

Low-frequency vibrational states in Spectrosil-WF

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The heat capacity of Spectrosil-WF (vitreous silica containing <20 ppm of OH) in the temperature range from 2 to 16 K as well as the Raman measurements are presented. The heat capacity is similar to that of Spectrosil-B (vitreous silica containing 1200 ppm of OH) but is about 20% higher than the Heralux (vitreous silica containing 130–180 ppm of OH). The density of low-frequency vibrational states, $g(\nu)$, has been determined. It has been found that the form of $g(\nu)$ is nonquadratic, which can be explained on the basis of a soft-potential model. About 110 atoms participate in a soft mode. The Raman and infrared coupling constants have similar dependence on frequency. These are explained on the basis of a single-coupling-constant bond model. It is found that the form of the Raman coupling constant cannot be explained on the basis of Martin-Brenig theory.

INTRODUCTION

Vitreous materials exhibit physical properties that 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 tunneling states,¹ although the microscopic origin of these states is still unclear. Another feature shared by all the vitreous materials in the temperature range 2 to 20 K is a broad peak when C/T^3 is plotted against T . It has been shown² that a consistent description of these anomalies is possible in terms of a soft-potential model,^{3,4} an extension of the two-level tunneling model to include soft vibrations in the picture. Experimentally, one finds both two-level states and soft harmonic vibrations existing with the sound waves in glasses.^{5,6} These findings support the soft-potential model. The soft-potential model describes both the tunneling and the soft vibrational motion in terms of soft anharmonic potentials with locally varying parameters. However, neither the two-level tunneling model nor its extension gives any justification for the existence of soft localized modes. More recently⁷ it has been shown that the peak in C/T^3 and the second increase in thermal conductivity with increasing temperature 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. Therefore, the most marked differences between density of vibrational states, $g(\nu)$, in crystals, glasses, and liquids become most apparent when the frequency ν is low ($\nu < 3$ THz).

Four different techniques are commonly used to study the low-frequency vibrational states in glasses. These are Raman scattering, infrared absorption, inelastic neutron scattering, and heat capacity. In the past^{8,9} it has been claimed that $g(\nu)$ at low frequencies in amorphous ma-

terials is proportional to ν^2 . Therefore, the room-temperature Raman spectra reflect the Raman coupling constant and can be interpreted according to the Martin-Brenig theory.¹⁰ However, the experimentally measured low-temperature heat capacities of amorphous materials dictate that $g(\nu)$ must have a nonquadratic dependence on ν . In our previous work^{6,11,12} on Heralux (vitreous silica containing 130–180 ppm of OH) and vitreous Se, it was shown that the form of $g(\nu)$ determined from low-temperature heat capacities is nonquadratic and the values are identical to those determined from inelastic-neutron-scattering studies. Therefore, any analysis of the Raman data based on the Debye density of states $g_D(\nu)$ is not satisfactory.

In the vitreous state SiO_2 exists in a variety of forms and is commercially available under a large number of different names such as Spectrosil-WF containing less than 20 ppm of OH, Spectrosil-B containing 1200 ppm of OH, and Heralux containing 130–180 ppm of OH. In an attempt to identify the nature of the low-frequency vibrational states, the heat capacity, Raman scattering, and infrared absorption of Spectrosil-WF are presented. Low-frequency vibrational states in Spectrosil-B and Heralux are also determined from heat-capacity data and are presented in this paper.

MEASUREMENT OF HEAT CAPACITY

The heat capacity of a small sample (221.0 mg) of Spectrosil-WF was measured using a standard heat-pulse technique¹³ over the temperature range 1.5 to 16 K. A flat surface was ground on the silica sample which was then attached to a silicon-on-sapphire bolometer¹⁴ using silicone oil. The results, corrected for addenda, are shown in Fig. 1. Heat capacities of Spectrosil-B¹⁵ and Heralux⁶ measured with this system are also shown in this figure for comparison. Values of C , believed to be accurate to 3%, are in close agreement with measurements on Spectrosil-B but are 20% higher than those of Heralux⁶ and Amersil.¹⁶

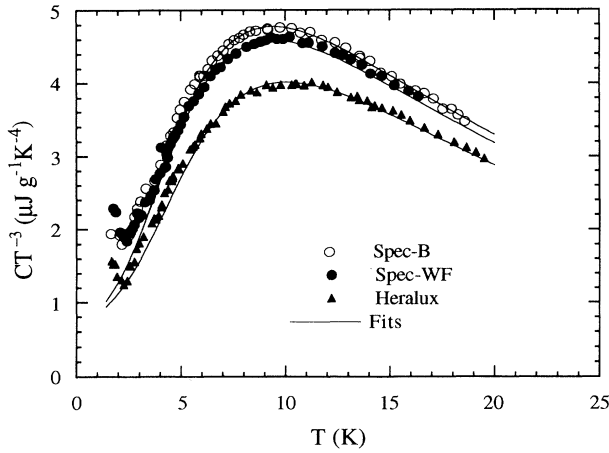


FIG. 1. The heat capacities of Spectrosil-WF, Spectrosil-B, and Heralux. Solid curves are fit to the experimental data as explained in the text.

RESULTS

The heat capacities of Spectrosil-WF (OH less than 20 ppm) and Spectrosil-B (OH content 1200 ppm) within the experimental accuracy of the system are similar but about 20% larger than Heralux (OH content 130–180 ppm). Therefore, the difference in the measured heat capacities of Spectrosil-WF, Spectrosil-B, and Heralux is not due to OH content. Raman measurements at room temperature¹² and infrared measurements¹⁷ at 77 K in Spectrosil-WF and Spectrosil-B on the samples used in heat-capacity measurements are also similar and, therefore, support these heat-capacity results.

Infrared transmission spectra of all three materials were taken at room temperature with a Perkin-Elmer model 577 spectrometer. This spectrometer gives the percent transmission as a function of wave number from 4000 cm^{-1} down to 200 cm^{-1} . The spectrum for Spectrosil-WF does not show any absorption due to OH. This confirms the negligible amount of OH in this sample. For Heralux, the decrease in the percent transmission at 3690 cm^{-1} is about 50%, whereas for Spectrosil-B, the percent transmission at 3690 cm^{-1} is almost negligible. This confirms that the amount of OH in Heralux is lower than in Spectrosil-B and is higher than in Spectrosil-WF, in accordance with the supplier's data.

The Raman spectra were taken in the region 10–150 cm^{-1} at the Applications Laboratory at Lille and the infrared-absorption data are by Hutt.¹⁷ It is to be noted that all three measurements are on the same sample.

DISCUSSION

For a density of vibrational states $g(\nu)$, the heat capacity C is given by

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

where h is the Planck constant, k is the Boltzmann constant, and $x = h\nu/kT$.

In the absence of the translational symmetry in glasses,

the Raman measurements are sensitive to all vibrational modes. The Raman intensity $I(\nu)$ can be written in the following form:^{18,19}

$$I(\nu) = C(\nu)g(\nu) \frac{1 + n(\nu, T)}{\nu}, \quad (2)$$

where $n(\nu, T)$ is the Bose function and $C(\nu)$ is the Raman coupling constant. The tensorial nature of $I(\nu)$ has been ignored in Eq. (2) because experimentally no polarization dependence has been observed at low frequencies ($\nu < 3$ THz). The Raman measurements are temperature dependent. The coupling constant is written as follows:

$$C(\nu) = |\mathbf{V}_R(\nu)|^2, \quad (3)$$

with

$$\mathbf{V}_R(\nu) = \alpha \mathbf{E}, \quad (4)$$

where α is the first-order polarizability change due to an electric field \mathbf{E} associated with the incident light. Since $C(\nu)$ cannot be determined independently, the Raman measurements do not give a direct measure of $g(\nu)$ but provide a product of $g(\nu)$ and $C(\nu)$.

The temperature-independent infrared absorption $\alpha(\nu)$ can be written in the following form:

$$\alpha(\nu) = M(\nu)g(\nu), \quad (5)$$

where $M(\nu)$ is the vibrational coupling constant for infrared absorption and $g(\nu)$ is once again the density of lattice vibrational states. According to Bell and Hibbins-Butler,²⁰ $M(\nu)$ can be written as

$$M(\nu) = |\mu(\nu)|^2, \quad (6)$$

where $\mu(\nu)$ is the derivative of the intrinsic dipole moment of the material with respect to the normal coordinates for a mode with frequency ν . Once again, it is not possible to determine $M(\nu)$ independently and therefore, it is not possible to determine $g(\nu)$ from infrared measurements.

In the case of inelastic scattering of neutrons, the one-phonon scattering cross section is given by²¹

$$\frac{d^2\sigma^{(1)}}{d\Omega d\nu} = \frac{k_f}{k_i} \frac{3hN}{2\pi} \frac{g(\nu)}{\nu} n(\nu, T) I^{(1)}(\mathbf{Q}), \quad (7)$$

where $\mathbf{Q} = \mathbf{k}_f - \mathbf{k}_i$, and \mathbf{k}_f and \mathbf{k}_i are the final and incident-neutron wave vectors, N the number of the atoms, and

$$I^{(1)}(\mathbf{Q}) = \left| \sum_j b_j e^{-w_j} e^{i\mathbf{Q} \cdot \mathbf{R}_j} (\mathbf{Q} \cdot \mathbf{e}_j) / M_j^{1/2} \right|^2, \quad (8)$$

where b_j is the coherent scattering length, \mathbf{R}_j the position vector, M_j the mass, and \mathbf{e}_j the displacement amplitude of atom j . The polarization vectors are related to the actual displacement \mathbf{u}_j by $\mathbf{u}_j = M_j^{1/2} \mathbf{e}_j$ and normalized so that $\sum_j \mathbf{e}_j^2 = 1$.

On the assumption that the \mathbf{Q} dependence of $I^{(1)}(\mathbf{Q})$ is the same for all modes in the frequency range 0.3 THz $< \nu < 2$ THz, $g(\nu)$ is obtained by scaling the inelastic intensities to give a common curve. Therefore, with this assumption it is possible to obtain $g(\nu)$. In the case of

Heralux,⁶ it has been observed that the $g(\nu)$ values determined from the neutron scattering are slightly different in detail from those determined from heat capacities. Due to these differences, the estimated heat capacity of Heraldux using $g(\nu)$ determined from neutron scattering, 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 $I^{(1)}(Q)$ is the same for all modes in the low-frequency regime.

It is clear from Eq. (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 $g(\nu)$ without any unknown coupling constants but have the disadvantage of involving the convolution of $g(\nu)$ with the temperature derivative of the Bose function. Therefore, the heat capacities have poor frequency resolution and the details in $g(\nu)$ are lost.

In order to explain the heat capacity of Amersil, Flu-bacher *et al.*¹⁶ have assumed $g(\nu) \propto \nu^2$ and three monochromatic modes at 9, 22, and 40 cm^{-1} . However, the Raman, infrared-absorption and neutron-scattering data confirm the nonexistence of such monochromatic modes in vitreous materials.

According to the Debye theory at low frequencies $g(\nu) \propto \nu^2$ and C/T^3 is constant at low temperatures. C/T^3 values in amorphous materials in excess of the Debye predicted value indicate a nonquadratic $g(\nu)$ greater than that calculated from measured sound velocities. The increase in C/T^3 with increasing temperature means that $g(\nu)$ must increase more rapidly than ν^2 up to a frequency of, say ν_0 . After reaching a maximum, the decrease in C/T^3 values with an increase in T implies that the increase in $g(\nu)$ is now less rapid than ν^2 . Therefore, one may assume the following form for $g(\nu)$:

$$\begin{aligned} g(\nu) &= A\nu^2 + B\nu^4, & \nu \leq \nu_0, \\ g(\nu) &= D\nu, & \nu_0 \leq \nu \leq \nu_{00}, \\ g(\nu) &= E, & \nu \geq \nu_{00}. \end{aligned} \quad (9)$$

At higher frequencies ($\nu > 3$ THz) any form of $g(\nu)$ can be assumed, as this region of the spectrum 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 nonzero. Therefore, $g(\nu)$ cannot be zero and it is realistic to assume a nonzero form of $g(\nu)$. The constants D and E in Eq. (9) can be determined in terms of A , B , ν_0 , and ν_{00} . Since the Raman data provide strong evidence that the vibrational states in glasses in the range 0.2 to 1.5 THz are harmonic, in contrast to the two-level tunneling states known to contribute to heat capacity below 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., $A = 3V/2\pi v_D^3$, where V is the volume and v_D is the Debye velocity. If v_l and v_t are the longitudinal and the transverse sound velocities, respectively, then

$$3/v_D^3 = 1/v_l^3 + 2/v_t^3. \quad (10)$$

With $g(\nu)$ represented by Eq. (9), Eq. (1) has three unknowns, i.e., B , ν_0 , and ν_{00} and can be solved using the computer library subroutines for integration to determine these constants for a reasonable agreement to the experimentally observed heat-capacity data. It is worth noting that the function in the 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 the contribution is then from a larger number of modes. The narrowness of this function at low temperatures helps to define $g(\nu)$ fairly accurately for a particular value of $C(T)$. During the calculations, it was observed that a variation of ± 0.03 THz (1 cm^{-1}) in the value of ν_0 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 sensitive to the form of $g(\nu)$ and fairly accurate and absolute values of $g(\nu)$ at low frequencies can be obtained by adopting this procedure.

The form of $g(\nu)$ as described above provides a rather poor fit to the 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 ν_{00} and $g(\nu)=0$ for $\nu > \nu_{00}$ also provides the same fit. However as already explained, a nonzero form of $g(\nu)$ in this region of the spectrum should be used. But what about the kinks at ν_0 and ν_{00} ? These were introduced to provide a mathematical form of $g(\nu)$ for computational purposes. They do not have any physical significance and thus cannot be real. Therefore, $g(\nu)$ can be smoothed at these kinks. The smooth forms of $g(\nu)$ along with the Debye density of states $g_D(\nu)$ for Spectrosil-WF, Spectrosil-B, and Heraldux are shown in Fig. 2 and the fit to the heat-capacity data is shown by solid curves in Fig. 1. At low temperatures, the fit is kept lower than measured values as the tunneling states may still be contributing to the heat capacities. It is clear from this fit that the smooth forms of $g(\nu)$ shown in Fig. 2 are nearly a true representative of the actual density of states in silica glasses. It may be noted that the values of $g(\nu)$ for Heraldux are the same as given elsewhere.⁶

A plot of $g(\nu)/g_D(\nu)$ against ν for Spectrosil-WF

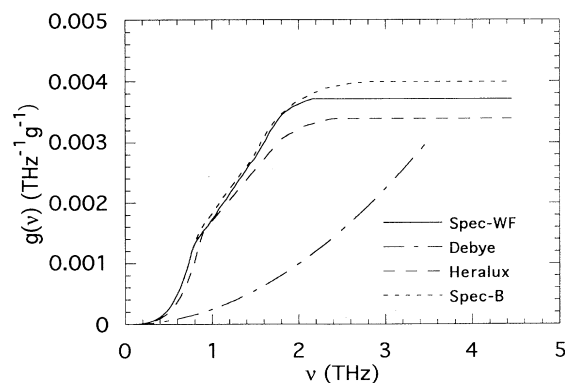


FIG. 2. The density of low-frequency vibrational states for Spectrosil-WF, Spectrosil-B, and Heraldux.

shows that the ratio is maximum at about 0.75 THz and for $\nu \geq 4$ THz, the ratio is less than unity. The nonquadratic form of these $g(\nu)$ values for $\nu < 0.75$ THz is in agreement with theoretical work based on the coherent-potential approximation by Galperin, Karpov, and Kobuz.²² It may be noted that $g(\nu)$ values obtained in this work are very reliable as it has been seen in the past⁶ that the $g(\nu)$ values obtained from heat capacities are very similar to those obtained from inelastic scattering of neutrons.

For Heralux, Buchenau, Nucker, and Dianoux²³ have given $g(\nu)$ as a sum of $g_D(\nu)$ and additional states. This division raises a number of problems. For example, nondispersive sound waves are known to exist at low frequencies from Brillouin scattering ($\nu < 30$ GHz) and phonon-interference experiments ($\nu < 500$ GHz). Analysis of thermal conductivity κ of vitreous silica based on this suggests that the sound waves are reasonably well defined below 1 THz but in order to explain the plateau in κ between 4 and 20 K, the mean-free path for the transverse waves must be smaller than the wavelength at higher frequencies. Furthermore, above 4 THz, total $g(\nu)$ as calculated from the heat capacities or neutron scattering is less than $g_D(\nu)$ in direct contradiction to the postulate of nondispersive sound waves. It is, therefore, concluded that the well-defined nondispersive sound waves exist below 1 THz but not at higher frequencies. The division of $g(\nu)$ into $g_D(\nu)$ and additional states is not adequate and must not be made.

Using the values of $g(\nu)$ shown in Fig. 2, the Raman-scattering and infrared-absorption coupling constants for Spectrosil-WF have been determined and are shown in Fig. 3. It may be seen from this figure that they have very similar frequency dependences and confirm our earlier results^{24,25} that both Raman and infrared experiments at low frequencies can be explained with a single-coupling-constant bond model and there is no need to introduce separate charge and structural correlation lengths for infrared and Raman experiments. In both cases a vibrational correlation function $C(\nu)$ is the important physical parameter. A similar vibrational function has been used by Jackle and Frobose²⁶ when calcu-

lating the neutron inelastic structure factor in glasses, and this suggests that a complete synthesis of neutron, infrared, and Raman measurements, based on this idea, should be possible in the low-frequency regime ($\nu < 3$ THz).

The Martin-Brenig theory¹⁰ as normally applied assumes that the Raman coupling constant $C(\nu)$ is

$$C(\nu) \propto \nu^2 \exp[-(2\pi\nu\sigma/v_s)^2], \quad (11)$$

where v_s is the velocity of sound and σ is the structural correlation range. It is clear from Fig. 3 that the Raman coupling constant cannot be represented by Eq. (11). Therefore, the Martin-Brenig model as normally applied is not valid if the $g(\nu)$ values determined from heat capacities are used. The experimental work by Malinovsky *et al.*²⁷ also confirms the present conclusions regarding the Martin-Brenig approach. It is easy to see what is going wrong. Martin and Brenig calculate the contribution of a plane wave of wave vector \mathbf{q} , and this is usually taken to represent the Raman scattering in the glass of angular frequency $\omega = v_s \mathbf{q}$. This is consistent with the normal assumption $g(\nu) \propto \nu^2$, but both these approximations are valid only at very low frequencies. In a real glass, higher frequency vibrational modes ($\nu > 0.3$ THz) are either strongly attenuated plane waves or localized vibrations. The word localized is used here not to imply the lack of thermal transport, but to indicate that a vibrational mode will involve a large range of wave vectors \mathbf{q} if analyzed into plane waves. When using the Martin-Brenig model, the contribution at angular frequency ω should be calculated by summing over the appropriate \mathbf{q} vectors, most conveniently accomplished by means of a spectral function. This does not appear to have been done, but will clearly lead to a constant $C(\nu)$ at higher frequencies where a broad range of \mathbf{q} is expected.

A possible explanation for the enhanced $g(\nu)$ as compared to $g_D(\nu)$ in vitreous silica is the crossover from sound waves at low frequencies to vibrations of crystallites or fractals.^{28,29} Fractals of size 5–10 nm have been assumed to predict this enhancement in $g(\nu)$. The clusters proposed by Phillips²⁹ comprise 6.6 nm size β -cristobalite crystallites, the surfaces of which are non-coalescing and saturated with Si=O double bonds. This assumption of the size of the crystallites is totally incompatible with the neutron-diffraction studies³⁰ where the width of the diffraction pattern indicates a correlation length of no more than 1 nm. Assuming the presence of 1 nm size β -cristobalite crystallites in vitreous silica, the model calculations³⁰ for the neutron-diffraction pattern give rise to three peaks below 0.53 nm^{-1} , whereas, experimentally only two peaks are observed. Since this region of the diffraction pattern is most sensitive to intermediate-range order, the presence of fractals or β -cristobalite crystallites of size 5–10 nm is out of the question. Further evidence against the presence of β -cristobalite crystallites in vitreous silica comes from the study of the devitrification process in pure bulk vitreous silica. This process has been observed to start from the surface of the sample and to proceed inward,³¹ which is contrary to what would be anticipated for a material with

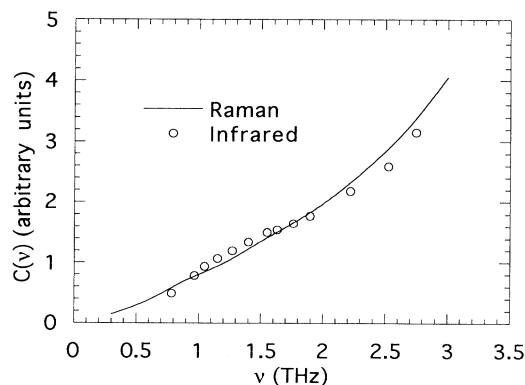


FIG. 3. The Raman (solid line) and infrared (dots) coupling constants for Spectrosil-WF, using $g(\nu)$ determined from heat capacities as shown in Fig. 2.

paracrystallites. It is, therefore, concluded that the experimental evidence does not support the fractal model.

A more convincing explanation about the nature of these additional states is based on inelastic-neutron-scattering studies, heat-capacity measurements, and model calculations.⁶ It was shown that in vitreous silica (Heralux) the additional states can result from relative rotational motion of almost rigid SiO₄ tetrahedra. Model calculations also support this picture.³² It was also shown that the frequencies would approach zero in a structure based on linked tetrahedra so that the structure would become locally unstable, giving rise to two-level potentials consistent with what are known as tunneling states at low temperature.³² Thus, the model based on microscopic motion of rigid tetrahedra provides explanations both for the heat capacity and the presence of double-well potentials.

Using the approach adopted by Buchenau,³³ one can calculate the number of atoms N_s of mass M participating in a soft vibrational or tunneling mode. In the present case, the minimum in C/T^3 is at about 2.4 K but it is not possible to determine the first broad maximum in $g(\nu)$ from heat-capacity data. For $T=16$ K, the estimated values of C/T^3 as a function of upper limit of the integration in Eq. (1) are shown in Fig. 4. It is clear from this figure that the C/T^3 values are not sensitive to the form of $g(\nu)$ for $\nu > 3$ THz but the inelastic-neutron-scattering data⁶ predict a decrease in the values of $g(\nu)$ for $\nu > 3$ THz. Therefore, a very approximate value of the frequency where the first broad maximum in $g(\nu)$ occurs, is about 3 THz. Using this value of frequency, the estimated value of $N_s a^2$ is $3.7 \times 10^{-44} / M \text{ m}^2 \text{ kg}^{-1}$. For simplicity it may be assumed that all the atoms are similar with an average mass of about $3.32 \times 10^{-26} \text{ kg}$, then $N_s a^2$ is $1.1 \times 10^{-18} \text{ m}^2$. Since a should be of the order of 0.1 nm, there are about 110 atoms participating in a tunneling or soft mode which are nearly the same as determined by Buchenau³³ in Heralux.

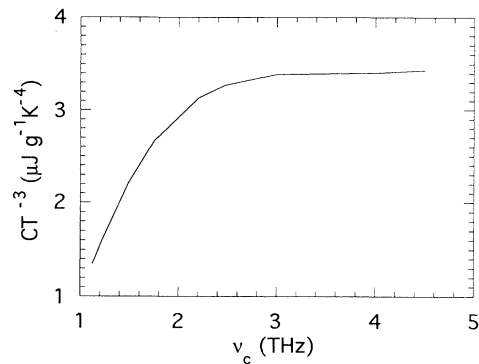


FIG. 4. Estimated values of C/T^3 as a function of ν_c at $T=16$ K, where ν_c is the upper limit of integration in Eq. (1).

CONCLUSION

The estimated form of the density of low-frequency vibrational states in Spectrosil-WF is nonquadratic. The enhanced $g(\nu)$ as compared to the Debye density of states can be attributed to rotational motion of almost rigid SiO₄ tetrahedra. Such degrees of freedom also provide a possible explanation for the presence of two-well tunneling states. The forms of the Raman and infrared coupling constants are similar and can be explained on the basis of a single-bond-coupling-constant model. The Raman coupling constant cannot be represented according to the Martin-Brenig theory if the $g(\nu)$ values determined from heat capacities are used. About 110 atoms participate in a soft mode.

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