

Low-Temperature Specific Heat and Brillouin Scattering Measurements on Hydrogen-Bonded Glasses

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Abstract. We review specific-heat and Brillouin-scattering experiments, that have been conducted as a function of temperature on different hydrogen-bonded glasses. Specifically, we have measured the low-temperature specific heat for a set of glassy alcohols: normal and fully-deuterated ethanol, 1- and 2- propanol, and glycerol. In addition, we are currently performing Brillouin-scattering experiments on the same glasses in order to obtain their sound velocities and hence their Debye coefficients. First acoustic measurements conducted on 1- and 2- propanol are presented.

INTRODUCTION

Glasses are known to exhibit universal properties at low temperatures very different from those of crystalline solids. At very low temperatures, $T < 1$ K, the specific heat depends approximately linear on temperature, $C_p \propto T$, in contrast to the expected Debye's behavior $C_p \propto T^3$ found in crystals. At $T > 1$ K, C_p still deviates from that cubic dependence, presenting a broad maximum in C_p/T^3 , what is originated from a difference or excess in the vibrational density of states $g(\nu)$ at low frequencies over the crystalline Debye behavior, leading to a ubiquitous maximum in $g(\nu)/\nu^2$, which is known as the "boson peak". It seems therefore interesting to study these issues in molecular glasses such as simple alcohols, which also allow a direct comparison with the corresponding properties in crystalline phases of the same substance.

EXPERIMENTAL RESULTS

Ethanol exhibits an interesting polymorphism presenting three different solid phases [1] at low temperature: (i) a fully-ordered (monoclinic) crystal; (ii) an orientationally-disordered (cubic) crystal or "glassy crystal"; (iii) the ordinary structural (amorphous) glass. We have measured their specific

heats at low temperature, both for normal (H-) and fully-deuterated (D-) ethanol [2-4]. Fig. 1 shows the obtained C_p/T^3 data for D-ethanol. As can be seen, the glassy crystal phase exhibits the same *glassy behavior* as the structural glass, in contrast to the the Debye behavior of the stable crystal at low temperatures. Very similar curves [5] were obtained for the two isomeric phases of propanol and for glycerol.

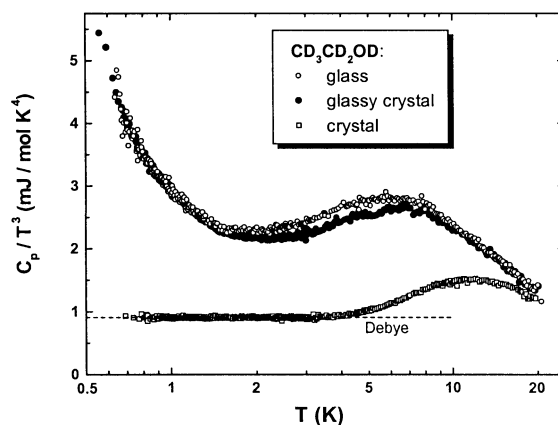


FIGURE 1. Low-temperature specific heat C_p/T^3 data of (amorphous) glass, "glassy crystal", and stable (monoclinic) crystal phases of fully-deuterated ethanol.

We have shown [5] that a consistent analysis of the low-temperature specific heat of glasses can be done based upon the Soft-Potential Model (SPM), by fitting the data in a C_p/T vs T^2 representation to a quadratic polynomial

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

with C_{TLS} being the contribution from two-level systems, C_{sm} that from additional "soft modes" within the SPM, and C_D the expected Debye coefficient. To be consistent, the fits must be performed in the temperature range $0 < T < 3/2 T_{\min}$, or up to a close temperature which lies in the middle between T_{\min} and T_{\max} , the temperatures where the minimum and maximum of C_p/T^3 occur, respectively. In Table 1, we present the results of these fits for all the glassy alcohols that we have measured.

In order to check the validity of this method, it is very interesting to obtain independently the Debye coefficient C_{Debye} from elastic measurements. From published data of sound velocity and density of glassy glycerol, we estimated [5] $C_{Debye} = 0.835 \text{ mJ mol}^{-1} \text{ K}^{-4}$, in good agreement with the fitted C_D .

With such an aim, we plan to measure the longitudinal v_L and transverse v_T sound velocities at low temperatures for all these glassy alcohols, by means of right-angle Brillouin scattering experiments. By extrapolating preliminary results to zero kelvin, we would obtain v_L (v_T) = 3125 (1562) m/s and 3008 (1508) m/s, and hence $C_{Debye} = 1.45 \text{ mJ mol}^{-1} \text{ K}^{-4}$ and $1.7 \text{ mJ mol}^{-1} \text{ K}^{-4}$, for 1-propanol and 2-propanol, respectively, only in rough agreement with the fitted C_D coefficients of Table 1. Further Brillouin measurements are currently in progress.

TABLE 1. Specific-heat data of glassy alcohols. Fit parameters and coefficients are defined in the text.

	<u>H-ethanol</u>		<u>D-ethanol</u>		<u>1-propanol</u>	<u>2-propanol</u>	<u>Glycerol</u>
	Glass	Glassy crystal	Glass	Glassy crystal	Glass	Glass	Glass
P_{mol} (g mol ⁻¹)	46.1		52.1		60.1	60.1	92.1
T_{\min} (K)	2.3	2.6	2.1	2.3	1.8	1.6	2.0
T_{\max} (K)	6.1	6.8	6.0	6.4	6.7	5.0	8.7
C_{TLS} (mJ mol ⁻¹ K ⁻²)	1.2	1.27	1.05	1.13	0.424	0.516	0.157
C_D (mJ mol ⁻¹ K ⁻⁴)	1.55	1.45	1.80	1.72	1.77	2.54	0.855
C_{sm} (mJ mol ⁻¹ K ⁻⁶)	0.0432	0.0288	0.0572	0.0419	0.0367	0.0845	0.0139

CONCLUSION

We have measured the low-temperature specific heat of several well-known alcohols (H- and D-ethanol, 1- and 2-propanol, and glycerol) both in glassy and crystalline states. In contrast to the Debye behavior found in the latter, all glassy phases (including the "glassy crystal" of ethanol, i.e. a crystal with mere orientational disorder) strongly exhibit the universal low-temperature behavior typical of all glasses, namely a linear contribution to C_p at the lowest temperatures due to two-level systems and a broad peak in C_p/T^3 or "boson peak", in excess of the Debye contribution from lattice vibrations.

Furthermore, the very similar qualitative and quantitative behavior observed [1-5] in the "glassy crystal" phase of ethanol in comparison with that of the true (amorphous) glass, provides a strong evidence for the irrelevance of the lack of long-range crystalline order characteristic of amorphous solids to account for the universal properties of glasses.

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