PHYSICAL REVIEW B VOLUME 31, NUMBER 2 15 JANUARY 1985

Low-temperature behavior of vitreous silica containing neon solute

G. X. Mack and A. C. Anderson
Department of Physics, University of Illinois at Urbana-Champaign, 1110 West Green Street, Urbana, Illinois 61801
(Received 20 July 1984)

The low-temperature specific heat, thermal-expansion coefficient, and thermal conductivity have been measured in vitreous silica with and without Ne solute. Changes introduced by the Ne may be attributed to an added population of localized excitations of unknown microscopic description. These changes are similar to those introduced by the addition of K_2O, Na_2O, or H_2O to vitreous silica.

I. INTRODUCTION

Amorphous solids harbor a broad energy spectrum of localized, low-energy excitations[1] which dominate most properties at temperatures $T \lesssim 1$ K. The specific heat C, for example, varies as

$$C = AT^n \tag{1}$$

with $n \approx 1$ whereas, in a dielectric crystal, $C \propto T^3$. An interesting discovery was the reversible increase in the coefficient A of Eq. (1) with the introduction of He or Ne solute into vitreous silica.[2] In the present paper, we investigate further the influence of Ne on the low-temperature behavior of vitreous silica through measurements of specific heat, thermal expansion, thermal conductivity, and ultrasonic velocity. We find that addition of Ne to SiO_2 has a similar effect as the addition, for example, of K_2O. The results are presented in Sec. III. First we review briefly two models proposed for the localized excitations.

II. MODELS OF THE LOCALIZED EXCITATIONS

The work on Ne or He solute in vitreous silica was discussed in terms of a "cavity" model,[3] whereas most investigations of low-temperature properties of amorphous solids utilize a "tunneling-states" model.[4,5] Therefore, we will compare the assumptions and predictions of the two models, which were proposed simultaneously.

The potential-energy wells used in the two models are depicted in Fig. 1(a) which represents the potential energy of a Ne atom as a function of a general coordinate x. The cavity model assumes a single potential well as on the left of Fig. 1(a). The potential is modeled as a roughly cubic box of size L, and this results in the energy levels shown by Fig. 1(b). The broad spectrum of excitation energies E_1 (required to fit the specific heat, for example) derives from a spectrum of cavity sizes L.

The tunneling model assumes the presence of a double well as on the right of Fig. 1(a). This is approximated as two overlapping harmonic wells and results in the energy levels shown under Fig. 1(c). The harmonic-well ground state is split by an energy $E = (\Delta^2 + \Delta_0^2)^{1/2}$ where Δ is the asymmetry shown in Fig. 1(a) and Δ_0 arises from tunneling through the barrier between the two wells. The broad spectrum of energies E required by experimental data derives from a distribution in both Δ and Δ_0. The tunneling model produces a two-level state (TLS); that is, a ground state and an excited state at energy E, well separated from higher energy levels E_1. In pure vitreous silica, ultrasonic data have demonstrated the presence of "intrinsic" TLS excitations.[1] Hence the tunneling-states model is the better choice to account for the excitations intrinsic to silica glass.

We now consider the He or Ne solute in vitreous silica. Measurements of He and Ne solubility in vitreous silica indicate the presence of $\approx 10^{21}$ cm^{-3} sites available for the occupation of solute atoms.[6,7] These sites are associated with the myriad of diffusion channels which pass He and Ne (but not Ar), and possibly account for the $\approx$ 20% smaller mass density of vitreous silica as compared to crystalline quartz. A typical diffusion channel might be represented by the potential of Fig. 1(a), with $V(x)$ appearing somewhat different for He than for the more massive Ne. (Solubility studies indicated a factor of $\approx$ 2 fewer sites available for Ne.) The solute atoms could re-

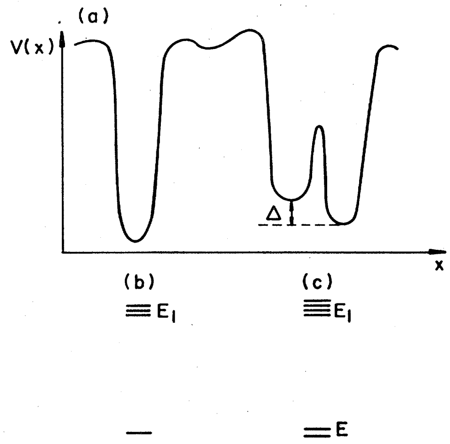

FIG. 1. (a) Schematic representation of the potential energy $V(x)$ of a Ne atom in vitreous silica versus a generalized coordinate x. (b) Energy-level diagram for the single potential well immediately above. (c) Energy-level diagram for the double well immediately above.

side in either or both types of wells shown in Fig. 1(a). The appropriate model to ascribe to the additional excitations associated with the solute atoms cannot be determined solely from specific-heat measurements.

III. EXPERIMENTAL DETAILS AND RESULTS

The vitreous silica samples[8] were two $3.0\times0.48\times0.28$ cm^3 rods of Spectrosil WF. The Ne was 99.996% pure containing ≤5 ppm H_2O. One silica sample was placed in a pressure chamber, which was then flushed with Ne at 20 °C and 200 atm (2×10^7 Pa), again at 200 °C and 130 atm, and finally at 200 °C and 80 atm. The pressure was then increased to 240 atm at 600 °C for 40 h. The chamber was cooled before the pressure was released. The Ne concentration introduced under these conditions was expected to be $\approx 4\times10^{19}$ cm.$^{-3}$ The samples were stored at liquid-nitrogen temperature between measurements.

The thermal conductivity κ was measured by the two-heater method. That is, two heaters were spaced a distance L along the sample of cross-sectional area A. A thermometer was mounted at one end of the sample, the other end was attached mechanically and thermally to the refrigerator. Switching heater power $\dot{Q}$ from one heater to the other created a temperature change of ΔT at the thermometer. The thermal conductivity is given by the expression $\kappa=L\dot{Q}/A\Delta T$. The data are shown in Fig. 2. The results are so nearly the same with and without the Ne that the data for pure silica are represented by the solid line.

The specific heat C was computed from the thermal equilibration time τ of the sample using the relation $C=\pi^2\kappa\tau/4L^2$ where L is here the total length of the sample. The data, shown in Fig. 3, have been divided by T^3 to exhibit deviations from the Debye phonon contribution to pure silica[9] represented by the dashed line. The added specific heat created by the Ne solute is also shown in Fig. 3. These data may be compared with the earlier results of Ref. 2 shown by the solid curve. The latter data, obtained for a Ne concentration of 4.2×10^{19} cm^{-3}, have been scaled by a factor of 0.6 in Fig. 3. This suggests that the actual Ne concentration in our sample may have been closer to 3×10^{19} cm^{-3}.

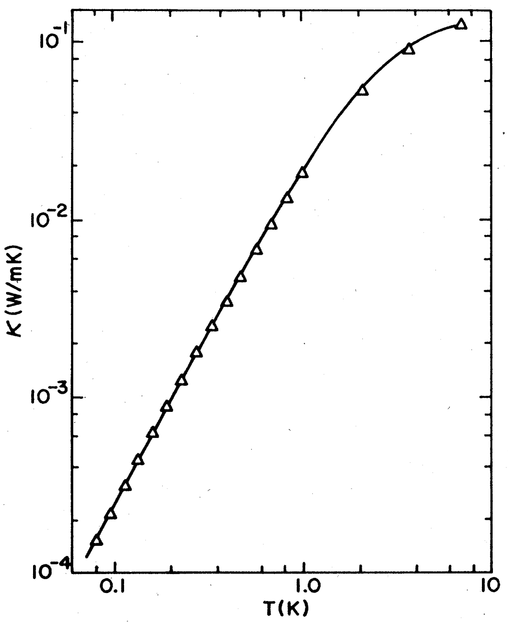

FIG. 2. Thermal conductivity κ, versus temperature T. Solid line, pure vitreous silica; △, silica plus Ne solute.

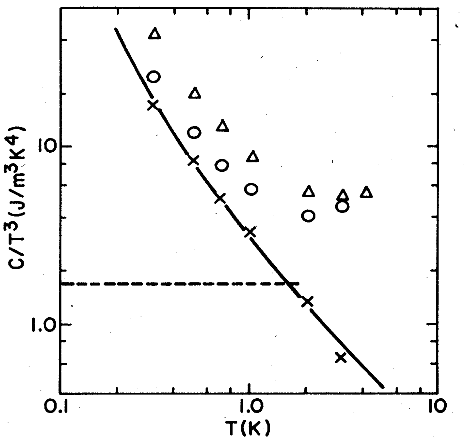

FIG. 3. Specific heat C, divided by T^3, versus temperature T. ○, pure vitreous silica; △, silica plus Ne solute; ×, contribution attributed to the Ne; solid line, contribution attributed to Ne, from Ref. 2; dashed line, phonon contribution.

The linear thermal-expansion coefficient α was obtained in a dilatometer discussed previously.[10,11] The absolute accuracy is $\approx$ 20% based on calibration runs against pure Cu made before and after each run. The data are shown in Fig. 4, where α has been divided by T^3 to show departures from the T^3 contribution expected for phonons. Our data for pure silica agree within 10% with an earlier measurement[11] represented by the solid line.

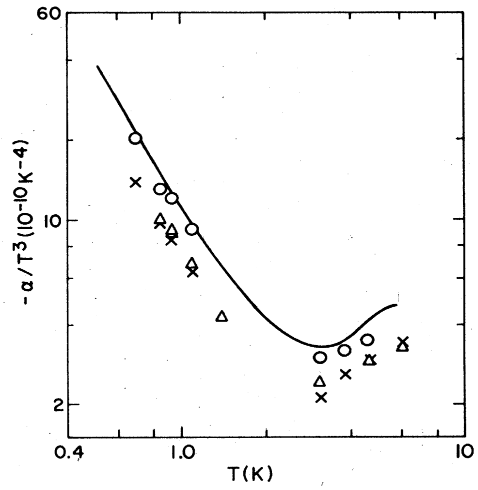

FIG. 4. Negative linear thermal-expansion coefficient α, divided by T^3, versus temperature T. ○, pure vitreous silica; △, ×, silica plus Ne solute (two independent runs); solid line, earlier data on pure silica, Ref. 11.

Data from two independent runs indicate that the presence of Ne reduces α by $\approx$ 30%.

Transverse ultrasonic velocities v were measured to an accuracy of 1% by a standard pulse-echo technique at room temperature and a frequency of 10^7 Hz. For pure silica we obtained $v = 3.77\times10^5$ cm/sec and, for the sample containing Ne, $v = 3.73\times10^5$ cm/sec. To within the accuracy of the measurements, the ultrasonic velocity is not changed by the introduction of Ne. Therefore, the phonon contribution to the specific heat is the same with or without Ne solute, and is properly represented by the dashed line in Fig. 3.

We would like to know the glass transition temperature T_g for the sample containing Ne. However, an actual measurement of T_g as in a scanning calorimeter would simply allow the Ne to diffuse out of the sample. We therefore note that, since the presence of Ne solute did not change the phonon velocity v, the solute is unlikely to have changed the glass transition temperature.[12]

In Ref. 2, both He and Ne solute were observed to increase the specific heat of vitreous silica. We have used only Ne since its diffusion constant is smaller than for He and we were therefore assured of a more constant concentration of Ne for the four properties measured. With respect to He, it has been reported[13] that exposure of vitreous silica to ^{4}He at low temperature can increase the specific heat. However, others[14,15] report that the heat capacity of silica is not increased through normal contact with He gas. The He must be introduced at high pressure and temperature.[2]

IV. DISCUSSION

Introduction of Ne into vitreous silica contributes an additional specific heat $C \approx AT^n$ with $n \approx 1$. The coefficient A increases with increasing Ne concentration,[2] but should become constant after the $\approx 10^{21}$ cm^{-3} available sites become filled. The most simple explanation is that the additional excitations reflected in the increased specific heat are associated explicitly with Ne atoms. These excitations would have a broad distribution of energies to give a specific heat roughly linear in T.

Not all of the available sites give rise to the conjectured low-energy excitations. If all the excitations were TLS, for example, the number N having energy $E \lesssim 1$ K would be given by the integral $Nk\ln 2 = \int_0^{1.0\,K}(C-C_p)dT/T$ where C_p is the specific heat of pure vitreous silica. This computation gives $N \approx 3\times10^{17}$ cm^{-3} for the data of Fig. 3. Therefore, the ratio of N to the number of Ne atoms present in our sample is $\approx 10^{-2}$, and the ratio of N to the total number of available sites is $\approx 3\times10^{-4}$.

The added excitations must couple only weakly to thermal phonons since the presence of Ne does not decrease the thermal conductivity. At low temperatures, it is known that phonons transport heat in glasses.[16] Therefore, the conductivity may be written

$$\kappa = 4.08\times10^{10}T^3 l/v^2 \ (\mathrm{W/cm\,K}) , \tag{2}$$

where l is the mean free path of phonons having average velocity v. In glasses, l is limited by phonon scattering from the TLS. Since κ and v are independent of the Ne solute, l must be also. Therefore, the thermal phonons are scattered only by the TLS intrinsic to the silica, and not by the added excitations.

Yet there must be a finite coupling of the new excitations to strain fields, since the presence of Ne solute reduces the magnitude of the thermal expansion coefficient as seen in Fig. 4. Of greater interest, however, is the average expansion contributed by each 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. The Γ computed from the *total* C and α of pure silica and silica containing Ne solute are plotted in Fig. 5, which shows the decrease in expansion per excitation when averaged over both the intrinsic TLS population plus the added excitations. If instead we deduce Γ from the added specific heat shown in Fig. 3 and the (algebraically) added expansion coefficient, then $\Gamma \approx +11$ near 0.8 K. That is, the added excitations contribute, on the average, a positive expansion as compared to the negative expansion coefficient of the TLS intrinsic to pure silica.

In brief, addition of Ne to vitreous silica appears to create a broad energy spectrum of localized excitations. The coupling of these new excitations to strain fields is sufficient to provide a (positive) contribution to thermal expansion, but not sufficient to scatter phonons significantly. Both the "cavity" model and the "tunneling" model of Sec. II have been ascribed to these excitations.[2,17] However, our measurements cannot distinguish which model might be more appropriate to the added excitations. Low-temperature ultrasonic attenuation measurements could be helpful.[1]

We note that a similar, understood phenomenon occurs in the crystalline superconducting alloy.[18] NbTi$_{0.05}$. The Ti impurity creates a local potential well which can trap interstitial H. The H tunnels between equivalent sites

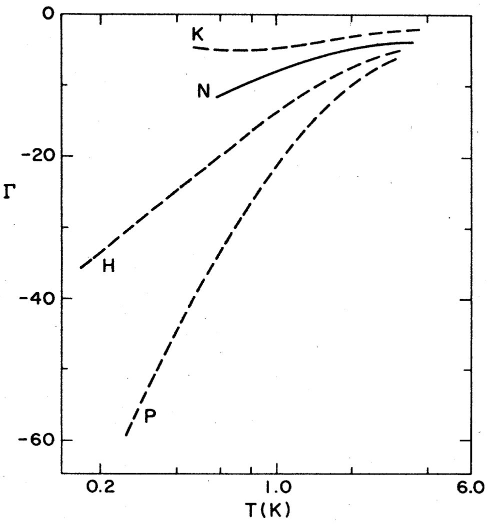

FIG. 5. Grüneisen parameter Γ versus temperature T. Solid line N, present results on vitreous silica containing $\approx$0.1 mol % Ne solute. Dashed lines from Ref. 11: P, pure silica; H, silica containing $\approx$0.1 mol % H_2O; K, silica containing 10 mol % K_2O.

around the Ti (or other impurity) giving rise to an energy spectrum similar to Fig. 1(c). At large ($\approx$ 5%) concentration of Ti, the wells elastically interact producing a broad spectrum of excitation energies. The low-temperature specific heat contributed by the H is given roughly by Eq. (1), and the coefficient A can be increased by diffusing in more H. The one apparent difference between $NbTi_{0.05}$ and vitreous silica is that the alloy, being crystalline, does not contain an intrinsic set of TLS. Therefore, with no solute present, $NbTi_{0.05}$ should have a Debye specific heat proportional to T^3.

An entirely different, alternative scenario for vitreous silica would have the Ne or He solute only modify the existing population of TLS. This seems unlikely since the density $\bar{P}$ of TLS (per unit of energy) and the coupling γ of TLS to phonons would both have to vary in a manner to leave the thermal conductivity unchanged after introduction of the solute. That is, the l of Eq. (2) is proportional[1] to $(\bar{P}\gamma^2)^{-1}$, which must be independent of Ne concentration. We therefore assume that the solute does introduce a new set of excitations distinguishable from the intrinsic TLS.

We move next to a surprising and more speculative observation, namely, that the changes in the low-temperature properties of vitreous silica with addition of chemically inactive Ne are similar to changes caused by the addition of K_2O or Na_2O. The specific heat is increased, the magnitude of the expansion coefficient is decreased, and the thermal conductivity is essentially unchanged by the presence of the dopant.[12] Rather similar behavior has been noted[19] for silica containing H_2O. Since more data are available for the K_2O system,[12] the following discussion will be directed primarily to potassium silicate glasses.

Both Ne and K_2O dopants create excitations having a positive average expansion coefficient at low temperatures. Figure 5 compares the net Grüneisen parameters for pure silica and silica doped with H_2O, Ne, and K_2O.

The K_2O-doped samples[12] obey the empirical relation[20] $l \propto T_g$ where l is the phonon mean free path of Eq. (2). This is also true for Ne since, as indicated above, neither l nor T_g are changed by the presence of Ne.

It is tempting to conclude that the K_2O, as a "network filler," can fall into the same kind of sites as would be occupied by the Ne or He. Indeed, studies of He diffusion in alkali silicate glasses indicate that the open volume accessible for the He is decreased with increasing alkali concentration.[7] Support for the above view is also found from silica doped with H_2O, in which the OH^- creates TLS distinct from those intrinsic to the silica.[21]

Additional support is found in the specific-heat data. For Ne solute, the specific-heat contribution $C \approx AT^n$ increases with solute concentration but should become constant after the $\approx 10^{21}$ cm^{-3} available sites are filled. No measurements are available for K_2O for samples containing less than 5 mol%, and 5 mol% would fill the available sites. Indeed the coefficient A of Eq. (1), which is larger than that of pure silica by a factor of ≈ 10, decreases slightly[12] with further addition of K_2O beyond 5 mol%. The ratio of excitations N (having $E \lesssim 1$ K) to available sites is $\approx 3\times 10^{-4}$ as computed above for Ne, while for 8 mol% K_2O this ratio is $\approx 10\times 10^{-4}$. The number N accounts for only a small fraction of the dopant present in the sample, namely, $\approx$1% for Ne and $\approx$0.1% for K_2O or H_2O.[12,22] Thus the specific heat reveals several similarities between Ne and K_2O dopants suggesting that the K_2O may fall into the same kind of sites as would be occupied by the Ne.

Of course, the view of K_2O solely as a network filler is too simplistic. For vitreous silica doped with Na_2O, for example, the sodium also partially disrupts the SiO_2 network[23] (at least at concentrations of $\gtrsim 5$ mol%). This disruption is reflected in the reduced glass transition temperature T_g of alkali silicate glasses. Nevertheless, the effects of Ne and K_2O dopants on the low-temperature behavior of vitreous silica are remarkably similar.

In conclusion, we have measured at low temperature the specific heat, thermal expansion, and thermal conductivity of vitreous silica containing Ne solute. The changes produced by the Ne may be attributed to new or added localized excitations, presumably associated with the trapping of Ne atoms within the interstices of the silica network.[24] The nature of the localized excitations, whether cavity modes or tunneling states, cannot be determined from our data. The changes produced by the chemically inactive Ne are similar to the effects produced by the addition of K_2O, Na_2O, or H_2O to vitreous silica.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation—Low Temperature Physics—under Grant No. DMR83-03918. We thank Dr. Lazarus for the use of a high-pressure apparatus.

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[1] *Amorphous Solids*, edited by W. A. Phillips (Springer, Berlin, 1981).

[2] M. H. van Maaren, J. E. Olijhoek, and C. Parlevliet, Solid State Commun. **35**, 867 (1980).

[3] H. B. Rosenstock, J. Non-Cryst. Solids **7**, 123 (1972).

[4] P. W. Anderson, B. I. Halperin, and C. Varma, Philos. Mag. **25**, 1 (1972).

[5] W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

[6] J. E. Shelby, J. Appl. Phys. **47**, 135 (1976).

[7] J. E. Shelby, in *Treatise on Materials Science and Technology*, edited by M. Tomozawa and R. H. Doremus (Academic, New York, 1979), Vol. 17 (Glass II), p. 1.

[8] The Spectrosil WF was obtained from the Thermal American Fused Quartz Co., Change Bridge Road, Montville, NJ 07045.

[9] M. Rothenfusser, W. Dietsche, and H. Kinder, Phys. Rev. B **27**, 5196 (1983).

[10] D. A. Ackerman and A. C. Anderson, Rev. Sci. Instrum. **53**, 1657 (1982).

[11] D. A. Ackerman, A. C. Anderson, E. J. Cotts, J. N. Dobbs,

W. M. MacDonald, and F. J. Walker, Phys. Rev. B **29**, 966 (1984).

[12] W. M. MacDonald, A. C. Anderson, and J. Schroeder Phys. Rev. B. **31**, 1090 (1985).

[13] R. A. Fisher, J. Non-Cryst. Solids **41**, 251 (1980).

[14] J. L. Vorhaus and A. C. Anderson, J. Non-Cryst. Solids **17**, 241 (1975).

[15] D. A. Ackerman and A. C. Anderson, J. Non-Cryst. Solids **45**, 229 (1981).

[16] M. P. Zaitlin and A. C. Anderson, Phys. Rev. B **12**, 4475 (1975).

[17] J. C. Phillips, Phys. Rev. B **24**, 1744 (1981).

[18] K. Neumaier, H. Wipf, G. Cannelli, and R. Cantelli, Phys. Rev. Lett. **49**, 1423 (1982).

[19] S. Hunklinger, L. Piche, J. C. Lasjaunias, and K. Dransfeld, J. Phys. C **8**, L423 (1975).

[20] C. L. Reynolds, J. Non-Cryst. Solids **30**, 371 (1979).

[21] M. v. Schickfus, S. Hunklinger, and K. Dransfeld, Phys. Rev. Lett. **43**, 1817 (1979).

[22] T. L. Smith and A. C. Anderson, Phys. Rev. B **19**, 4315 (1979).

[23] J. Kruger, Phys. Chem. Glasses **13**, 9 (1972).

[24] After submission of our manuscript, similar results for the specific heat and thermal conductivity of He in vitreous silica have been published by S. Grondey, G. V. Lecomte, and H. V. Lohneysen, J. Non-Cryst. Solids **65**, 139 (1984).