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Loosely bound particles in amorphous solids

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The density of tunneling states deduced from the thermal conductivity of vitreous silica is much smaller than that required to explain the low-temperature specific heat of vitreous silica. We show that this discrepancy can be reconciled by introducing the cavity—loosely-bound-particle model. The loosely bound particles contribute part of the specific heat at low temperature, but not to the phonon scattering anomalies. Numerical calculation of the specific heat and the thermal conductivity of SiO_2-Suprasil glass is given. Our discussion suggests that introduction of inert atoms into a glass will greatly increase its low-temperature specific heat, but its thermal conductivity may not be changed significantly.

I. INTRODUCTION

Over the past decade, extensive experimental and theoretical investigations have been made of the thermal, acoustic, and dielectric properties of amorphous solids at low temperature. It has been observed that, for a wide range of amorphous materials, these properties are anomalous, in contrast to those of crystalline dielectrics. Below 1 K, the specific heat has been found to be quasilinearly temperature dependent, while the thermal conductivity has shown roughly a T^2 dependence.[1,2] With decreasing temperature, the sound velocity[3,4] of amorphous dielectrics does not increase monotonically towards its value at $T=0$, but reaches a maximum and decreases steadily at lower temperature. Other anomalies, such as ultrasonic attenuation[5,6] and phonon echoes[7] have also been found. Of the many theoretical models[8,9] proposed to explain these anomalies, the so-called "tunneling model" proposed by Anderson, Halperin, and Varma,[10] and independently by Phillips[11] has been the most successful. It assumes that the localized excitations in the amorphous state are associated with the quantum-mechanical tunneling of some entity which can sit more or less equally well in two equilibrium positions. The microscopic origin of the tunneling state remains an unresolved problem. This makes the theoretical development more difficult.

A crucial question in the phenomenological development of the tunneling model is whether there exists a consistent set of tunneling-model parameters which can explain both the low-temperature specific heat and the phonon-scattering anomalies[3-7] (i.e., thermal conductivity, ultrasonic attenuation, sound velocity, and phonon echoes). This issue has been seriously considered by Black,[12] and also by Black and Halperin.[13] They conclude that, if only the "standard tunneling level" (see Sec. II) is assumed, the density of the tunneling states deduced from the phonon-scattering data is too small to be consistent with that deduced from the specific heat. They then discussed the possibility of the existence of "anomalous" tunneling levels, which only contribute to the specific heat, not to the phonon-scattering anomalies. A similar suggestion is also discussed by Hunklinger *et al.*[14] In the present work, we suggest a possible mechanism which may satisfy the requirement of the anomalous level. We will also give a quantitative calculation of the contribution of the suggested excitations to the specific heat. The mechanism is as follows. In an amorphous solid, because of its disordered nature, there may exist some microscopic cavities. A particle (single atom or molecule, or a group of atoms or molecules) trapped in a cavity may be weakly attached to the rest of the lattices (see Fig. 1). These loosely bound particles contribute to the specific heat at low temperatures, but weakly couple with phonons. More detailed discussions on this model will be given in Sec. III. We note that this has been discussed to some extent by Rosenstock.[15,16]

II. TUNNELING MODEL

We briefly review here the main results of the tunneling model and also give a quantitative discussion of the difficulties of the model in consistently explaining the large body of experimental results. When a broad range of relaxation time is assumed,[17] the long-time-scale specific heat contributed from the tunneling levels is calculated by[18,19]

$$C_1=\int_0^{E_{\max}} dE\, E^2[4k_BT^2\cosh^2(E/2k_BT)]^{-1}P(E)\eta(E)\ . \tag{1}$$

Here E is the energy splitting, $P(E)$ is the density of the tunneling states, and $\eta(E)$ represents the quantity $\frac{1}{2}\ln(4\tau_{\max}/\tau_{\min})$, where τ is the relaxation time;

$$\tau^{-1}=\left[\frac{M_l^2}{v_l^5}+2\frac{M_t^2}{v_t^5}\right]\frac{E^3}{2\pi\rho\hbar^4}\coth\left[\frac{E}{2k_BT}\right]\ . \tag{2}$$

The coupling parameters M_α reduce to $\gamma_\alpha(\Delta_0/E)$ on making the usual assumption that the dominant coupling of the phonons with the tunneling levels is through the modulation of E.[20] Here Δ_0 is the overlap energy. The minimum of the relaxation time reaches when $\Delta_0=E$. We get

$$\tau_{\min}^{-1}=\left[\frac{\gamma_l^2}{v_l^5}+2\frac{\gamma_t^2}{v_t^5}\right]\frac{E^3}{2\pi\rho\hbar^4}\coth(E/2k_BT)\ . \qquad (3)$$

The phrase "standard tunneling model" here refers to the model for which the coupling constants γ_α are the same for all the tunneling states. In the original tunneling model,[10,11] this is not necessarily the case.

The phonons are scattered by the tunneling levels through the resonant process and the relaxation process. The resonant process occurs when a phonon of frequency ω is absorbed by a state of energy $E=\hbar\omega$ and later reradiated in a different direction. At low temperature ($T \lesssim 1$ K), the resonant scattering is dominant. The phonon inverse mean free path due to the resonant process is given by

$$l_{\alpha,\mathrm{res}}^{-1}(\omega)=\left[\frac{\pi\gamma^2}{\rho v^3}\right]_\alpha \omega P(\hbar\omega)\tanh\left[\frac{\hbar\omega}{2k_BT}\right]\ . \qquad (4)$$

The thermal conductivity can be calculated from

$$\kappa=\frac{1}{3}\sum_\alpha\int_0^{\omega_D}\frac{\hbar^2\omega^4e^x l_\alpha(\omega)}{2\pi^2v_\alpha^2k_BT^2(e^x-1)^2}d\omega\ , \qquad (5)$$

where $x=\hbar\omega/k_BT$. To simplify our numerical calculation, we assume a constant density of states $P(E)=P_0$. At low temperature, we get

$$C_1=\tfrac{1}{6}\pi^2k_B^2P_0\eta(E=2.4k_BT)T\ , \qquad (6)$$

$$\kappa=\frac{\rho k_B^3}{6\pi\hbar^2}\left[\sum_\alpha\frac{v_\alpha}{P_0\gamma_\alpha^2}\right]T^2\ . \qquad (7)$$

By fitting to the experimental data of the thermal conductivity, we are able to get the value of the product $P_0\gamma_\alpha^2$. Since the coupling parameters have been measured independently for vitreous silica,[5,7] $\gamma_l=1.6$ eV and $\gamma_l^2 \simeq 2\gamma_t^2$, the density of states P_0 is determined. Using the experimental data from Zeller and Pohl,[21] $\kappa=33$ erg/cm K at $T=0.1$ K, and $v_l=5.81\times10^5$ cm/sec and $v_t=3.73\times10^5$ cm/sec, we get $P_0\gamma_l^2=1.73\times10^8$ erg cm^{-3} or $P_0=2.64\times10^{31}$ erg^{-1}cm^{-3}. On the other hand, if we assume that all the specific heat at $T=0.1$ K are contributed from the standard tunneling states, its density of states can also be determined directly from Eq. (6). From Zeller and Pohl,[21] $C=1.0$ erg g^{-1}/K at $T=0.1$ K, we have $P_0\eta(E=0.24k_B)=3.2\times10^{32}$ erg^{-1}g^{-1}. Assuming that the time scale in the specific heat measurement is $\tau_{\max}=10$ sec, we have, for vitreous silica,

$$\eta=\tfrac{1}{2}\ln[6.19\times10^9(E/k_B)^3\coth(E/2k_BT)]\ . \qquad (8)$$

This gives $\eta(E=0.24k_B)=9.2$. Therefore, $P_0=7.66\times10^{31}$ erg^{-1}cm^{-3}. It is almost three times larger than that calculated from thermal conductivity. We note that the density of states deduced from other ultrasonic properties is comparable with that from the thermal conductivity.

One possible way to go around this difficulty is to assume that the coupling parameter γ is energy dependent. The average of it may give a smaller value and hence bring P_0 into consistent with the one calculated from the specific heat. Since the energy dependence of γ is not known yet, the reduction of the coupling parameter cannot be predicted. Moreover, this assumption suffers the following challenges.

First, as is proved in Ref. 2, an energy-dependent density of states of the form $P(E)=P_0(E/k_B)^\nu$ will give a $T^{1+\nu}$ term in the specific heat, and a $T^{2-\nu}$ term in the thermal conductivity, at low temperature. The temperature dependence of the thermal conductivity in the vitreous silica is $T^{1.9\pm0.1}$, while that of the specific heat is $T^{1.30}$ (Suprasil W). When the energy dependence of the coupling parameter γ is considered, we would have $P(E)\gamma^2(E)\sim E^{0.1\pm0.1}$ and $P(E)\sim E^{0.3}$. This gives $\gamma^2(E)\sim E^{-(0.2\pm0.1)}$. This shows that the coupling parameter γ would increase with decreasing energy. After scaling $\gamma(E)$ and recalculating P_0, we are still not able to make P_0 consistent with the one calculated from the specific heat and the one calculated from the thermal conductivity.

Second, the specific heat is very sensitive to the exact nature of the sample (chemical composition, impurity content, sample preparation), whereas the thermal conductivity is rather independent of these details. For example, for As_2S_3 at 0.1 K, the specific heat increases by a factor of up to 3 between samples of different purities before any significant changes appear in the thermal conductivity.[22] If both of the thermal conductivity and the specific heat are only contributed from the tunneling states, we would be forced to conclude that $P_0\bar{\gamma}^2$ remains constant, P_0 increases by a factor of up to 3, and hence $\bar{\gamma}$ is reduced by a factor of up to 1.73, for samples of different purities. Here the overbar means average. Why the impurities are so weakly coupled with the phonons is to be explained.

Finally, short-time-scale specific-heat measurement[23] shows that only part of the total specific heat of glasses can be ascribed to the tunneling levels. This part has an extremely wide distribution of the relaxation time and shows the predicted logarithmic time dependence. The rest of the specific heat may be contributed from other sources.

III. CAVITY—LOOSELY-BOUND-PARTICLE MODEL

With the comments of Sec. II in mind, we now have to seek other possibilities to remedy the difficulties. Since the difficulties arise from the density of states deduced from the specific heat and from the thermal conductivity, we are led to adopt the following point of view.[12,13] Most of phonon-scattering anomalies are attributed to interactions between phonons and the tunneling levels. The specific heat, however, is contributed partly from the tunneling states, while the rest are from different local excitations.

We notice that there are several requirements that the unknown excitations have to satisfy. (1) The model should be general; it should not depend on the details of structure. (2) The coupling between the phonons and the unknown excitations should be weak. (3) The energy of the excitations should be small (low-lying modes), which then gives large contribution to the specific heat at low temperature. (4) It should present an explanation of the sample dependence of the specific heat. (5) Like the tunneling levels, these excitations should also present a quasilinearly temperature-dependent specific heat at low temperature. We note that this can be realized by postulating a weakly energy-dependent density of states. For, as we proved in the Appendix, any excitation with a constant density of states, extending from a sufficiently low energy to a sufficiently high energy, will contribute a linearly temperature-dependent term in the specific heat. We suggest that the following cavity—loosely-bound-particle model may satisfy the above requirements.

As is mentioned in the Introduction, cavities are more likely to occur in disordered solids, in comparison with crystalline solids (see Fig. 1). We point out that the existence of the cavities does not contradict either the "continuous random-network" model or the "random close-packing" model. The usual justification of these models is that they yield reasonable agreement with diffraction studies of the radial distribution function. As can be seen in the next section, the number of cavities is so small that it will not affect the measurement of the radial distribution function.

Consider a loosely bound particle in a cavity with linear size L. In the limit case, the particle can be considered to be free. The Schrödinger equation can readily be solved to yield

$$E_n=\sigma(n_1^2+n_2^2+n_3^2),\quad n_1,n_2,n_3,=1,2,3,\ldots\,, \tag{9}$$

$$\sigma=\frac{\pi^2\hbar^2}{2mL^2}\,, \tag{10}$$

where m is the mass of the particle. For $L=5$ Å, and m the mass of an oxygen atom, $m=2.66\times10^{-23}$ g, we have $\sigma=8.2\times10^{-17}$ erg. This is equivalent to 0.594 K or 7.8×10^{10} Hz. We see that it is small.

For simplicity, we assume that all the loosely bound particles are the same. From the Appendix, the specific heat contributed from these particles can be easily computed:

$$C_2=\int_{\sigma_{\min}}^{\sigma_{\max}} 3kP_2(\sigma)\left[\frac{Z_2(\sigma/k_BT)}{Z(\sigma/k_BT)}-\frac{Z_1^2(\sigma/k_BT)}{Z^2(\sigma/k_BT)}\right]d\sigma\,, \tag{11}$$

where $P_2(\sigma)$ is the density of states, and

$$Z(x)=\sum_{n=1}^{\infty} e^{-xn^2}\,, \tag{12}$$

$$Z_1(x)=\sum_{n=1}^{\infty} xn^2e^{-xn^2}\,, \tag{13}$$

$$Z_2(x)=\sum_{n=1}^{\infty} (xn^2)^2e^{-xn^2}\,. \tag{14}$$

Assuming $P_2(\sigma)=n_2(\sigma/k_B)^\nu$, we have

$$C_2=3k_B^2T^{1+\nu}n_2\int_{x_{\min}}^{x_{\max}} x^\nu\left[\frac{Z_2(x)}{Z(x)}-\frac{Z_1^2(x)}{Z^2(x)}\right]dx\,, \tag{15}$$

here $x=\sigma/k_BT$. We note that $\nu=0$ corresponds to a cavity distribution $P(L)\sim1/L^3$. This makes the assumption that the density of states is approximately constant more reasonable.

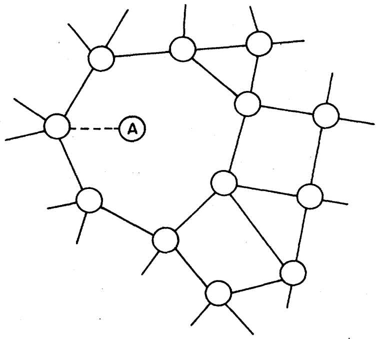

FIG. 1. Schematic representation of a disordered solid, showing a cavity and a loosely bound particle A. The circles represent the rest of lattices.

Using the parameters given in the next section, we can estimate $C_2\sim3.5\times10^{-2}$ erg g^{-1}K^{-1} at $T=0.01$ K. Extrapolating the experimental data of vitreous silica to this temperature gives $C\sim4.5\times10^{-2}$ erg g^{-1}K^{-1}. We see that the loosely bound particles may give large contribution to the specific heat at low temperature.

As can be seen in the next section, the average linear size of the cavities is about 4 Å for vitreous silica. Most phonons at low temperature have wavelengths much longer than this size. This shows that the cavities have little effect on the propagation of the phonons. On the other hand, being isolated from the rest of the lattice, a loosely bound particle in a cavity will weakly couple with the phonons. In the limit case, where the particle is free, there is no coupling between the phonons and the particle.

The influence of the sample preparation and the chemical composition on both the number and the size of the cavities is readily seen. The way the impurities affect the low-temperature specific heat can be explained as follows. For an impurity which weakly interacts with the solid network under consideration, like most of inert atoms, it will possibly enter an empty cavity and become a loosely bound particle. For an impurity which strongly interacts with the network, like OH in vitreous silica, it may replace an atom in the network and the latter may become a loosely bound particle (in the case of the OH impurity, the situation may be more complicated, because the OH group may itself consist of a tunneling state[24]). This interpretation is consistent with the measurements of the specific heat of vitreous silica after sorbing helium and neon atoms.[25,26] Large contribution to the specific heat from these inert atoms is found. We predict further that the thermal conductivity will have no significant change.

IV. NUMERICAL RESULTS ON SiO$_2$-SUPRASIL GLASS

In this section, we will calculate the specific heat and the thermal conductivity of vitreous silica (Suprasil), by employing the tunneling model and the cavity—loosely-bound-particle model. The specific heat is

$$C=C_D+C_1+C_2\ . \tag{16}$$

Here C_D is the Debye specific heat, $C_D=8.0T^3$ erg g^{-1}K^{-1}. Because the Debye temperature of the vitreous silica is about 340 K, and the temperature range under study is less than 10 K, the above expression of C_D is expected to be satisfactory. C_1 is the specific heat contributed from the tunneling states. The density of the tunneling states has been derived by the author,[18] which is

$$P(E)=n_0\left[\frac{\Delta}{k_B}\right]^{0.2} e^{-D(\Delta-\Delta_c)^2}\frac{d\Delta}{dE}\ , \tag{17}$$

$$\frac{d\Delta}{dE}=\frac{E/\Delta}{(E/\Delta)^2+(E^2-\Delta^2)(\{0.2Ae^{-t_0^2}/\Delta^{1.8}[1+A\Delta^{0.2}e^{-t_0^2}+\mathrm{erf}(t_0)]\}-1.2B\Delta^{0.4})}\ . \tag{18}$$

The asymmetry Δ and the energy E is related by

$$E^2=\Delta^2\{1+[1+A\Delta^{0.2}e^{-t_0^2}+\mathrm{erf}(t_0)]^2e^{-B\Delta^{2.4}}\}\ . \tag{19}$$

Here

$$A=\hbar\omega_0(2B/\pi)^{1/2}\ , \tag{20}$$

$$B=m\omega_0\bar{c}^{\,2}/2\hbar\ , \tag{21}$$

$$\mathrm{erf}(t_0)=\frac{2}{\sqrt{\pi}}\int_0^{t_0}e^{-t^2}dt\ , \tag{22}$$

and

$$t_0=(\sqrt{\pi}A\Delta^{0.2})^{-1}\ , \tag{23}$$

m is the mass of the tunneling entity, ω_0 is the frequency of an oscillator in the double-well potential, D characterizes the distribution width of the asymmetry, and $\bar{c}$ is related to the distribution center of the potential-minima separation.

C_2 is the specific heat contributed from the loosely bound particles. We assume $\nu=0.3$ in using Eq. (15).

The thermal conductivity is calculated from Eq. (5), with[19]

$$l_\alpha(\omega)=[l_{\mathrm{res},\alpha}^{-1}(\omega)+l_{\mathrm{rel},\alpha}^{-1}(\omega)]^{-1}+l_{\min}\ . \tag{24}$$

The inverse of the phonon mean free path due to resonant scattering by the tunneling levels has been given in Eq. (4). The mean free path due to relaxation process is mathematically complicated.[18,19] It can be integrated only for $\omega\tau_{\min}\ll 1$ and $\omega\tau_{\min}\gg 1$. We have

$$l_{\mathrm{rel},\alpha}^{-1}(\omega)=\frac{1}{4}\left[\frac{\pi\gamma^2}{\hbar\rho v^3}\right]_\alpha\left[\frac{\hbar\omega}{k_BT}\right]\int_0^{E_{\max}}dE\,P(E)\mathrm{sech}^2\left[\frac{E}{2k_BT}\right],\ \text{for } \omega\tau_{\min}\ll 1\ , \tag{25}$$

$$l_{\mathrm{rel},\alpha}^{-1}(\omega)=\left[\frac{\gamma^2}{3\rho v^3}\right]_\alpha\sum_\beta\left[\frac{\gamma^2}{2\pi\rho\hbar^4v^5}\right]_\beta\frac{1}{k_BT}\int_0^{E_{\max}}dE\,2E^3P(E)\left[\sinh\left[\frac{E}{k_BT}\right]\right]^{-1},\ \text{for } \omega\tau_{\min}\gg 1\ . \tag{26}$$

$l_{\min}$ is some constant. Following Zaitlin and Anderson,[27] we will use Eqs. (25) and (26) as interpolations.

Figures 2–4 show our fit to the experimental data. Most of the specific heat at $T\gtrsim 2$ K is contributed from the tunneling states, while that at $T\lesssim 0.5$ K is from the loosely bound particles. For example, at $T=0.1$ K, the loosely bound particles contribute almost $\frac{3}{4}$ of the specific heat.

By fitting the thermal conductivity to the experimental value at $T=0.1$ K, n_0, the constant in the density of the tunneling states, is determined to be $n_0=2.06\times10^{34}$ erg^{-1}cm^{-3}. The other parameters are as follows: $A=0.6/k_B^{0.2}$, $B=0.003/k_B^{2.4}$, $\Delta_c=66k_B$, $D=1.26\times10^{-3}/k_B^2$, $n_2=3.5\times10^{32}$ erg^{-1}g^{-1}, $\sigma_{\max}=1.5k_B$, $\sigma_{\min}=0.005k_B$, $l_{\min}=8\times10^{-6}$ cm, and $E_{\max}=80k_B$.

At temperature $T\lesssim 0.3$ K, the density of the tunneling states can be expressed as[18]

$$P(E)=(n_0e^{-D\Delta_c^2}/5^{0.6})(E/k_B)^{0.2}$$

$$=(3.24\times10^{31}\ \mathrm{erg}^{-1}\mathrm{cm}^{-3})(E/k_B)^{0.2}\ .$$

The information on the local potential of the tunneling entity can be obtained from A, B, Δ_c, and D.[18] Suppose

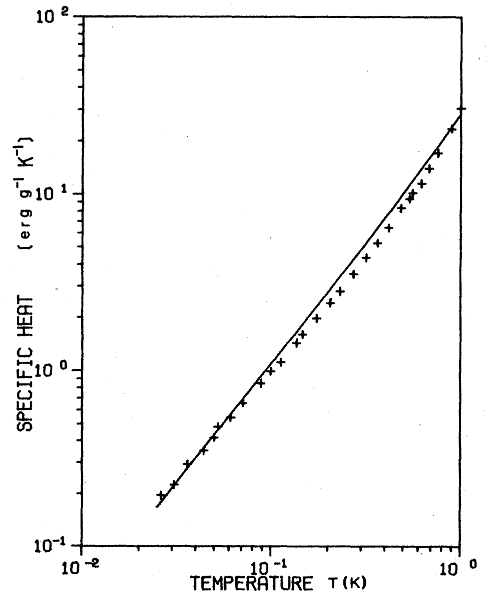

FIG. 2. Specific heat of vitreous silica below 1 K. The experimental data (+) are from Ref. 2. Below 0.5 K, a major part of the specific heat is contributed from the loosely bound particles.

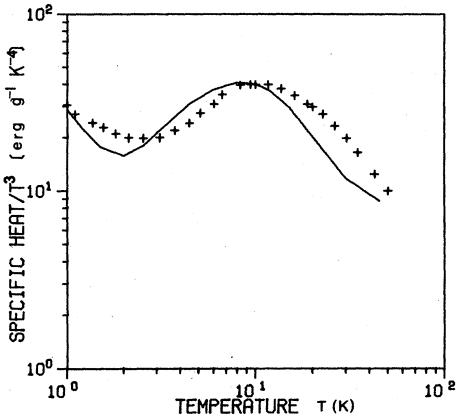

FIG. 3. Specific heat of vitreous silica above 1 K. The experimental data (+) are from Ref. 21. For 1 K $< T <$ 15 K, the tunneling states give major contribution.

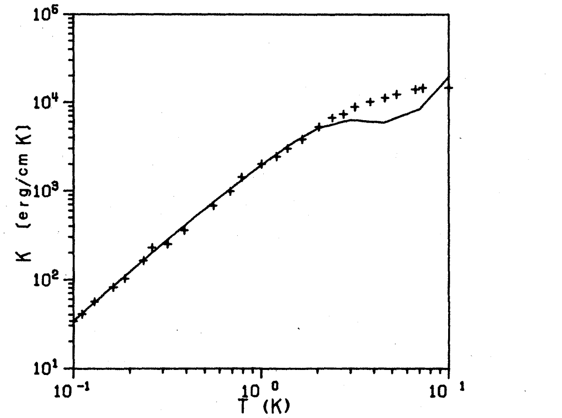

FIG. 4. The thermal conductivity of vitreous silica. The experimental data (+) are from Ref. 21.

that the tunneling entity is the SiO_2 molecule. Then the frequency of oscillation of the entity in the harmonic potential is $\omega_0=1.8\times10^{12}$ Hz. The distribution width of the asymmetry is $1/D^{1/2}=2.4\times10^{-3}$ eV. From $\bar{c}=A/53.3k_B^{1.2}$, the distribution center of the potential-minima separation can be calculated to be $\chi_c=\bar{c}\Delta_c^{1.2}=2.86$ Å, and its distribution width $\alpha=\bar{c}/D^{0.6}=1.03$ Å. If the tunneling entity is the SiO_4 unit, then $\chi_c=2.31$ Å and $\alpha=0.84$ Å.

The information on the loosely bound particles are included in the parameters n_2, $\sigma_{\max}$, and $\sigma_{\min}$. Suppose that the loosely bound particles are the "nonbridging" oxygens. Then $\sigma_{\max}$ corresponds to the smallest cavity size of $L_{\min}=3.15$ Å. The averaged energy of the particles is calculated to be $\bar{\sigma}=0.85k_B$, which corresponds to a cavity with $\bar{L}=4.19$ Å. The density of the loosely bound particles is estimated to be $6.5\times10^{16}/\mathrm{cm}^3$. This shows that as long as there is one loosely bound oxygen atom out of 10^6 SiO_2 molecules, the major part of the specific heat at low temperature will be contributed from those oxygens. Furthermore, the OH content in SiO_2-Suprasil is 1200 ppm. Suppose the hydroxyl enters the SiO_2 network through the replacement of a bridging oxygen atom by two OH groups.[28] To contribute major part of the specific heat at $T\lesssim0.1$ K, only $\frac{1}{200}$ of the replaced oxygen atoms are required to become loosely bound.

The parameter $\sigma_{\min}$ is not sensitive to the specific heat for $T\gtrsim0.05$ K. $\sigma_{\min}=0.005$ K corresponds to a cavity size of $L\sim50$ Å. Cavities of this size might be expected to have some effects on phonon-scattering properties. However, the cavities are distributed according to $1/L^{3.6}$, for the density of states $P_2(\sigma)\propto(\sigma/k)^{0.3}$. The number of cavities having $L\sim50$ Å is about four orders of magnitude smaller than that having $L\sim5$ Å. At $T\sim1$ K, where the cavities having $L\sim5$ Å give contribution to the specific heat, the phonon scattering by large-size cavities ($L\sim50$ Å) is negligible. At $T=0.05$ K, the cavities having $L\sim20$ Å give large contributions to the specific heat. However, at this temperature, most phonons will have wavelength about 10^4 Å, much larger than the linear size of any cavity. The effect of large-size cavities on the phonon-scattering properties is therefore negligible even at very low temperature.

V. SUMMARY AND CONCLUSION

The tunneling model successfully explains the major features of both the specific-heat anomaly and the ultrasonic anomalies. However, the density of states deduced from thermal conductivity seems too small to explain the low-temperature specific heat. As is shown in Sec. II, it seems hard to remove this difficulty by assuming an energy-dependent coupling parameter. That the specific heat is very sample dependent, while the thermal conductivity is rather independent of structural details, is also an issue to be explained. We have shown that it is possible to settle these problems by introducing the cavity—loosely-bound-particle model. The influence of sample preparation, chemical composition, and impurity content on the specific heat can readily be explained. In addition, because the loosely bound particles are weakly coupled with phonons, their influences on the ultrasonic properties are minor. Numerical calculations on SiO_2-Suprasil glass show that a density of 6.5×10^{16} cm^{-3} of the loosely bound particles will contribute about $\frac{3}{4}$ of the specific heat at $T=0.1$ K. At $T\gtrsim2$ K, the contribution from these particles is negligible.

APPENDIX

In this appendix, we prove a theorem which states that any excitation with a constant density of states, extending from a sufficiently low energy to a sufficiently high energy will contribute a linearly temperature-dependent term to the specific heat.

Proof. The partition function of a single excitation is a function of the energy and the temperature,

$$Z=Z(\beta E)\ . \tag{A1}$$

Its thermal averaged energy is then

$$\bar{E}=\frac{\partial\ln Z(\beta E)}{\partial\beta}=-k_BTx\frac{d\ln Z(x)}{dx}\ . \tag{A2}$$

Here $x=\beta E$ and $\beta=1/k_BT$. The specific heat contributed from this excitation is

$$c(E)=\frac{d\bar{E}}{dT}=k_Bx^2\left[\frac{d^2\ln Z}{dx^2}\right] . \tag{A3}$$

The specific heat contributed from all the excitations is then

$$C=\int n(E)c(E)dE=k_B^2Tn\int x^2\frac{d^2\ln Z(x)}{dx^2}dx\ , \tag{A4}$$

where $n(E)$ is the density of states.

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