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Low-temperature behavior of potassium and sodium silicate glasses

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In a study of the low-temperature anomalies which appear in disordered solids we have measured the specific heat, thermal conductivity, thermal expansion, and dielectric dispersion for a carefully prepared series of $(SiO_2)_{1-x}(K_2O)_x$ and $(SiO_2)_{1-x}(Na_2O)_x$ glasses. Each sample had a known glass transition temperature T_g, mass density, phonon velocities, covalency, and density and concentration fluctuations. The only significant correlation occurred between the phonon mean free path and the glass-transition temperature. No explicit support was found for any model developed to explain the specific heat and/or thermal conductivity of glasses.

I. INTRODUCTION

In an attempt to gain a better understanding of the low-temperature anomalies which appear in disordered materials, we have made a systematic study of a series of alkali-silicate glasses. The following paragraphs discuss these anomalies only in the detail required for the discussion of results found in Sec. III.

At temperatures below ≈ 1 K, nearly all amorphous solids[1] and many disordered crystals[2] have been found to exhibit remarkably similar ("universal") properties. The temperature dependencies of the specific heat and thermal conductivity are approximately $C \propto T$ and $\kappa \propto T^2$, respectively, and the magnitudes of C and κ are roughly independent of chemical composition. Ultrasonic and dielectric dispersion have frequency and temperature dependencies which are now recognized as being typical of the glassy state. All of these properties have been attributed to a set of localized excitations. These excitations may be modeled most simply as two-level states (TLS), that is, a ground state plus one excited state at energy E well separated from other excited states of higher energy. The TLS have a broad, nearly constant, spectrum of excitation energies E. Interaction of the TLS with the strain fields of phonons allows for thermal equilibration. If this interaction is attributed to a coupling constant γ, then the equilibration time τ is proportional to γ^{-2}. In addition to the broad spectrum in E, there is a broad spectrum[3-5] in τ.

Assuming a constant TLS density $n(E)=n$ (per unit energy interval), the specific heat of a nonmetallic glass receives a contribution

$$C \propto nT \qquad (1)$$

in addition to the T^3 phonon contribution. In Eq. (1) it is assumed that C is measured over a period of time $\gtrsim \tau_{\max}$, the longest TLS equilibration time present in the sample. Acoustic-phonon attenuation l^{-1} experiences two contributions from the TLS. One is a resonant contribution

$$l_{\rm res}^{-1}(E) \propto \gamma^2 E \int n(E,\tau)\,d\tau \propto \gamma^2 E \bar{P} \ , \qquad (2)$$

where $\bar{P}$ is the density of TLS interacting most strongly with phonons. Generally it is found that

$$n/\bar{P} = \eta \approx 10 \ . \qquad (3)$$

The second attenuation mechanism is a "classical" relaxation contribution

$$l_{\rm rel}^{-1} \propto \gamma^4 \bar{P} \ . \qquad (4)$$

Thermal phonons at $T \lesssim 1$ K primarily experience $l_{\rm res}^{-1}$ giving a thermal conductivity

$$\kappa \propto \rho v T^2/\gamma^2 \bar{P} \ , \qquad (5)$$

where ρ is mass density and v is an average phonon velocity. If an effective electric dipole moment p_0 is associated with each TLS, the real component ϵ' of the ac dielectric constant ϵ has a minimum near $T \approx 0.1$ K with a temperature dependence

$$\frac{\Delta\epsilon'}{\epsilon'} \propto \bar{P} p_0^2 \ln T \qquad (6)$$

at lower temperatures.

Continuing this conventional representation of TLS, the TLS should contribute a linear thermal-expansion coefficient[1,6]

$$\alpha \propto n\gamma \ . \qquad (7)$$

However, measurements[7] of thermal expansion indicate values of γ orders of magnitude smaller than obtained for $(\gamma^2)^{1/2}$ from ultrasonic attenuation measurements.[8] This discrepancy indicates that a localized TLS cannot be characterized in terms of E and τ alone. One must add the information that the energy splitting E of (roughly) half the TLS increase under an applied strain while, for the other half, E decreases.

After more than a decade of extensive study, the microscopic identity of the TLS has yet to be discovered. A phenomenological model assumes that the TLS arise from the tunneling of some entity of atomic size between two potential-energy wells.[9,10] Another model which has attracted attention recently has the TLS appearing as the low-temperature continuation of high-temperature mass diffusion.[11] The TLS occur in regions of lower-than-average mass density which are intrinsic to this free-volume model of the glass transition.[12,13] This latter model predicts

$$n \propto V_f / T_g \ , \tag{8}$$

where V_f is free volume and T_g is the glass-transition temperature.[14] In Eq. (8), V_f establishes the total number of TLS present while T_g reflects the energy range over which the excitation energy E is distributed.

A number of other models have been proposed.[1,15] Some assume that the anomaly in κ is independent of that observed in C, that the phonon scattering responsible for κ is nonresonant in character.[16] However, such models do not account for the observed ultrasonic dispersion, which is closely related to κ.

In an attempt to provide a test of the theoretical models, we have made a systematic study of a well-characterized series of alkali-silicate glasses. The study includes measurements of light scattering, specific heat, thermal conductivity, dielectric dispersion, and thermal expansion. The results are presented in Sec. II and are compared with previous work. A discussion of the results is presented in Sec. III. Section III also comments on the behavior of glasses at temperatures above ≈ 1 K, which at present is less understood than the temperature range below 1 K.

II. EXPERIMENTAL DETAILS AND RESULTS

Five samples were used in the low-temperature study of potassium silicate glasses as no previous measurements were available for this system. The K_2O content ranged from 0—20 mol %. Since some earlier data are available for the sodium silicate glasses, only two samples in this system were used, namely 0 and 27 mol %. Potassium silicate has the advantage that it has a smaller probability of devitrifying than does sodium silicate.[17] In the following sections the data are presented graphically. The data in tabular form will be available in Ref. 6.

A. Sample preparation and characterization

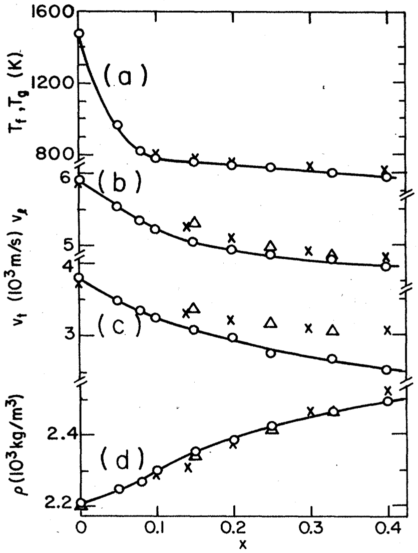

FIG. 1. Measured properties of silicate glass samples versus mole fraction x of K_2O (solid line and ○) or Na_2O (×). (a) Glass-transition temperature T_g for Na_2O (Refs. 21 and 22) and fictive temperature T_f for K_2O (present results and Ref. 20). (b) Longitudinal and (c) transverse phonon velocities. △, K_2O (Ref. 23); ×, Na_2O (Ref. 24). (d) Mass density. △, K_2O, (Ref. 23); ×, Na_2O (Refs. 24 and 25).

For convenience we will refer to the samples as $(SiO_2)_{1-x}(K_2O)_x$ or $(SiO_2)_{1-x}(Na_2O)_x$. For $x = 0$ we used a sample of high-purity silica.[18] The potassium silicate samples contained $x(\mathrm{K}) = 0.05$, 0.08, 0.10, and 0.20 mole fraction of K_2O, while the sodium silicate sample contained $x(\mathrm{Na}) = 0.27$ mole fraction of Na_2O. High-purity raw materials were mixed together and melted in a platinum-rhodium crucible heated in a small electric glow-bar furnace under an inert (Ar or N_2) atmosphere. The crude, prefused glass was homogenized by stirring the entire melt at high temperature for about 6 h. This stirring process removed most of the larger gas bubbles brought about by the chemical reactions in the mix. The remaining small bubbles were removed in the "fining" operation where the temperature of the homogeneous melt was slightly reduced by 75—100 °C. After sufficient time, the melt was poured into stainless-steel molds and, upon solidification, each sample was placed into an annealing furnace. All bulk glasses were annealed for 6 h at a temperature T_f corresponding to a viscosity of 10^{13} P, and then rate cooled to room temperature. Each sample was cut into shapes appropriate to the individual measurements. Samples prepared in this manner have been used previously in studies of light scattering.[19,20]

The fictive temperature T_f is very near the glass transition T_g. The fictive temperatures for our samples are shown in Fig. 1(a). Also plotted in Fig. 1(a) are values of T_g obtained from the literature.[21,22]

The longitudinal (v_L) and transverse (v_T) phonon velocities at a frequency of 2×10^{10} Hz were obtained at room temperature from Brillouin scattering measurements.[20] The results are shown in Figs. 1(b) and 1(c) and are compared with measurements[23,24] made at ultrasonic frequencies. The discrepancy between the two types of measurements (with increasing x) may arise from differences in sample preparation. Also shown in Fig. 1(d) are the measured mass densities[23—25] versus concentration x. The velocity and density data are used in the analyses of specific-heat and thermal-conductivity data.

We will also explore in Sec. III the effect of chemical bonding on the low-temperature behavior of the silicate glasses. Deviations from the Cauchy relation $c_{12} = c_{44}$ are conventionally taken as a criterion for the presence of noncentral forces.[26] The c_{ij} are elastic constants measured from the Brillouin scattering data. Ratios of c_{44}/c_{12} are shown in Fig. 2(a). The approach of $c_{44}/c_{12} = 1$ with increasing concentration implies an increase in the ionic character of the atomic bonding within the glass. An empirical measure of covalency may be obtained from the Poisson ratio σ, since σ decreases with increasing degree of covalency.[27] The Poisson ratios of the

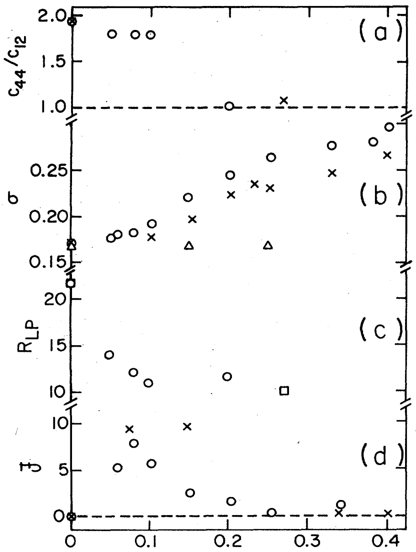

FIG. 2. Measured properties of silicate glass samples versus mole fraction x of K_2O (○) or Na_2O (×). (a) Ratio of elastic constants c_{44}/c_{12}. The dashed line is the Cauchy relation $c_{44}=c_{12}$. (b) Poisson's ratio σ. △, K_2O, determined from ultrasonic data, Ref. 23. (c) Function R_{LP} (see text) proportional to density fluctuations (□, Na_2O). (d) Function $\mathscr{F}$ (see text) proportional to concentration fluctuations. The K_2O data (○) for $\mathscr{F}$ have been multiplied by a factor of 10.

silicate samples, Fig. 2(b), reflect a decrease in covalency with increasing concentration.

In Sec. III we will look for correlations between phonon scattering and microscopic fluctuations in the glasses. A measure of density and concentration fluctuations can be obtained from the Rayleigh-Brillouin light scattering data. Conventionally the Landau-Placzek ratio is used to express the scattering magnitude. The Landau-Placzek ratio is the ratio of central or Rayleigh intensity to the intensity of the Brillouin lines. However, for a two-component glass such as $(SiO_2)_{1-x}(K_2O)_x$ the Landau-Placzek ratio depends on both density and concentration fluctuations. We therefore divide the ratio into a term, R_{LP}, which reflects only density fluctuations[28] and another, $\mathscr{F}$, which reflects only concentration fluctuations.[29] The quantity R_{LP} represents the variation in density fluctuations (as a function of x) that would be present if every oxide unit had the same mass. The quantity $\mathscr{F}$ is, in addition, corrected[29] for the variation in optical properties with concentration. Thus $\mathscr{F}$ provides a better indication of the fluctuations experienced by phonons rather than photons. The quantities R_{LP} and $\mathscr{F}$ are plotted versus concentration in Fig. 2. The amplitude of the density fluctuations is roughly the size of the SiO_2 unit, i.e., several Å, while the concentration fluctuations lie in the 15–100-Å range.[28]

We have an empirical test of the separation of the light scattering data into the terms R_{LP} and $\mathscr{F}$. Theoretically one would expect, in thermal equilibrium, the statistical dependence $R_{LP} \propto T$ (and proportional to the isothermal compressibility). If the sample is held a long time at a temperature T_f and then "quenched," as for our samples, then $R_{LP} \propto T_f$. Using the data of Fig. 2(c) for R_{LP} and the data of Fig. 1(a) for T_f, we find the ratio R_{LP}/T_f is indeed constant ($=0.0145\ K^{-1}$) to 6%. This agreement between R_{LP} and T_f provides confidence that the separation into "density" and "concentration" fluctuations is correct.

B. Specific heat

The specific-heat data were obtained using a signal-averaging technique.[30] The samples were roughly cubic in shape and ≈ 1 cm in size. Each sample was rigidly clamped to, yet thermally isolated from, the refrigerator by thin sapphire plates.[31] At temperatures T below ≈ 1 K, a significant time-dependent specific heat was observed for all finite concentrations of K_2O or Na_2O. A time-dependent specific heat at $T \lesssim 1$ K is characteristic of glassy solids[5] and is also observed in some disordered crystals[32] which exhibit "glassy" behavior at low temperatures. The time dependence manifested itself through the nonexponential temperature response following application of the heat pulse, see Fig. 3. At the lowest temperatures the total specific heat of a sample having $x \neq 0$ is somewhat uncertain because of this long-internal equilibration time.

The total specific heat C of our samples is presented in Figs. 4 and 5, where C has been divided by T^3 to emphasize departure from Debye behavior. The Debye specific heats,

$$C_D/T^3 = 4.08\times 10^{10}[(1/v_L)^3 + 2(1/v_T)^3]\ \ (\mathrm{J/m^3K^4})\ , \quad (9)$$

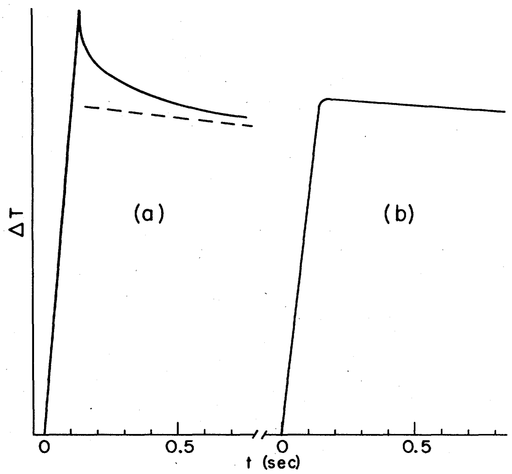

FIG. 3. Temperature versus time during a heat-capacity measurement on (a) $(SiO_2)_{0.95}(K_2O)_{0.05}$ and (b) $(B_2O_3)_{0.95}(K_2O)_{0.05}$ demonstrating the effect of the long internal equilibration time of the silicate sample. $T=0.36$ K; $\Delta T/T \approx 0.1$. The dashed line in (a) represents the (nearly) exponential time dependence extrapolated from later times for the silicate sample, and is used to compute the total specific heat of the sample. Deviation of the data, the solid line, from the dashed line represents a deviation from an exponential response. Although not evident in this figure, the curve in (b) is slightly nonexponential, a behavior not observed in our measurements on single-crystal LiF.

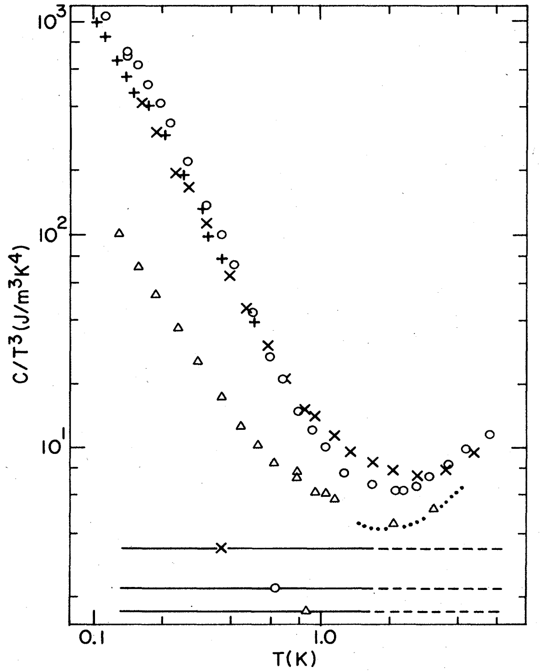

FIG. 4. Total specific heat of silicate glasses divided by T^3, the cube of the temperature. △, $x=0$; $x(\mathrm{K})=0.05$; ×, $x(\mathrm{K})=0.20$; +, $x(\mathrm{K})=0.20$ measured with a different technique (Ref. 34); dotted line, $x=0$ (Vitreosil) from Ref. 35. The horizontal lines indicate the Debye phonon contributions, see text.

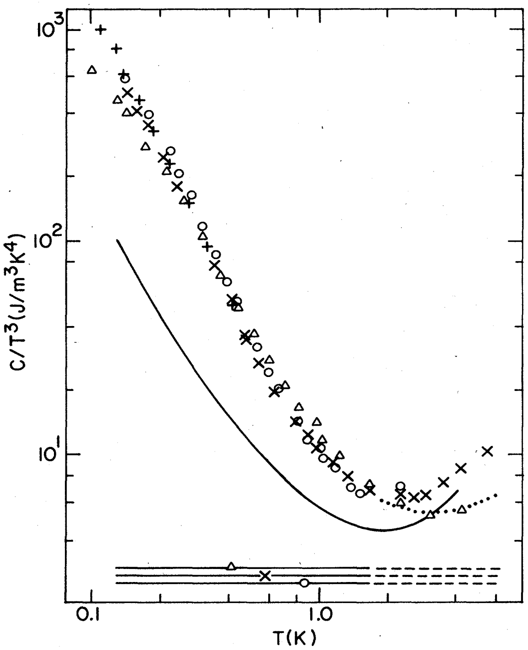

FIG. 5. Total specific heat of silicate glasses divided by T^3. Solid line, $x=0$, from Fig. 4; ○, $x(\mathrm{K})=0.08$; ×, $x(\mathrm{K})=0.10$; +, $x(\mathrm{K})=0.10$ measured by a different technique (Ref. 34); △, $x(\mathrm{Na})=0.27$; dotted line, $x(\mathrm{Na})=0.25$ from Ref. 25 (which agrees with Ref. 36 but not with Ref. 37). The horizontal lines indicate the Debye phonon contributions, see text.

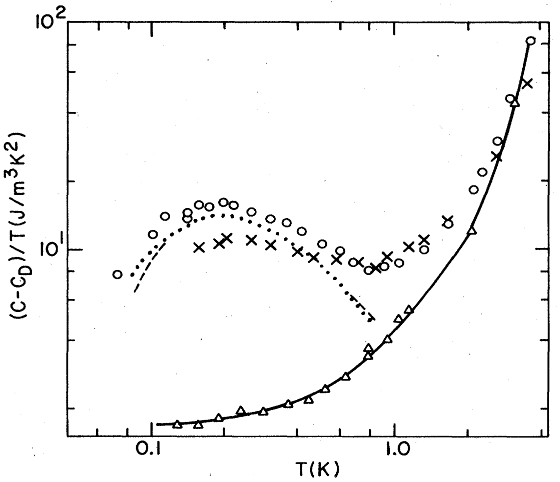

FIG. 6. Total specific heat C minus the Debye phonon contribution C_D, divided by T. △ and solid line, $x=0$; ○, $x(\mathrm{K})=0.05$; ×, $x(\mathrm{K})=0.20$; dotted line, $x(\mathrm{K})=0.05$ minus $x=0$; dashed line, calculated from the Einstein model with an Einstein temperature of 0.47 K.

have been computed using the velocity data of Fig. 1 and are included as the horizontal lines at the bottom of Figs. 4 and 5. These lines are continuous only at $T<2$ K, indicating the range in energy for which it has been demonstrated[33] that no velocity dispersion occurs for pure silica (see Sec. III B).

Also included in Figs. 4 and 5 (represented by +) are data obtained on the $x(\mathrm{K})=0.10$ and 0.20 samples using a different technique.[34] These data were obtained a year prior to the present data. We aborted this earlier measurement as we were surprised that the specific heat was larger than that of SiO_2 by a factor of 10 near 0.1 K, and that there occurred a long internal equilibration time. We remeasured the OH content as a precaution, since potassium silicate glasses are hygroscopic, but the OH content remained at ≈ 20 ppm. The agreement between the earlier specific-heat data and our present results is reassuring, as two different measurement techniques were used.

The dotted lines in Figs. 4 and 5 indicate that our results are in good agreement with earlier data obtained at higher temperatures.[25,35–37] The only comparable low-temperature measurements[38] are for $x(\mathrm{Na})=0.25$. The data reported for this sample are similar in temperature dependence to the present sample having $x(\mathrm{Na})=0.27$, but lie $\approx 20\%$ lower in magnitude.

The excess specific heat $C-C_D$, i.e., that not contributed by phonons, is roughly linear in T at $T \lesssim 1$ K. This excess specific heat has been plotted in Figs. 6 and 7 as $(C-C_D)/T$ to remove most of this temperature dependence. It will be noted that, for $x(\mathrm{K}) \neq 0$, the excess specific heat decreases with increasing x and also that a broad "hump" or maximum appears near 0.2 K. This hump is similar to that arising from the presence of a small quantity of iron.[38] However, in the present measurements all samples used the same starting material and were subjected to the same treatment. Hence iron impuri-

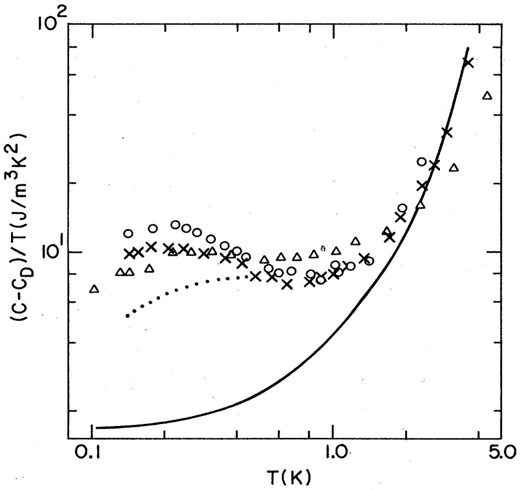

FIG. 7. Total specific heat C minus the Debye phonon contribution C_D, divided by T. Solid line, $x=0$ from Fig. 6; ○, $x(\mathrm{K})=0.08$; ×, $x(\mathrm{K})=0.10$; △, $x(\mathrm{Na})=0.27$; dotted line, $x(\mathrm{K})=0.10$, "prompt response" (see text).

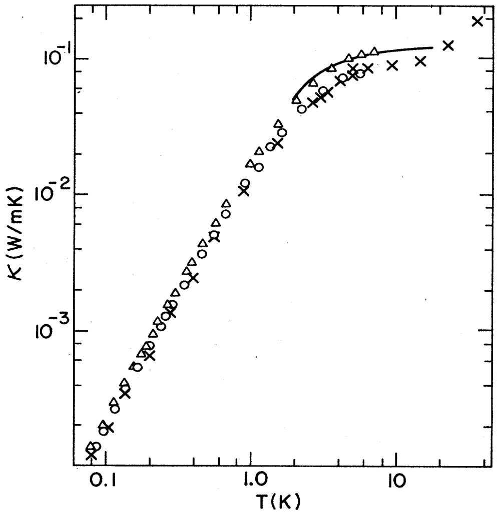

FIG. 8. Thermal conductivity of silicate glasses. △, $x=0$; ○, $x(\mathrm{K})=0.05$; ×, $x(\mathrm{K})=0.20$ (Ref. 39); solid line, $x=0$ (low-OH Infrasil, Ref. 40).

ty cannot explain the variation of the magnitude of the hump with concentration x. For $x(\mathrm{Na})=0.27$, a maximum does not appear in $(C-C_D)/T$. Rather, a "shoulder" appears near 0.2 K, a feature which is also evident in the earlier data[38] on $x(\mathrm{Na})=0.25$.

In Fig. 6 it may be noted that, at $T\gtrsim 3$ K, the presence of K_2O does not increase the excess specific heat above that observed for pure SiO_2 (the solid line). If the data for $x=0$ are subtracted from that for $x(\mathrm{K})=0.05$, one obtains what might be considered the additional specific heat contributed to the $x(\mathrm{K})=0.05$ sample by the K_2O. This "K_2O" contribution is indicated by the dotted line in Fig. 6. We note that the K_2O contribution is rather well represented by an ensemble of $\approx 10^{17}$ /cm^3 Einstein oscillators having an Einstein temperature of 0.47 K. (The Einstein specific heat is represented by the dashed line in Fig. 6.) The suggestion of an Einstein contribution is purely speculative, but is mentioned here to emphasize that the specific-heat data are open to different interpretations.

An estimate of the number N of low-energy excitations contributing to the excess specific heat may be obtained from the integral $Nk\ln(m)\approx\int_0^{1\,\mathrm{K}}(C-C_D)dT/T$, where m is expected to be a small number. This computation indicates that the ratio of N to the number of K or Na ions present is 10^{-4}–10^{-3} for the energy range below 1 K.

In Fig. 7 the dotted line represents, for $x(\mathrm{K})=0.10$, roughly the "prompt-response" specific heat computed a short time after the heat pulse in Fig. 3(a). It indicates the fraction of excitations which are in good thermal contact with the phonons. The prompt response was computed on a time scale of ≈ 1 sec, while the total specific heat was determined on a time scale of ≈ 50 sec.

Finally, it may be seen in Fig. 7 that above ≈ 2.5 K the presence of Na_2O decreases the excess specific heat below that found in pure SiO_2. This is in agreement with the more extensive data reported in Refs. 24 and 25 for the $(SiO_2)_{1-x}(Na_2O)_x$ system.

C. Thermal conductivity

The thermal conductivities κ were measured using either a two-heater arrangement or the more conventional two-thermometer method. The sample dimensions were approximately $2.0\times0.2\times0.5$ cm^3. The data reproduced to within 5% when samples were remounted and remeasured months apart by different experimentalists using different techniques. The results, displayed in Figs. 8 and

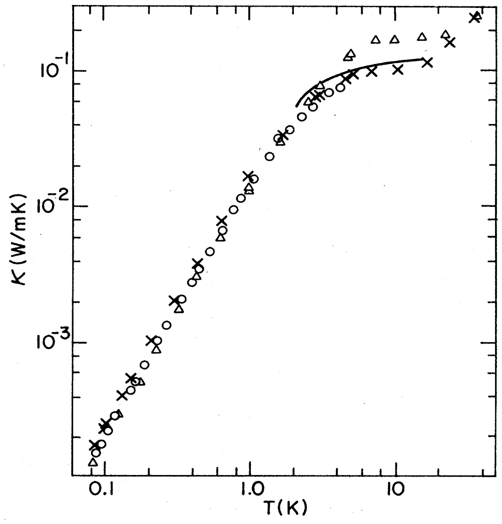

FIG. 9. Thermal conductivity of silicate glasses. ○, $x(\mathrm{K})=0.08$; × $x(\mathrm{K})=0.10$ (Ref. 39); △, $x(\mathrm{Na})=0.27$ (Ref. 39); solid curve as in Fig. 8 for reference. Data of Ref. 38 for $x(\mathrm{Na})=0.25$ at $T<2$ K cannot be distinguished from that of $x(\mathrm{Na})=0.27$.

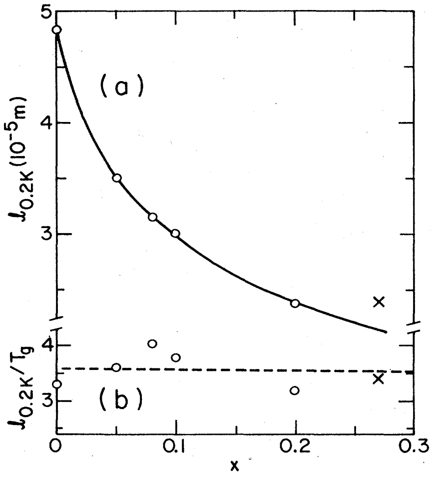

FIG. 10. (a) Phonon mean free path $l_{0.2\text{ K}}$, computed at 0.2 K, versus K_2O (○) or Na_2O (×) concentration x. (b) Plot of $l_{0.2\text{ K}}/T_g$ (in units of 10^{-8} m/K) versus x demonstrating the dependence $l_{0.2\text{ K}} \propto 1/T_g$.

9, appear to be in good agreement with earlier measurements.[38–40]

The thermal conductivity at $T \lesssim 2$ K is roughly independent of K_2O or Na_2O content. In the "plateau" range above 2 K, the K_2O appears to reduce κ slightly, while Na_2O increases κ as observed in the more extensive measurements reported in Ref. 24.

Since it is known that phonons carry the low-temperature heat flux in glasses,[41] the thermal conductivity may be approximated as

$$\kappa = 1.36\times 10^{10} l T^3[(1/v_L)^2+2(1/v_T)^2] \ \text{(W/mK)}\,, \tag{10}$$

where l is the phonon mean free path. Using values of κ at $T=0.2$ K, where the low-temperature behavior of κ is well established, the mean free path $l(x)_{0.2\text{ K}}$ may be computed using the velocity data of Fig. 1. The result is shown in Fig. 10(a). The concentration dependence of $l_{0.2\text{ K}}$ is similar to that of the glass-transition temperature T_g of Fig. 1(a). Indeed, a plot of $l_{0.2\text{ K}}/T_g$ in Fig. 10(b) is independent of concentration x to within the uncertainties in our measurements. It should be noted that the value of $l_{0.2\text{ K}}$ obtained by different authors for vitreous silica varies somewhat (assuming the phonon velocities are the same for all samples). This variation may reflect the presence of impurities[42] or different thermal histories.[43] The use of the data of Ref. 44, for example, would give $l_{0.2\text{ K}}/T_g \approx 4.3\times 10^{-8}$ m/K.

D. Thermal expansion

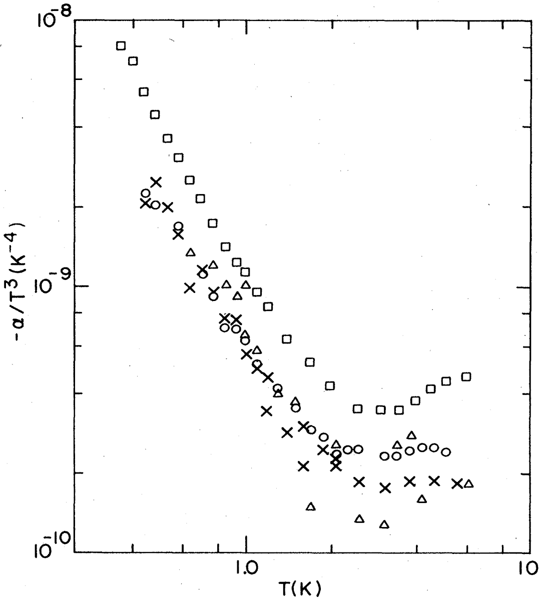

FIG. 11. Thermal-expansion coefficient α divided by T^3. □, $x=0$ (Ref. 7); ×, x(K)=0.05; △ x(K)=0.08; ○, x(K)=0.10. Note that all values are negative.

The linear thermal-expansion coefficients α of four samples were measured using a dilatometer discussed previously.[7,45] The samples were rods typically 0.2–0.3 cm in width and 2–3 cm in length. The results are plotted in Fig. 11 as α/T^3 to emphasize departure from the T^3 dependence expected for phonons. The data for x(K)=0.05, 0.08, and 0.10 clearly lie below that of pure silica, but we cannot say if there is any significant difference between the three samples with $x(\text{K})\neq 0$ because of the large scatter in the data. Part of the scatter is attributed to the short length of the samples having $x(\text{K})\neq 0$.

It is of greater interest to obtain the average thermal expansion per excitation. A related quantity in common use is the Grüneisen parameter Γ defined as $\Gamma = 3\alpha B/C$, where B is the bulk modulus obtained from the velocities of Fig. 1. Since α and C are only weakly dependent on x for $0.05 \leq x \leq 0.10$, we have averaged C and α for the three samples x(K)=0.05, 0.08, and 0.10 to obtain the Grüneisen parameter represented in Fig. 12 by the solid

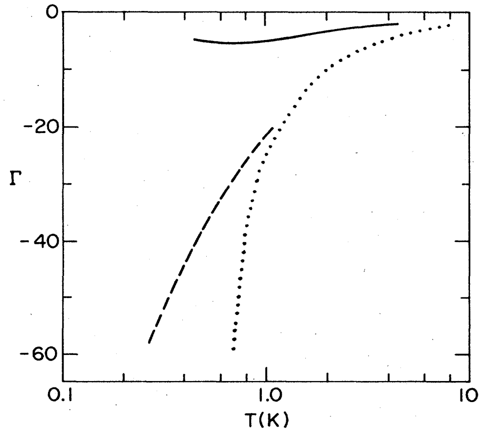

FIG. 12. Grüneisen parameter Γ of silicate glasses computed from the total measured specific heat and total measured thermal-expansion coefficient. Dashed line, $x=0$; solid curve, averaged for x(K)=0.05, 0.08, and 0.10; dotted line, "direct" measurement from Ref. 46.

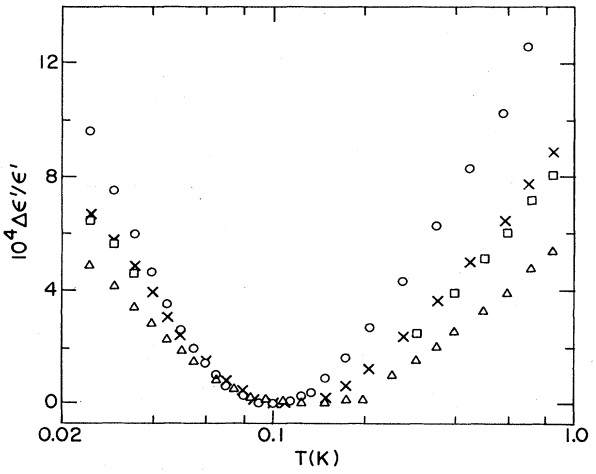

FIG. 13. Variation in dielectric constant ϵ' with concentration and temperature at 10^4 Hz, normalized to the minimum near 0.1 K. △, $x(\mathrm{K})=0.05$; □, $x(\mathrm{K})=0.08$ (some data omitted); ×, $x(\mathrm{K})=0.10$; ○, $x(\mathrm{K})=0.20$.

curve. This result for $x(\mathrm{K})\neq 0$ may be contrasted with Γ of pure silica indicated by the dashed line.[7] The dotted line represents Γ deduced[46] from a measurement of the temperature change caused by the uniaxial extension of a sample having $x=0$. The reduction in the magnitude of α or Γ with addition of K_2O is qualitatively similar to the reduction observed[25] at $T>2$ K with addition of Na_2O.

E. Dielectric dispersion

A three-terminal capacitance bridge[47] was used to measure the real (ϵ') and imaginary (ϵ'') components of the dielectric constant ϵ of samples having an area of ≈ 2 cm^2 and a thickness of ≈ 0.03 cm. At $T\gtrsim 10$ K the behavior of ϵ for $x(\mathrm{K})=0.10$ and 0.20 was similar to that observed previously in Ref. 48 (see Ref. 49 for Na_2O in silica).

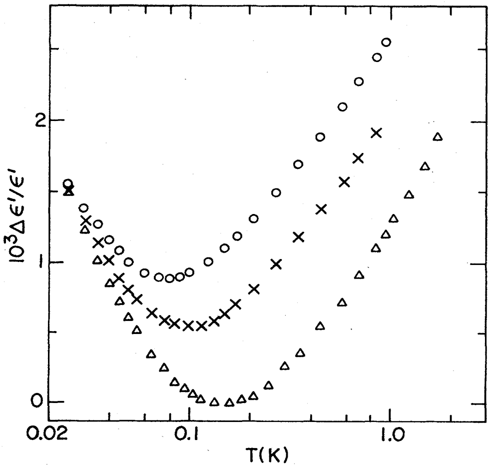

FIG. 14. Variation in dielectric constant for $x(\mathrm{K})=0.20$ with frequency ν and temperature T, normalized near 0.025 K. ○, $\nu=5$ kHz, ×, $\nu=10$ kHz; △, $\nu=30$ kHz. The minimum varies as $\nu^{1/3}$ as for other glasses. The ϵ' of pure vitreous silica would be a horizontal line.

We are primarily interested in the behavior of ϵ below 1 K. Figure 13 shows the dependence of ϵ' on concentration and temperature at fixed frequency, while Fig. 14 shows the temperature and frequency dependence for fixed concentration. The minimum in ϵ' observed near 0.1 K is typical of glassy solids. We note that the temperature dependence of ϵ', both above and below the minimum, qualitatively increases with increasing concentration of K_2O.

III. DISCUSSION

The discussion is divided into two subsections. Section III A explores the results of temperatures $\lesssim 1$ K and the theoretical models developed to account for the low-temperature behavior. Section III B examines behavior observed at $T\gtrsim 1$ K.

A. The temperature regime below 1 K

We examine the influence of glass-transition temperature, atomic bonding, density or concentration fluctuations, and alkali concentration on the low-temperature behavior of the silicate glasses.

1. Glass-transition temperature; free-volume model

It has been suggested that there may be a correlation between the properties of glasses below ≈ 1 K and the glass-transition temperature T_g. An empirical relationship has been observed[50] between T_g and the phonon mean free path l for a variety of amorphous solids. This relationship may be expressed as

$$l_{0.2\,\mathrm{K}} \approx 4\times 10^{-8} T_g \ \ (\mathrm{m})\ , \tag{11}$$

to within $\approx 30\%$ for a factor of ≈ 8 change in T_g. Here l is measured at 0.2 K, a temperature in the T^2 regime well below 1 K, yet at a sufficiently high temperature that measurements of κ should be reliable. As may be seen in Fig. 10, we obtain $l_{0.2\,\mathrm{K}}=3.6\times 10^{-8}T_g$ (m), to within $\pm 10\%$ for a factor of 2 change in T_g. This result provides additional support for the empirical relationship presented in Eq. (11).

Neutron irradiation increases the thermal conductivity of vitreous silica[51] which in turn, by Eq. (11), implies an increase in T_g. It has been suggested[44] that a fictive temperature T_f may be substituted for T_g for irradiated quartz, and that T_f can be deduced from measurements of the intensity I of small-angle x-ray scattering ($I\propto T_f$ as in Sec. II A). There are problems with this viewpoint. A fictive temperature refers to the temperature at which the glass sample would be in thermal equilibrium in its irradiated state, but there is no equilibrium state of silica having a density as large as that of some neutron irradiated samples.[51,52] The assigned T_f may also require an extrapolation by a factor of 2 beyond the temperature range of the x-ray studies[53] of I versus T_f. Finally, the change in thermal conductivity and other properties saturate as a function of neutron fluence, while the scattering intensity I continues to increase beyond this range. Nevertheless, if we use this approach to obtain an equivalent T_g for *neutron fluences at or below saturation,*[44,51] we obtain $l_{0.2}/T_g \approx 3.5\times10^{-8}$ (m/K) to within $\approx$20% for a factor of 2 change in T_g. Thus neutron irradiated silica appears to fit the pattern observed for the alloy glasses of Fig. 10, and for glasses in general as expressed by Eq. (11).

A phonon mean free path can also be obtained from ultrasonic measurements made on a series of silicate and fluoride glasses.[54] The results are expressed in terms of parameters used in the tunneling-state model, but they may be converted to $l_{0.2\,\mathrm{K}}$ using expressions for ultrasonic attenuation found in Ref. 55. We find that $l_{0.2\,\mathrm{K}}/T_g$ is constant to within 20% for a change in T_g by a factor of 3. The numerical constant in Eq. (11) is obtained provided the relation $\hbar\omega = 2.4kT$ is used to express the dominant phonon frequency ω appropriate to the temperature T.

In summary, there is extensive evidence that the phonon mean free path at temperatures below 1 K is proportional to the glass-transition temperature, and that the constant of proportionality is essentially the same for a number of dielectric glasses.[56]

It was also suggested[50] that the excess specific heat, $C-C_D$, may vary inversely as T_g. A quantitative comparison between $C-C_D$ and T_g is awkward because $C-C_D$ has a different temperature dependence for different glasses as may be seen, for example, in Figs. 6 and 7. One technique[57] has been to fit the data below $\approx$0.4 K with the expression $C-C_D = aT^n$ with $n\approx 1$. The data of Ref. 57 for a series of $Ca(NO_3)_2$-KNO_3 glasses containing H_2O are shown in Fig. 15(a). Here $(C-C_D)T_g/T^{1.16}$ is constant to $\approx$10% for a narrow 30% range in T_g. In calculating $C-C_D$, the authors used one value of C_D for all samples. If the likely variation of C_D with T_g was taken into account, the data of Fig. 15(a) would more nearly lie on a horizontal line.

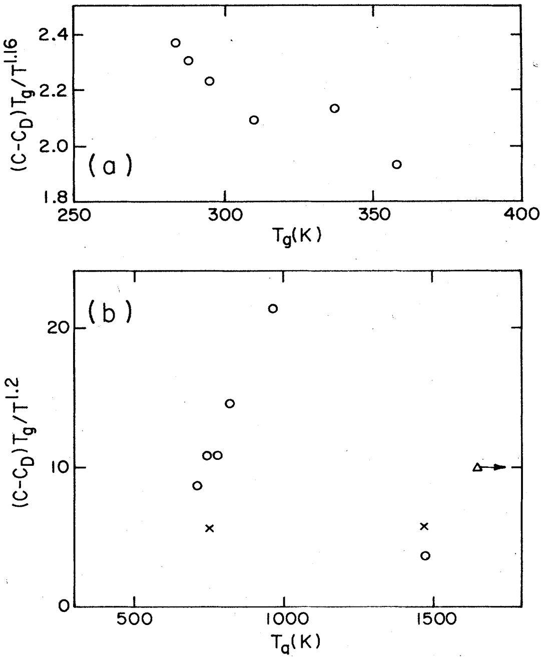

FIG. 15. Excess specific heat, $C-C_D$, of a series of $[Ca(NO_3)_2$-$KNO_3]$ glasses containing H_2O (Ref. 57), multiplied by $T_g/T^{1.16}$, versus glass-transition temperature T_g. Units of 10^4 erg/g K$^{1.16}$. (b) Excess specific heat of silica glasses, multiplied by $T_g/T^{1.2}$, versus T_g. ○, present data; × and △, data of Ref. 57 with △ at $T_g \approx 3600$ K (see note after Ref. 57). Units of 10^4 erg/cm^3 K$^{1.2}$ = 10^3 J/m^3 K$^{1.2}$.

The same authors[57] suggested a similar relationship between $C-C_D$ and T_g for silicate glasses. Their data are shown by the × and △ symbols in Fig. 15(b). However, when our data (the circles) are added, it is seen that $(C-C_D)T_g/T^{1.2}$ varies by a factor of 5 for a factor of 2 change in T_g.

The arbitrary treatment of the data shown in Fig. 15 is not important. An alternative analysis in which $T_g\Delta S$ is plotted versus T_g does not change the qualitative results. Here $T_g\Delta S = T_g\int_0^{1\,\mathrm{K}}(C-C_D)dT/T$, which is more independent of the detailed temperature dependence of $C-C_D$. The qualitative result is that the excess specific heat does not scale with $1/T_g$ for a wide variety of dielectric glasses.

It may be significant that the correlation between low-temperature properties and T_g occurs for thermal conductivity and ultrasonic dispersion, properties related to those TLS which couple most strongly to phonons. Those TLS have the most rapid equilibration times, and are represented by the density $\bar{P}$ discussed in Sec. I.

A free-volume model[13] developed to explain phenomena near the glass-transition temperature, may explain the T_g dependence of the low-temperature properties.[11] The argument gives

$$n \approx N/T_g\ , \tag{12}$$

where N is the total number of TLS per unit volume. The total N is proportional to the free volume in the glass, and is expected to be essentially independent of material and cooling rate.[11] Indeed, a conventional approximation for the free-volume fraction is found to be constant for a number of polymers,[58] but less so for a series of glasses.[22] With N a constant, the free-volume model predicts $n \propto 1/T_g$.

We have noted above that, in general, n is not found to vary as $1/T_g$. On the other hand, $l_{0.2\,\mathrm{K}}$ has been seen to vary as T_g. By using Eqs. (5) and (10),

$$l_{0.2\,\mathrm{K}} \propto \rho v^3/\gamma^2\bar{P} \propto T_g\ . \tag{13}$$

As may be seen in Fig. 1, ρ and v vary with T_g, and γ^2 has also been reported to have a T_g dependence.[54] However, the quantity $\rho v^3/\gamma^2$ averaged over the three phonon modes is constant[54] to ±15% for a factor of 3 change in T_g. Hence, to this accuracy,

$$\bar{P} \propto 1/T_g \tag{14}$$

is obtained from the thermal-conductivity data. In addition, $\bar{P}$ may be measured explicitly by ultrasonic techniques,[54] and the results are consistent with $\bar{P}\propto 1/T_g$.

In summary, it appears that the density of TLS coupled strongly to phonons, $\bar{P}$, may vary as $1/T_g$, whereas the total TLS density does not. This clearly is not the implication of the free-volume model.

For completeness, we mention one other prediction of the free-volume model. Since N is proportional to the free volume, and the free volume is roughly proportional to temperature T near the glass transition, the free volume and N can be modified by quenching a sample from temperatures T_A near, but less than, T_g. This has been done for glassy metals,[59] both normal and superconducting. Although the samples could not be held at T_A long enough to establish equilibrium (glassy metals often crystallize first), it was observed that $\kappa_{0.2\,\mathrm{K}} \propto T_A^{-1}$. This result is consistent with $\bar{P} \propto T_A$, or $N \propto T_A$, as predicted by the model. But again, it is the quantity $\bar{P}$ rather than n which appears to be involved.

2. *Covalency*

We detect for $T \lesssim 1$ K no significance correlation between the change in average bonding, shown in Figs. 2(a) or 2(b), and the specific heat, the thermal conductivity (or $l_{0.2\,\mathrm{K}}$), or the thermal expansion (or Γ). This result is contrary to the speculation[60] that covalency is essential to the existence of TLS. The same conclusion as to the importance of covalency has been derived from measurements on glassy metals.[61]

3. *Mass and concentration fluctuations; geometric models*

An obvious correlation exists between the density fluctuations, represented by R_{LP} in Fig. 2, and the phonon mean free path l. We have shown that $l_{0.2\,\mathrm{K}} \propto T_g$ (Sec. III A 1) and that $R_{\mathrm{LP}} \propto T_g$ (Sec. II A), therefore $l_{0.2\,\mathrm{K}} \propto R_{\mathrm{LP}}$. This relationship is the opposite of what would be expected if phonons were being scattered by the density fluctuations. Rather, it is possible that the correlation simply reflects the variation of the TLS density $\bar{P}$ with the concentration x. In brief, the important correlation may be $\bar{P} \propto 1/R_{\mathrm{LP}}$, or $\bar{P} \propto 1/T_g$ as discussed already in Sec. II A *1*.

We detect no other correlations between the mass or concentration fluctuations of Fig. 2 and the properties of silicate glasses at temperature below 1 K. In particular, the concentration fluctuations of size 10–100 Å do not scatter phonons having a similar wavelength. (The dominant phonon wavelength near 0.2 K is ≈ 1000 Å.) Therefore, we find no support for models of thermal conductivity in glasses which attribute the phonon scattering to static geometric or structural fluctuations.[16] Nor do we find support for "cellular" models of the specific heat.[15]

4. *Alkali concentration; tunneling-states model*

Adding K_2O, Na_2O, or H_2O to vitreous SiO_2 increases the specific heat[62] (Figs. 4 and 5), increases the dielectric response[63] (Fig. 13), decreases the expansion coefficient[7] (Fig. 11), and leaves the thermal conductivity essentially unchanged[62] (Figs. 8 and 9). It is therefore reasonable to include $(SiO_2)_{1-x}(H_2O)_x$ in a discussion of alkali-silicate glasses.

In Sec. II B it was demonstrated that the specific heat of $(SiO_2)_{1-x}(K_2O)_x$ could be represented by the addition of a set of Einstein oscillators, each having the same frequency, to the intrinsic TLS of pure silica. This result is probably accidental, as the same fit cannot be made for $(SiO_2)_{1-x}(Na_2O)_x$ of Fig. 7 or for OH in SiO_2 (Ref. 62). In addition, the dielectric response shown in Figs. 13 and 14 arises from the addition of K_2O, and this response has frequency and temperature dependencies indicative of TLS. Therefore we will assume that essentially all of the localized excitations found in samples containing alkali oxides may be treated as TLS.

For low concentrations (≈ 1000 ppm) of H_2O it appears[7,63,64] that the OH introduces a new, additional set of TLS to the "intrinsic" set already present in pure SiO_2. The question arises whether the present rather large concentrations of K_2O or Na_2O also introduce a new set of TLS.

The tunneling-states model[9,10] is sufficiently pliable that it can be fitted to the present data by assuming a more complicated range of phenomenological parameters than has been customarily used for glasses. The tunneling-states model would require the conventional roughly flat or constant density of states $n(E)$ as for pure silica[51] but with an additional peak or maximum near $E \approx 0.5$ K. Long equilibration times τ would be ascribed to many of the TLS within this maximum to explain the observed time-dependent specific-heat data.[65] Also, the new excitations in the peak would have positive Grüneisen parameters Γ (as for OH, Ref. 7), whereas Γ for the intrinsic TLS is negative. Such a mathematical exercise has been carried out for the crystalline fast-ion conductor ZrO_2:Y_2O_3, which displays glassy behavior,[32] and the tunneling-states model could similarly be fitted to our data for silica samples. However, this tedious exercise would provide no additional physical insight. Thus our results neither support nor deprecate the tunneling-states model, nor do they confirm[66] the presence of a new, additional set of TLS.

As discussed in Sec. I, a TLS ensemble having known E and τ spectra is not sufficient to account for the thermal expansion of disordered solids. That is, Eq. (7) must be multiplied by a ratio of the form $\langle (n_+ - n_-)/(n_+ + n_-)\rangle$, where $n_+(n_-)$ represents the density of TLS for which E increases (decreases) with applied stress [the TLS expand (contract) the lattice when placed in the excited state], and where $\langle\ \rangle$ represents an average over all energy splittings E. The large change in $\langle (n_+ - n_-)/(n_+ + n_-)\rangle$ with addition of ≈ 8 mol % K_2O is reflected in the corresponding change in the Grüneisen parameters of Fig. 12. The ratio $(n_+ - n_-)/(n_+ + n_+)$ is not provided by any theory. It could be introduced into the phenomenological tunneling-states model at the expense of an additional set of adjustable parameters.

It has been asserted that, if electric dipole-dipole interactions are an important influence on the asymmetry of the two potential-energy wells giving rise to the TLS, then Γ should be reduced to a value near unity with increasing alkali concentration.[67] Indeed, Fig. 12 does show a large decrease in Γ as the concentration increases from $x(\mathrm{K}) = 0$ to ≈ 0.08. Unfortunately, the lack of resolution in our expansion measurements masks any change that may occur in Γ as concentration varies over the range $x(\mathrm{K}) = 0.05$ to 0.10.

The variation $\Delta\epsilon'/\epsilon'$ in the dielectric response increases with increasing K_2O concentration as may be seen in Fig. 13. Thus, by Eq. (6), the product $\bar{P}p_0^2$ must increase by a factor of 2 between $x(\text{K})=0.05$ and $x(\text{K})=0.20$. If $\bar{P}\propto 1/T_g$, the increase in $\bar{P}$ would be a factor of ≈ 1.3. Therefore the effective electric dipole moment p_0 increases by a factor of only $\approx\sqrt{1.5}$ or 24% for a factor of 4 increase in K_2O content. It is not certain that the subset of TLS having a finite p_0 is the same subset $\bar{P}$ that appears in Eq. (5) for the thermal conductivity. If it is the same subset, the density $\bar{P}$ increases smoothly with x in accordance with $\bar{P}\propto 1/T_g$, whereas p_0 increases a large amount between $x(\text{K})=0$ and 0.05, then remains rather constant. Briefly, the *microscopic* description of a TLS must change considerably at concentrations $x<0.05$. This is not a surprising result as 5% is already a large concentration. It would be interesting to study glasses having much smaller K_2O or Na_2O concentrations, but such samples are difficult to produce. It is likely that the low-temperature behavior would be similar to that observed for low concentrations of OH in vitreous silica.

B. The temperature regime above 1 K

We turn next to the temperature regime $T>1$ K. As stated above, the excess specific heat $C-C_D$ often has a temperature dependence of T^n at $T<1$ K with n slightly greater than unity. If this dependence is extrapolated above 1 K, it may be seen from Figs. 6 and 7 that the extrapolation cannot account for all of $(C-C_D)/T$. It is natural to inquire if phonon dispersion can account for the rise in C/T^3 above 1 K. That is, the dashed lines in Figs. 4 and 5 are not true representations of the phonon specific heat. It is known[33] that no phonon dispersion occurs in pure vitreous silica at frequencies up to 4.5×10^{11} Hz. For the purpose of illustration, assume that the average phonon velocity is a constant, v_U, at frequencies up to 5×10^{11} Hz, then drops abruptly to the value v_H for higher frequencies. The ratio of v_H/v_U required to account for $(C-C_D)/T$ near 3—4 K in Fig. 6 is $v_H/v_U=0.35$, a completely unreasonable result. A less abrupt and more realistic transition between v_U and v_H would dictate an even smaller ratio of v_H/v_U. Thus it is concluded that most of the increase in $(C-C_D)/T$ or C/T^3 above ≈ 2 K for pure vitreous silica does *not* arise from an acoustic-phonon contribution, but that additional excitations must be present. Whether the localized excitations having energies $E\gtrsim 1$ K are entirely TLS or only partly TLS is open to speculation.[68–70]

A well-resolved plateau appears near 10 K in the thermal conductivities plotted in Figs. 8 and 9. Several authors have suggested that the plateau may arise from a strong Rayleigh scattering of thermal phonons by microscopic fluctuations in the glass.[1,16] For a discussion of this possibility, we will refer to the two samples $x(\text{K})=0.20$ and $x(\text{Na})=0.27$, since both have roughly the same phonon velocity and the same conductivity[71] at $T<1$ K. The thermal conductivity in the plateau is larger for $x(\text{Na})=0.27$ by a factor of ≈ 2. Yet the density fluctuations are essentially the same for the two samples [R_{LP} of Fig. 2(c)], and the concentration fluctuations are roughly a factor of 10 larger for $x(\text{Na})=0.27$ [Fig. 2(d)]. This variation is in opposition to what would be expected if Rayleigh scattering were responsible for the plateau.

It has been stated in the literature[2,72] that there appears to be a relationship between the maximum in C/T^3 (which occurs near 10 K for vitreous silica) and the plateau in thermal conductivity. Further support for an inverse correlation is found in the present data. Using again the two samples[71] $x(\text{K})=0.20$ and $x(\text{Na})=0.27$, we repeat that the conductivity in the plateau is larger for $x(\text{Na})=0.27$. Indeed, the magnitude of C/T^3 (Figs. 5 and 7) is smaller for $x(\text{Na})=0.27$. This observation is explained phenomenologically if the additional localized modes responsible for the excess specific heat, the maximum in C/T^3, also scatter phonons thus creating the plateau in the thermal conductivity.

IV. CONCLUSIONS

Using a carefully prepared series of $(SiO_2)_{1-x}(K_2O)_x$ and $(SiO_2)_{1-x}(Na_2O)_x$ glasses, we have made measurements of light scattering and of the low-temperature dielectric constant, thermal conductivity, specific heat, and thermal expansion. From our results, combined with literature data, we find the following.

(i) An excellent correlation exists between thermal conductivity (at temperatures $T<1$ K) and the glass-transition temperature T_g, but not between specific heat and T_g. It may be that only the partial density $\bar{P}$ of localized excitations or TLS scales as $1/T_g$, rather than the total density n as predicted by the free-volume model. The TLS represented in $\bar{P}$ experience the strongest coupling with phonons.

(ii) No correlation is found between any measured property and either the density or the concentration fluctuations derived from light scattering data. This suggests that the thermal conductivity (phonon scattering) is little influenced by the microscopic variations of a glass.

(iii) Additional support is found for a correlation between a maximum in C/T^3 near 10 K and a plateau in the thermal conductivity near the same temperature. Evidence available at present suggests that both arise through localized, nonacoustic-phonon excitations of unknown description.

(iv) The tunneling-states model could be fitted to our data, but would require a more complicated spectrum of adjustable parameters than has customarily been used.

(v) The addition of 5 mol % K_2O to vitreous SiO_2 increases the density of localized excitations by a factor of ≈ 10 at temperatures below ≈ 0.4 K. These excitations appear to be additional TLS. It would be interesting to observe the density of TLS (and other properties) develop as the K_2O concentration is increased by small increments from zero. However, suitable samples are difficult to produce. We speculate that the behavior would be similar to that found in vitreous silica containing small concentrations of OH.

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