Heat capacity and thermal conductivity of LiCl.7H$_2$O

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Abstract. The heat capacity in the temperature range from 2 K to 20 K and the thermal conductivity in the temperature range from 2 K to 82 K of LiCl·7H$_2$O cooled at a rate of 5 mK s^{-1} has been measured. The general behaviour of both properties is very similar to that observed in other vitreous materials but there is no real evidence of the plateau region in the thermal conductivity of this material. The density of vibrational states has been determined from the heat capacity and it is non-quadratic in nature. The thermal conductivity data can be explained on the basis of scattering from point defect and tunnelling states. About 40 atoms are participating in a tunnelling or soft mode.

1. Introduction

Vitreous materials exhibit physical properties which are different from their crystalline counterparts. For example at low temperatures all vitreous materials show a linear term in heat capacity C, a T^2 dependence of thermal conductivity and saturable ultrasonic absorption. These anomalies point to an enhanced low-frequency vibrational density of states as compared to the Debye density of states and can be explained on the basis of two-level tunnelling states (Phillips 1972, Anderson et al 1972), although the microscopic origin of these states is still unclear. Another feature shared by all the vitreous materials in the temperature range 2 K to 20 K is a broad peak when C/T^3 is plotted against T.

LiCl·7H$_2$O can exist in liquid, supercooled liquid and amorphous states. The glass transition temperature is 140 K (Angell et al 1970, 1981). We have measured the heat capacity of this material over the temperature range from 2 K to 20 K and the thermal conductivity from 2 K to 85 K. The results are presented in this paper.

2. Measurement of heat capacity

The heat capacity of a small sample (93.9 mg) of LiCl·7H$_2$O was measured using a standard heat pulse technique (Bachmann et al 1972). The solution was poured into an aluminium boat attached to a silicon-on-sapphire bolometer (Early et al 1981) using silicone oil. The results, corrected for the addenda (aluminium boat, silicone oil, and bolometer etc) are shown in figure 1. Values of C are believed to be accurate to 3%.

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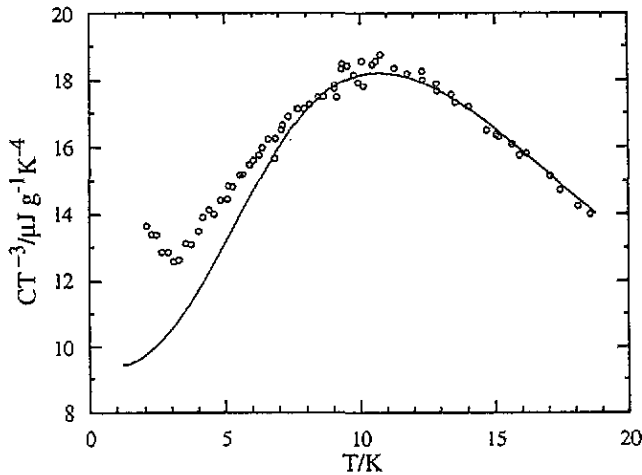‡ GEC–Marconi Hirst Research Centre, Wembley HA9 7PP, UK.

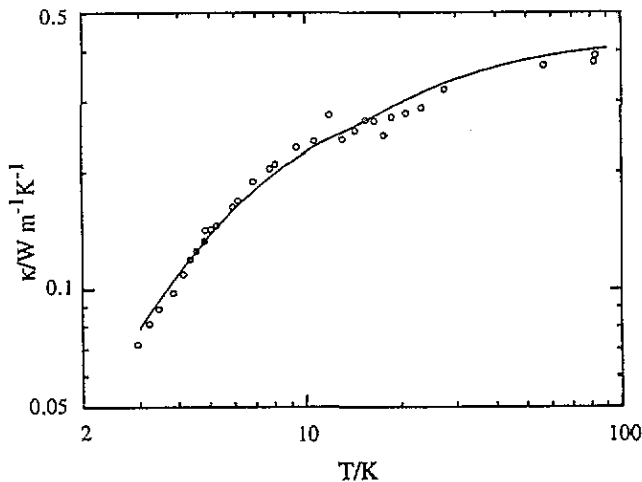**Figure 1.** The heat capacity of LiCl·7H$_2$O. The solid curve shows the quality of fit to experimental data using $g(v)$ values given in figure 3.

Figure 2. Thermal conductivity of LiCl·7H$_2$O. The solid curve is a fit using parameters given in the text.

3. Measurement of thermal conductivity

To measure the thermal conductivity of LiCl·7H$_2$O, a linear heat flow method has been used. A PTFE tube 40 mm long with 5 mm internal diameter and 0.36 mm wall thickness was mounted on an oxygen-free high-purity copper post attached to the tail piece of a cryostat. Rhodium + 0.5 at.% iron–chromel thermocouples in differential mode were soldered to Cu pins which passed through the PTFE tube at a separation of 25 mm and were used to determine the temperature difference ΔT across the sample. The form factor, defined as the ratio of the length to the cross-sectional area of the sample, was 1270 m^{-1}. The sample was heated from the top with a 1 kΩ resistor embedded in a copper cap which fitted at

the top of the PTFE tube and ran up to 4 mm into the solution-filled tube to make a good thermal link between the sample and the heat source. To measure the thermal conductivity, LiCl·7H₂O solution was poured into the PTFE tube and cooled in a nitrogen atmosphere at a rate of 5 mK s^{-1}. The temperature, T_1, at the bottom of the sample was measured with a standard RhFe thermometer. ΔT was kept less than 4% of T_1. The absolute temperature was taken as $T_1 + \Delta T/2$. The time taken by the specimen to reach a steady state was a few minutes at low temperatures and more than 5 hours at 80 K. To test the accuracy of the system, the PTFE tube was replaced with a rod of Spectrosil-B (vitreous silica) and its thermal conductivity was measured. Our results, with necessary corrections due to the conductance of wires (Ahmad 1986), were within ±5% of the reported measurements by Zeller (1971) and Zeller and Phol (1972). It is therefore believed that the measurements made with this system are accurate to ±5%. The thermal conduction of the PTFE cell (PTFE tube, thermocouples and other connecting wires) was measured separately (Ahmad and Adkins 1993) and varied from 49% to 11% of that of the LiCl·7H₂O between 82 K and 2.48 K. It was subtracted from the total thermal conductance to determine the conductance of the LiCl·7H₂O. The results plotted on a log–log scale are shown in figure 2.

4. Results and discussion

The results as shown in figure 1 clearly indicate that the shape of C/T^3 plotted against temperature for LiCl·7H₂O is similar to that observed in other glassy materials. There is a peak at about 11 K and at this temperature the value of C/T^3 is greater than the Debye limit (9.4 μJ g^{-1}K^{-4}) by a factor of approximately two, as determined from the speed of sound. For temperatures below 3 K, C/T^3 values increase with decreasing temperature and this is once again a characteristic shared by all the vitreous materials whose behaviour can be explained in terms of the two-level tunnelling model (Phillips 1972, Anderson *et al* 1972).

Above 2 K, the specific heat increases more rapidly than the Debye T^3 term. It has been shown (Buchenau *et al* 1992) that this anomaly can be explained in terms of a soft-potential model (Karpov *et al* 1983, Il'in *et al* 1987), an extension of the two-level tunnelling model including soft vibrations. Experimentally, one finds both two-level states (Phillips 1981) and soft harmonic vibrations (Buchenau *et al* 1986) existing with the sound waves in glasses. These findings support the soft-potential model. The soft-potential model describes both the tunnelling and the soft vibrational motion in terms of soft anharmonic potentials with locally varying parameters. However, neither the two-level tunnelling model nor its extension gives any justification for the existence of soft localized modes. More recently, Gil *et al* (1993) have shown that the peak in C/T^3 and the increase in the thermal conductivity can be explained within the framework of the soft-potential model without any additional parameters on the basis of a physically plausible assumption, which relates the asymmetry of the soft potential to thermal strains at the glass temperature.

The heat capacity C is given by

$$C = \frac{h^2}{kT^2} \int_0^\infty g(\nu)\nu^2 \frac{\exp(h\nu/kT)}{(\exp(h\nu/kT) - 1)^2} \, d\nu \qquad (1)$$

where $g(\nu)$ is density of vibrational states, h is the Planck constant and k is the Boltzmann constant. It is clear from (1) that unlike the other techniques for the determination of $g(\nu)$ such as neutron and Raman scattering and infrared absorption, the heat capacity

measurements give absolute values of $g(\nu)$ but have the disadvantage of involving an integral and thereby limiting the frequency resolution of the measurement. According to the Debye theory at low frequencies, $g(\nu) \propto \nu^2$ and C/T^3 is constant at low temperatures. However, there is a broad peak in the plot of C/T^3 as a function of temperature T as may be seen in figure 1. These C/T^3 values in excess of the Debye predicted value therefore indicate a non-quadratic form of $g(\nu)$. The increase in C/T^3 with increasing temperature means that $g(\nu)$ must increase more rapidly than ν^2 up to a certain frequency, say ν_0. After reaching a maximum, the decrease in C/T^3 values with increase in T implies that the increase in $g(\nu)$ is now less rapid than ν^2. Based on this approach, a procedure explained elsewhere (Ahmad 1991) has been used to determine the $g(\nu)$ values at low frequencies ($\nu < 4$ THz). The estimated values of $g(\nu)$ normalized to the Debye density of states $g_D(\nu)$ are shown in figure 3. The quality fit to the experimental data is shown by a solid curve in figure 1 which when extrapolated to $T = 0$ gives the limiting value calculated from an average sound velocity, i.e. 2.2 km s^{-1}. At low temperatures the calculated C/T^3 values are kept smaller than the measured values as the tunnelling states may still be contributing to the heat capacity. Raman data in glasses provide strong evidence that the vibrational modes in the range 0.2 THz to 1.5 THz are harmonic, in contrast to the two-level tunnelling states known to contribute to the heat capacity below 1 K. It is therefore realistic to separate the two contributions by extrapolating to the Debye limit. As may be seen from figure 3, $g(\nu)$ exceeds $g_D(\nu)$ below 2.2 THz. The ratio of $g(\nu)$ and $g_D(\nu)$ is maximum at about 1.2 THz. The form of these $g(\nu)$ values is non-quadratic and this result is in agreement with theoretical work using the coherent potential approximation by Galperin *et al* (1989). It may be noted that our procedure of determining $g(\nu)$ values from heat capacities is reliable—as previously seen (Buchenau *et al* 1986)—where the $g(\nu)$ values determined from heat capacity measurement of Heralux were identical to those obtained from inelastic scattering of neutrons.
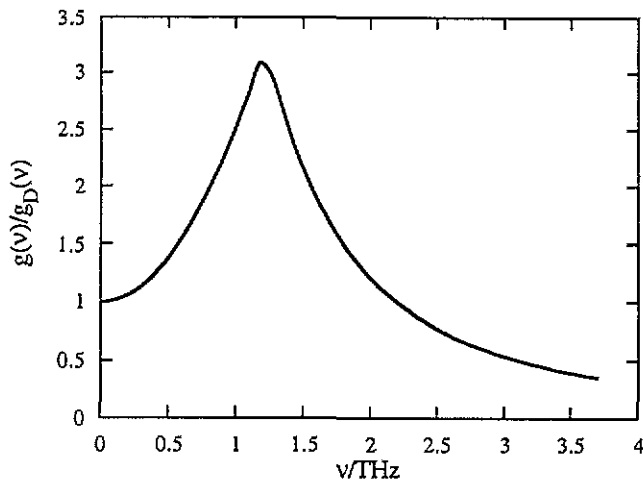

Figure 3. The density of low-frequency vibrational states normalized to the Debye density of states for LiCl·7H$_2$O.

The overall trend of the measured thermal conductivity κ of LiCl·7H$_2$O is very similar to that observed in other glasses but the plateau region observed between 10 K and 20 K is

not as prominent as in other vitreous materials (Phillips 1987). In fact, due to the scattering in the observed experimental data, there is no clear evidence of the plateau region.

κ can be expressed in the following integral form

$$\kappa(T) = \frac{1}{3} \int_0^\infty C(\nu, T) l(\nu, T) v(\nu, T) \, d\nu \tag{2}$$

where $C(\nu, T)$ is the heat capacity at temperature T for a mode of frequency ν as given by (1), $l(\nu, T)$ is the mean free path and $v(\nu, T)$ is the velocity of phonons. $C(\nu, T)$ can be determined using $g(\nu)$ shown in figure 3. The total mean free path $l(\nu)$ can be written as

$$1/l(\nu, T) = \sum_i 1/l_i(\nu, T) \tag{3}$$

where $l_i(\nu, T)$ is the mean free path for a particular scattering mechanism. In the case of vitreous materials, the point defects and tunnelling states are believed to be the scattering mechanisms. For tunnelling states the mean free path l_s (Jones 1982) is

$$l_s^{-1} = (h\nu/kB)\tanh(h\nu/kT) + \beta T^3/4B \qquad \text{for } h\nu/k > \beta T^3 \tag{4}$$

$$l_s^{-1} = (h\nu/kB)\tanh(h\nu/kT) + h\nu/4Bk \qquad \text{for } h\nu/k < \beta T^3 \tag{5}$$

where β and B are constant parameters. For point defects the scattering mean free path l_p is

$$l_p^{-1} = D\omega^4 \tag{6}$$

where D is a constant parameter and $\omega = 2\pi\nu$.

To fit the thermal conductivity data shown in figure 2, we have used a constant value of the sound velocity, i.e. 2.2 km s^{-1}. The other parameters D, β and B are 6×10^{-43} s^4 m^{-1}, 2×10^{-2} K^{-2} and 5.8×10^{-6} m K respectively. The upper limit in the integration in (2) is 3.7 THz. The quality of fit to experimental data is shown in figure 2 by a solid curve.

Using the approach adopted by Buchenau (1992), one can calculate the number of atoms N_s of mass M participating in a soft vibrational or tunnelling mode. In the case of LiCl·7H$_2$O, the minimum in C/T^3 is at about 3 K and the first broad maximum in $g(\nu)$ is at about 1.5 THz so that the estimated value of $N_s a^2$ is $4.7 \times 10^{-45} M$ m^2 kg^{-1}. For simplicity it may be assumed that all the atoms are similar with an average mass of about 1.2×10^{-26} kg, then $N_s a^2$ is 3.9×10^{-19} m^2. Since a should be of the order of 0.1 nm, there are about 40 atoms participating in a tunnelling or soft mode.

5. Conclusions

The measured specific heat behaviour of LiCl·7H$_2$O shares all the characteristics observed in other glassy materials such as a linear term in heat capacity and a broad peak in the C/T^3 plot. The thermal conductivity shows a T^2 dependence but there is no clear evidence of the plateau region similar to that observed in other glasses. The estimated form of the density of low-frequency vibrational states ($\nu < 4$ THz) in LiCl·7H$_2$O is non-quadratic. The number of atoms participating in a tunnelling or soft mode is about 40.

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