HEAT CAPACITY AND LOW-FREQUENCY VIBRATIONAL STATES OF SPECTROSIL-WF

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The heat capacity measurements of Spectrosil-WF (vitreous silica containing < 20ppm of OH) in the temperature range of 1.5K–17K are presented. An approach which can be used to determine the low-frequency (υ<3THz) density of lattice vibrational states $g(\upsilon)$ from heat capacities of vitreous materials has been briefly discussed. It has been found that the form of $g(\upsilon)$ at low-frequencies determined from the low temperature heat capacities of Spectrosil-WF is non-quadratic. Using the $g(\upsilon)$ values determined from heat capacities and the Raman measurements, the Raman coupling constant $C(\upsilon)$ has been determined. It is observed that $C(\upsilon)$ cannot be interpreted using Martin-Brenig theory.

Key words: Spectrosil-WF, Heat capacity, Neutron scattering, Raman scattering,

Introduction

The most marked differences between vibrational density of states in crystals, glasses and liquids become most apparent when the frequency (υ) is low (υ<3THz). In glasses four different techniques commonly used to study such states are the Raman scattering, infrared absorption, inelastic neutron scattering and heat capacity. In the past [1-3], it has been claimed that the $g(\upsilon)$ at low-frequencies in amorphous materials is proportional to υ^2. However, the experimentally measured low temperature heat capacities of amorphous materials dictate that $g(\upsilon)$ must have non-quadratic dependence on υ. In our previous work [4,5] on Heralux (Vitreous SiO_2 containing 130–180ppm of OH) and amorphous Se it was shown that the form of $g(\upsilon)$ determined from low temperature heat capacities is non-quadratic and the values are identical to those determined from inelastic neutron scattering studies.

In this paper we present our measurements of the specific heat of Spectrosil-WF (Vitreous SiO_2 containing <20ppm of OH) in the temperature range of 1.2–17 K. A method which has been repeated used [4,5] to determine the low-frequency density of vibrational states is explained. This method is then used to determine the $g(\upsilon)$ values to study their dependence on υ. The Raman measurements have been performed. Using the $g(\upsilon)$ values determined from heat capacities, the form of the Raman coupling constant $C(\upsilon)$ has been determined to test the Martin-Brenig theory [6] for Spectrosil-WF.

Experimental

Experimental measurement. The heat capacity of a small (221.0mg) sample was measured using a standard heat pulse technique [7] over the temperature range 1.5–17 K. A flat surface was ground on the sample which was then attached to a silicon-on-sapphire bolometer [8] using silicone oil. The additional heat capacity of the bolometer and supporting wires decreased from 10% at 1.5 K to less than 7% at 16 K. Values

of C, believed accurate to 3%, are shown in Fig 1. These are in close agreement with measurements on Spectrosil-B [9] and are about 20% higher than Heralux [4] and Amersil [10].

Data analysis. The heat capacity C is given by:

$$\frac{C}{T^3} = \frac{K^4}{h^3} \int_0^\infty \frac{g(\upsilon)}{\upsilon^2} \left[\frac{x^4 e^x}{(e^x - 1)^2} \right] dx \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where x=hυ/kT. According to the Debye theory at low frequencies, $g(\upsilon) \propto \upsilon^2$ and C/T^3 is constant at low temperatures and this is true for most crystalline materials. However, at low temperatures a broad peak in the plot of C/T^3 as a function of temperature T as can be seen in Fig. 1 is a characteristics of all the amorphous materials. These C/T^3 values in excess of the Debye predicted value, therefore, indicate a non-quadratic form of $g(\upsilon)$. The rise in C/T^3 with increasing temperature means that $g(\upsilon)$ must rise more rapidly than υ^2 upto
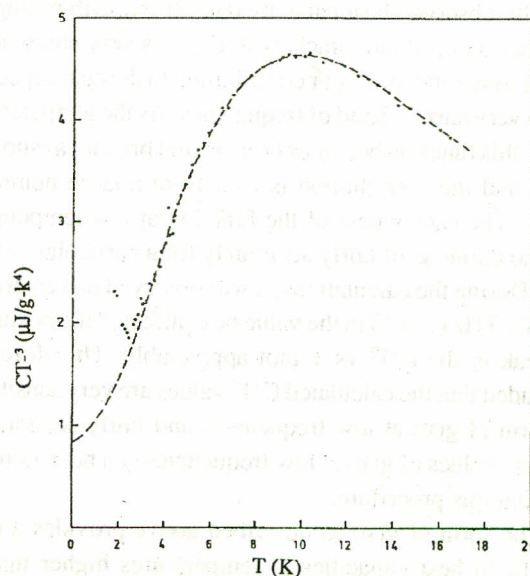

Fig. 1. The heat capacity of Spectrosil-WF. The dashed line is fit to the using $g(\upsilon)$ shown in Fig. 3.

a frequency, say υ_o. After reaching a maximum, the decrease in C/T^3 with increase in T implies that the rise in $g(\upsilon)$ is now less rapid than υ^2. Therefore, one can assume the following form for $g(\upsilon)$.

$$
\begin{aligned}
g(\upsilon) &= A\upsilon^2 + B\upsilon^4 & \upsilon \leq \upsilon_o \\
g(\upsilon) &= D\upsilon & \upsilon_o \leq \upsilon \leq \upsilon_{oo} \quad \text{..................... (2)} \\
g(\upsilon) &= E & \upsilon \geq \upsilon_{oo}
\end{aligned}
$$

At higher frequencies ($\upsilon > 2$THz) any form of $g(\upsilon)$ can be assumed, as this region is not well defined by the low temperature heat capacity data. However in this region of the spectrum, the observed Raman and inelastic neutron scattering are non-zero. Therefore, $g(\upsilon)$ cannot be zero and it is more realistic to assume a non-zero form of $g(\upsilon)$. The constants D and E in eq. 2 can be determined in term of A, B, υ_o and υ_{oo} Since the Raman data provides strong evidence that the vibrational states in glasses in the range of 0.2–1.5 THz are harmonic, in contrast to the two level tunneling states known to contribute to the heat capacity below about 2 K, it is, therefore, realistic to separate the two contributions by extrapolating the heat capacities to the Debye limit and the constant A can be determined from the sound velocities i.e. $A = 3V/2\pi V^3_D$, where V is the volume and V_D is the Debye velocity. If V_1 and V_t are the longitudinal and the transverse sound velocities respectively then

$$3/V^3 = 1/V^3_1 + 2/V^3t \text{... (3)}$$

With $g(\upsilon)$ represented by Eq. 2, the Eq. 1 has three unknowns i.e. B, υ_o and υ_{oo}. This equation can be solved using the computer library subroutines for integration to determine these constants for a reasonable agreement with the experimentally observed heat capacity data. It is worth noting that the function in square brackets in Eq. 1 is very sharp at low temperatures and the major contribution to the heat capacity is from a very narrow band of frequencies. As the temperature is raised, this function becomes broader and broader as shown in Fig. 2 and the contribution is then from a large number of modes. The narrowness of the function at low temperatures helps to define $g(\upsilon)$ fairly accurately for a particular value of C(T). During the calculations, it was observed that a variation of ± 0.03 THz (1cm^{-1}) in the value of υ_o affected the position of the peak in the C/T^3 vs T plot appreciably. Therefore, it is concluded that the calculated C/T^3 values are very sensitive to the form of $g(\upsilon)$ at low frequencies and fairly accurate and absolute values of $g(\upsilon)$ at low frequencies can be obtained by adopting this procedure.

The form of $g(\upsilon)$ as described above provides a rather poor fit to heat capacities at temperatures higher than the temperature of the peak in the C/T^3 curve. It was also observed that a slightly higher value of υ_{oo} and $g(\upsilon) = 0$ for $\upsilon > \upsilon_{oo}$ also

provides the same fit. However as already explained, a non-zero form of $g(\upsilon)$ in this region of the spectrum should be used. But what about the kinks at υ_o and υ_{oo}? These were introduced to provide a mathematical form of $g(\upsilon)$ for computational purposes. They don't have any physical significance and thus cannot be real. Therefore, $g(\upsilon)$ can be smoothed at these kinks. This smooth form of $g(\upsilon)$ provides C/T^3 in excellent agreement with experimental measurements as shown in Fig. 1. The ratio of $g(\upsilon)/g_D(\upsilon)$ is shown in Fig. 3 to emphasis the departure of $g(\upsilon)$ from Debye density of states $g_D(\upsilon)$.

Results and Discussion

Figure 1 shows that the C/T^3 plot of the specific heat of Spectrosil-WF as a function of temperature T has a broad peak at 9.75 K and the shape of the curve is similar to other glasses. In the peak region C/T^3 values are 4.617 μJ/gK^4. Below 2K, the rise in C/T^3 is due to two-level tunneling states.

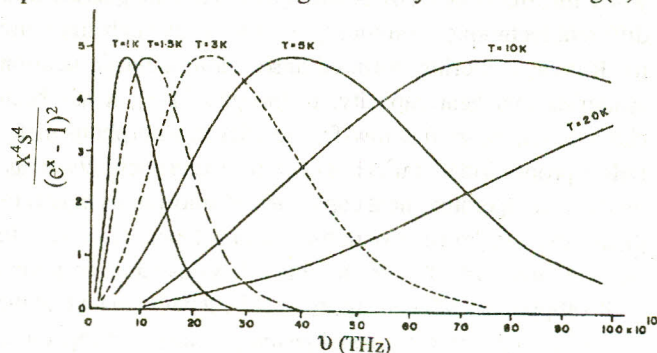The estimated values of $g(\upsilon)$ shown in Fig. 3 are non-quadratic in form. This Figure clearly indicates that $g(\upsilon)$ is

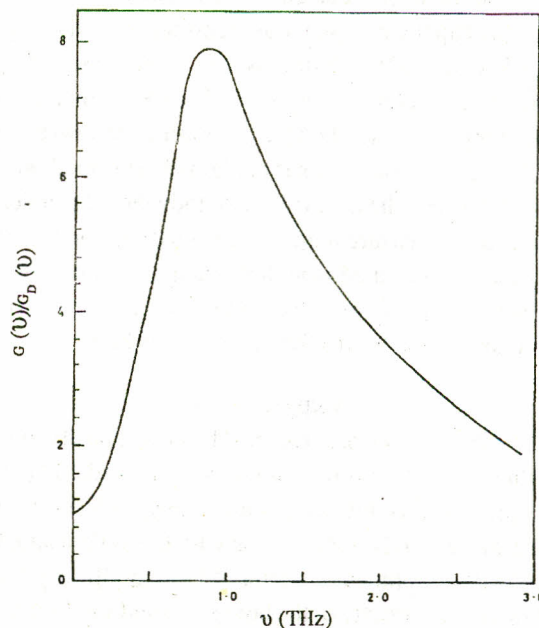Fig. 2. The plot of $x^4 e^x/(e^x - 1)^2$ as function of υ for different temperatures; $x = h\upsilon/kT$.

Fig. 3. The density of vibrational states in Spectrosil-WF.

higher than $g_D(\upsilon)$ for υ more than 3 THz and there is a peak in $g(\upsilon)/g_D(\upsilon)$ at about 0.8 THz. As shown elsewhere [4], this enhanced $g(\upsilon)$ is due to the rotation of almost rigid tetrahedra in SiO_2.

In the past [4,5] this procedure of calculating $g(\upsilon)$ from heat capacity has provided $g(\upsilon)$ values which were in reasonable agreement with those determined from neutron scattering studies for Heralux and Vitreous Se. This procedure has also been tested for many glasses (Spectrosil-B, quenched and annealed As_2S_3 and $GeSe_2$) and always a good fit to the heat capacities was possible [11]. There are some crystalline materials such as Ge and Cristobalite which also have a broad peak in the plot of C/T^3 against T at low temperature. However, the form of $g(\upsilon)$ given by Eq. 1 which fits the heat capacities of glasses does not provide a fit to the heat capacity data for these crystalline materials. In these materials, it is necessary to assume $g(\upsilon) \propto \upsilon^2$ along with delta functions (broad monochromatic mode) and the resulting $g(\upsilon)$ values are similar to those determined from the study of the lattice dynamics [12] of these materials. Therefore, the form of $g(\upsilon)$ given by Eq. 2 and smoothed at the kinks is only useful for vitreous materials. The heat capacity measurements, thus, give absolute values of $g(\upsilon)$ with no unknown coupling constants. However, these have the disadvantage of involving the convolution of $g(\upsilon)$ with the temperature derivative of the Bose function. Therefore, the heat capacities have poor frequency resolution and the details in the $g(\upsilon)$ are lost. The important point to be noted is that heat capacities provide non-quadratic form of $g(\upsilon)$ similar to that determined from neutron scattering measurements. Both these measurement show [4] that their are no sharp peaks (monochromatic modes) in $g(\upsilon)$ as proposed by Flubacher et al. [10]. These proposed modes have not also been observed in the Raman measurement taken in this work and the infrared absorption [13] in this material. Therefore the present work alongwith the literature [4,5,11] support that the form of $g(\upsilon)$ at low-frequencies is non-quadratic and the assumption $g(\upsilon) \propto \upsilon^2$ used elsewhere [1-3] is not valid, however this work support the theoretical work by Galperin et al. [14] that the density of low-frequency vibrational states in glasses is proportional to υ^4.

In the absence of translational symmetry in glasses, the Raman measurements are sensitive to all vibrational modes and according to Shuker et al. [15] and Jackle [16] the Raman intensity $I(\upsilon)$ can be written in the following form:

$$I(\upsilon) = C(\upsilon)g(\upsilon)[1+n(\upsilon,T)]/\upsilon \quad .... (4)$$

where $n(\upsilon, T)$ is the Bose function, and $C(\upsilon)$ is the Raman coupling constant. The tensorial nature of $I(\upsilon)$s has been ignored in Eq. 4 because experimentally no polarization dependence has been observed at low-frequencies ($\upsilon < 3THz$).

Therefore, the Raman measurements do not give a direct measure of $g(\upsilon)$ but provide a product of $g(\upsilon)$ and unknown coupling constant $C(\upsilon)$. In the past, in many glasses [1-3] the Raman studies have been used to derive the form of Raman coupling constant $C(\upsilon)$ by assuming a quadratic dependence of low-frequency vibrational states $g(\upsilon)$ on frequency υ. The resulting $C(\upsilon)$ is then interpreted in terms of Martin-Brenig model [6]. As normally applied this theory assumes that

$$C(\upsilon) \propto \upsilon^2 \exp[-(2\pi\upsilon\sigma/V_s)^2] \quad .... (5)$$

Where V_s is the velocity of sound and 2σ is the structural correlation range. To test this theory for Spectrosil-WF, the Raman scattering measurements were performed. Using the density of states $g(\upsilon)$ determined from heat capacities, the Raman coupling constant has been determined and the results are shown in Fig. 4. It is clear from this Figure that $C(\upsilon)$ cannot be represented by Eq. 5. Therefore, the Martin-Brenig as normally applied is not valid if $g(\upsilon)$ determined from heat capacities is used. The experimental work by Malinovsky et al. [17] also confirms the present conclusions regarding the Martin-Brenig approach.

The temperature independent infrared absorption can be written as

$$\alpha(\upsilon) = M(\upsilon)g(\upsilon) \quad .... (6)$$

where $M(\upsilon)$ is the vibrational coupling constant for infrared absorption and $g(\upsilon)$ is once again the density of lattice vibrational states. According to Bell et al. [18], $M(\upsilon)$ can be written as:

$$M(\upsilon) = |\,\mu\,(\upsilon)\,|^2 \quad .... (7)$$

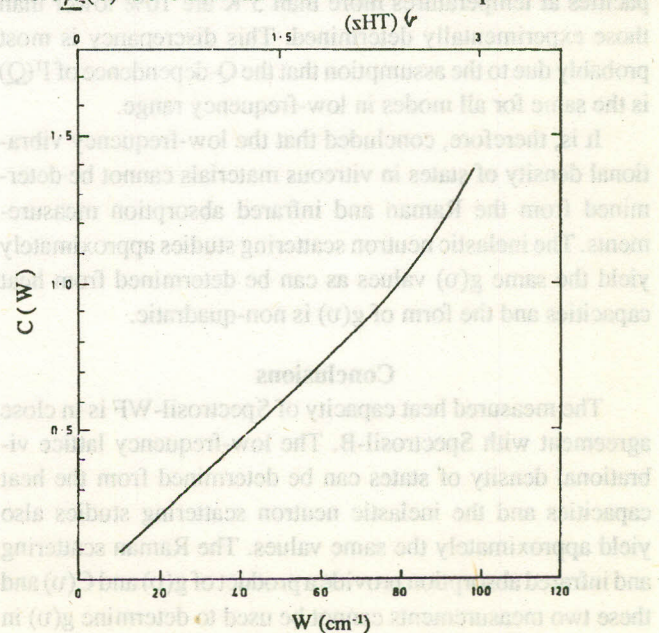where $\mu(\upsilon)$ is the derivative of the intrinsic dipole moment of

Fig. 4. Raman coupling constant for Spectrosil-WF.

the solid with respect to the normal coordinates for a mode with frequency υ. Therefore, it is also not possible to determine $g(\upsilon)$ from infrared measurements because of the unknown nature of $M(\upsilon)$. In a recent theoretical and experimental work [19] on Vitreous SiO_2 (Spectrosil-B), it has been shown that at low-frequencies a single coupling constant can be used for both the optical measurements. However, if $g(\upsilon)$ is to be determined from any of these optical measurements the coupling constant $C(\upsilon)$ must be known.

In case of neutron scattering, the one phonon scattering cross-section σ^1 according to Buchenau $et\ al.$ [4] is given by

$$\frac{d^2\sigma^1}{d\Omega d\upsilon} = \frac{k_f}{k_i}\frac{3Nh}{8\pi^2}\ \frac{g(\upsilon)}{\upsilon}\ n(\upsilon,\ T)\ I^1(Q) \ \dots\dots\dots\dots\ (8)$$

with $Q = \underline{k}_f - \underline{k}_i$ where $\underline{k}_f$ and k_i are the final and incident neutron wave vectors and

$$I^1(\underline{Q}) = |\ _j\Sigma b_j e^{-Wj}\ e^{iQ.Rj}\ (\underline{Q}.e_j)\ \sqrt{M_j}\ |^2$$

where b_j is coherent scattering length, $\underline{R}_j$ is the position vector, e^{-Wj} is the Debye-Waller factor, M_j is the mass and $\underline{e}_j$ is the displacement amplitude of atom j and $n(\upsilon,\ T)$ is the Bose function. The polarization vectors are related to the actual displacements $\underline{u}_j$ by $\underline{u}_j = \sqrt{M_j}\ .\ \underline{e}_j$ and normalized so that $\Sigma_j\underline{e}_j{}^2 = 1$. On the assumption that the Q-dependence of $I^1(\underline{Q})$ is the same for all modes in low-frequency range, $g(\upsilon)$ is obtained by scaling the inelastic scattering intensities to give a common curve [4]. Therefore, with the above mentioned assumption, it is possible to determine $g(\upsilon)$. In case of Heralux [4], it has been observed that the $g(\upsilon)$ values determined from neutron scattering are slightly different in detail from those determined from heat capacities. Due to these differences the estimated heat capacities at temperatures more than 5 K are 10% lower than those experimentally determined. This discrepancy is most probably due to the assumption that the Q-dependence of $I^1(\underline{Q})$ is the same for all modes in low-frequency range.

It is, therefore, concluded that the low-frequency vibrational density of states in vitreous materials cannot be determined from the Raman and infrared absorption measurements. The inelastic neutron scattering studies approximately yield the same $g(\upsilon)$ values as can be determined from heat capacities and the form of $g(\upsilon)$ is non-quadratic.

Conclusions

The measured heat capacity of Spectrosil-WF is in close agreement with Spectrosil-B. The low-frequency lattice vibrational density of states can be determined from the heat capacities and the inelastic neutron scattering studies also yield approximately the same values. The Raman scattering and infrared absorption provide a product of $g(\upsilon)$ and $C(\upsilon)$ and these two measurements cannot be used to determine $g(\upsilon)$ in

glasses. The form of the Raman coupling constant cannot be represented according the martin-Brenig theory if the $g(\upsilon)$ values determined from heat capacities are used.

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