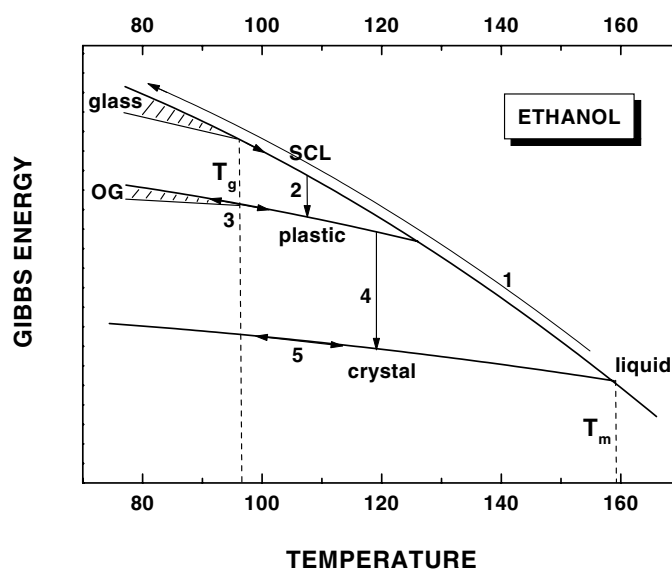
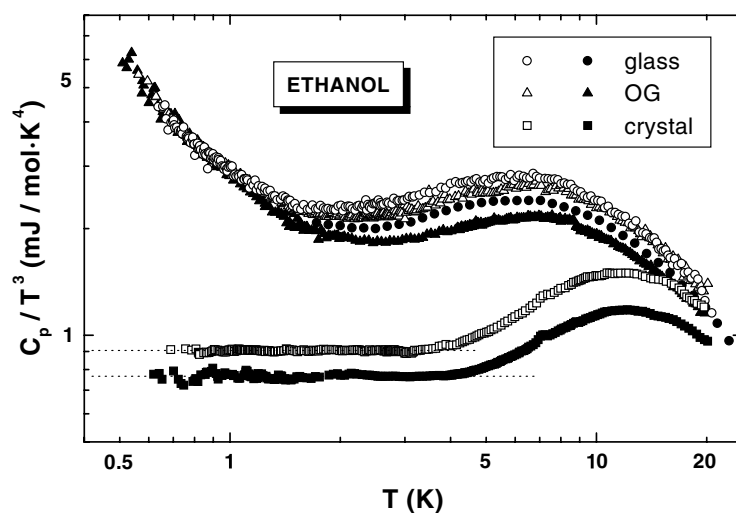


Figure 5. Schematic phase diagram of ethanol, indicating the thermal history followed to prepare and measure the different phases.

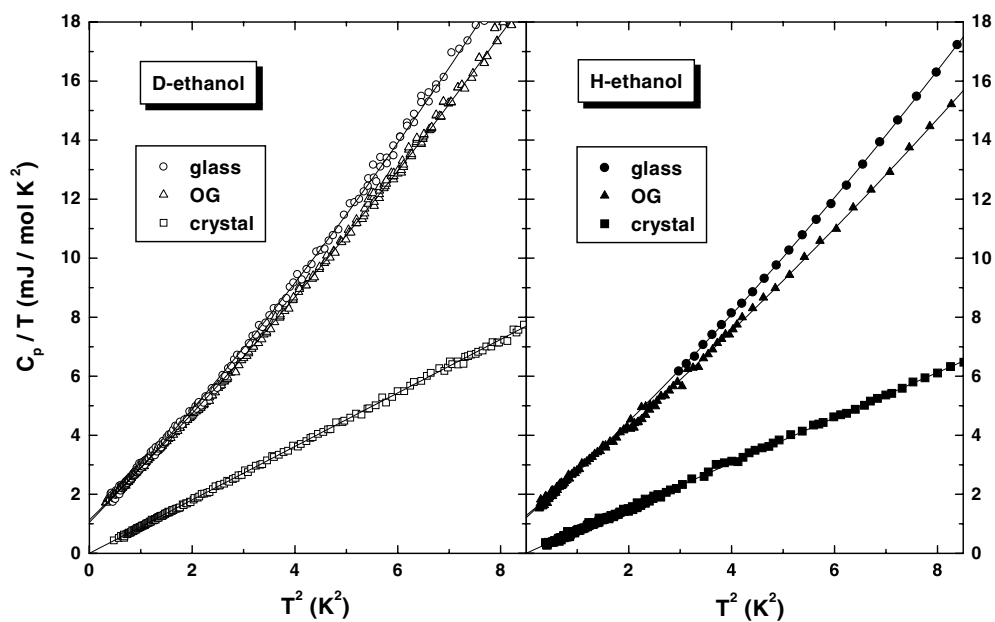
this phase after the transition has been completed, we obtain (3) the OG phase that is measured at low temperatures. We repeat the previous procedure and observe (see figure 2 of [14]) the *dynamic* OG  $\rightarrow$  plastic crystal transition, also at 95 K with a discontinuity about 80% of that of the glass  $\leftrightarrow$  SCL transition, in agreement with previous measurements [29]. After further heating, ethanol does not show any trace of the phase transition (2), therefore confirming that we had 100% of OG phase. When the (bcc) plastic crystal is further heated up to about 120 K, another first-order transition (4) into the (monoclinic) stable crystal phase takes place, following Ostwald's rule of stages. Once again, the new phase is cooled down (5), its specific heat is measured and it is subsequently heated up to liquid-nitrogen temperatures, where heat-capacity data do not show any evidence of glassy behaviour, as expected.

In figure 6, we display the specific heat  $C_p/T^3$  of the three low-temperature solid phases of both H-ethanol and D-ethanol for the whole measured low-temperature range in a double-logarithmic scale. As can be seen, both structural (amorphous) and orientational glasses exhibit a similar broad maximum in  $C_p/T^3$  at  $\sim 6$  K, well in excess of the specific heat of stable crystalline phases. Below 2 K, an upturn for the two *glassy* phases is observed, which is an indication of the presence of TLS excitations, and is in clear contrast to the typical Debye behaviour observed in the stable crystals. Nevertheless, the latter contribution can be better studied by means of the usual  $C_p/T$  versus  $T^2$  representation at the lowest temperatures, which is shown in figure 7. As can be observed there, amorphous and orientational glasses of ethanol, either hydrogenated (right) or deuterated (left), exhibit a very similar linear term in the specific heat (the intercept at  $T = 0$  in figure 7). The results of the same fitting procedure as previously used for glycerol and propanol are shown by solid lines in figure 7 and numerically in tables 1 and 2.

On the other hand, a direct data comparison between H- and D-ethanol has allowed us [15] to assess the isotopic effect on the different contributions to the low-temperature specific heat of ethanol. Firstly, we found again that lattice-vibrational (Debye) contributions to specific heat behave in a similar way for crystalline and non-crystalline networks. By assuming that the



**Figure 6.** Specific heat  $C_p/T^3$  of ordinary, structural glass (circles), OG (triangles) and crystal (squares) phases of both normal H-ethanol (full symbols) and fully deuterated D-ethanol (open symbols), for the whole measured low-temperature range in a log–log scale. Dotted lines show the corresponding Debye contributions to the specific heat obtained calorimetrically for the crystalline phases.



**Figure 7.** Low-temperature specific heat in a  $C_p/T$  versus  $T^2$  plot of structural glass (circles), OG (triangles) and crystal (squares) phases of both fully deuterated ethanol (left, open symbols) and hydrogenated ethanol (right, full symbols). Solid lines are least-squares fits, as explained in the text.

elastic moduli are the same, the sound velocities should be proportional to the inverse root of mass density, and hence  $C_D \propto M^{3/2}$ , where  $M$  is the molecular mass. Thus, 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 coefficients  $C_D$  between the crystals (1.18), between the OGs (1.19) and between the structural glasses (1.16). Hence, the mass difference itself seems to account naturally for the isotopic effect on the Debye contributions in all phases. Secondly, one can investigate the isotopic effect on the *glassy* excitations, i.e. TLSs and the boson peak. Concerning the latter, Theenhaus *et al* [31] recently studied the role of orientations and translation–rotation coupling in the microscopic dynamics of molecular liquids and glasses, finding a *boson peak* which originates from a localized and nonpropagating orientational mode coupled to translational, acoustic phonons. That ‘orientational peak’  $\omega_{op}$  exhibits an isotopic effect such as  $\omega_{op} \propto I^{-1/2}$ , where  $I$  is the moment of inertia. Since in our case [15] the ratio of moments of inertia is  $I_D/I_H = 1.23$ ,  $\omega_{op}$  should decrease a factor 0.90. By scaling  $\omega_{op}$  with the temperature  $T_{\max}$  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  $C_{\text{TLS}}$  of the glass by a factor 0.88 and that of the OG by a factor 0.89. These apparent correlations could be a signature of the common *orientational* origin of all glassy low-temperature excitations, either TLS or *soft* vibrations, though their full validity cannot be concluded only from these data.

#### 4. Summary and conclusions

In summary, we have reviewed and comparatively discussed specific-heat experiments, that we have conducted on different hydrogen-bonded glasses and crystals: glycerol, 1- and 2-propanol, and normal and fully deuterated ethanol.

By using a systematic method partly based upon the SPM to analyse these low-temperature specific-heat measurements, we have obtained consistently the density of TLS and soft modes for all studied glassy alcohols. The fact that, at least for glycerol and propanol, calorimetric and elastic Debye coefficients agree shows that the concept of acoustic ‘phonons’ and Debye’s theory can be applied to glasses up to a few kelvin or millielectronvolts. We want to emphasize that it is not merely that acoustic-like excitations or ‘in phase’ components [32] exist in glasses. The *quantitative* agreement found between the calorimetric  $C_D$  and the elastic data supports the view that ordinary, Debye-like acoustic phonons (i.e., with the usual linear dispersion relation) also exist in non-crystalline solids up to  $\sim 0.5$  THz.

Last but not least, we have shown that both structural glass and OG (i.e., a crystal with orientational disorder) phases of ethanol show, qualitatively and even quantitatively, the same glassy features in the low-temperature specific heat (TLSs and boson peak, the latter also observed by inelastic neutron scattering [13]), in accordance with very similar glass-transition phenomena [14, 29] between their corresponding ergodic and non-ergodic states. These results provide a *quantitative* confirmation of the fact that ‘glassy behaviour’ at low temperatures is not directly related to the lack of long-range crystalline order occurring in amorphous solids, but a more general characteristic of solids where some kind of disorder is able to *soften* the rigid vibrational spectrum of a crystalline lattice, and that the glass transition event (i.e., the freezing of an ergodic state into a non-ergodic one) seems to be a more general phenomenon than the kinetic arrest of an SCL into a non-crystalline solid.

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