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Soft surface phonons in porous glasses

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Enhancements above the specific heat of solid alkali-borosilicate glass were observed in the low-temperature specific heat of porous glasses with pore diameters of 22, 37, 60, and 140 Å. The effects are attributed to the presence of low-frequency surface vibrational modes in these glasses. The enhancements are probably controlled by the silica clusters and thus are not directly proportional to the apparent surface area. Since the specific heat of solid glass does not follow the Debye approximation even at lowest temperatures, the semi-infinite calculations of surface specific heat do not apply though rough qualitative agreement is found with experimental enhancements.

I. INTRODUCTION

The vibrational spectrum of any crystalline or amorphous solid is considerably altered when there is a significant fraction of atoms at or near the surface. Experimental evidence of this effect can be obtained by low-energy-electron diffraction,[1] neutron scattering,[2] from the low-temperature specific heat of samples with large surface areas, etc. Because of the presence of the surfaces on the solid, we expect the vibrational-frequency distribution $g(\omega)$ to have a contribution with the frequency dependence characteristic of two-dimensional solids, which is proportional to frequency ω in the low-frequency limit for the elastic continuum, in addition to the ω^2 dependence expected for three-dimensional solid. Thus the specific heat of a solid with large surface area should have a contribution varying as T^2 in the low-temperature limit, in addition to T^3 dependence characteristic of the infinite crystal. A more realistic description of the phonon density of states $g(\omega)$ based on lattice-dynamical calculations[3] involves the expansion of $g(\omega)$ with even and odd terms being contributed by bulk and surface, respectively, so that the heat capacity is of the form

$$C = BST^2 + AVT^3 + \cdots , \tag{1}$$

the even terms being the surface-phonon contributions and the odd ones the bulk-phonon terms. S and V stand for the surface area and the volume of the sample, respectively. The relative importance of the first term in (1) was evaluated for the semi-infinite and finite isotropic elastic continua[4] with B being expressed as a function of the longitudinal v_l and transverse velocity v_t of sound.

$$B = \frac{3\pi k_B^3 \zeta(3)(2v_t^4 - 3v_t^2 v_l^2 + 3v_l^4)}{h^2 v_t^2 v_l^2 (v_l^2 - v_t^2)} , \tag{2}$$

where $\zeta(3)$ is the Riemann zeta function, k_B and h are Boltzmann's and Planck's constants, respectively. Therefore, surface effects on the vibrational spectrum are demonstrated as enhancements in the lattice specific heat at low temperatures.

The physical origin of the enhancements can be easily understood by comparing the average frequency of the bulk samples with those of a solid with large surface area. Because of the missing neighbors of the atoms at or near the surface, their characteristic frequencies are lower than in the bulk and their amplitudes of vibrations are increased. The presence of these modes results in a decrease of the average phonon frequency and therefore in an enhanced specific heat at low temperatures. Experimental results indicating the presence of the surface effects in the specific heat of crystalline powders of NaCl,[5,6] MgO,[7] and Pb and In,[8] have been reported. Results presented here show enhancements of the specific heat in the amorphous samples with large surface area which are interpreted as arising from surface effects. The calculations for the semi-infinite elastic continuum should be more easily applicable to amorphous materials since they are isotropic. For crystalline solids, an averaging of the sound velocities is required, since B in (2) is expressed in terms of average values of these quantities.

II. EXPERIMENTAL

Several porous glasses with varying pore diameter were obtained from Dr. J. H. P. Watson (Corning Glass Works) and were of the same type as described in his experiments.[9] These glasses were typically prepared by leaching a phase separated alkali-borosilicate glass and thus removing the boron-rich phase. Development of glass into silica-rich and boron-rich phases occurs during a heat treatment carried at temperatures varying roughly between 500 and 700 °C. Higher development temperature and longer development time lead generally to lower surface area. Removal of the silica-deficient phase is accomplished by leaching with HNO_3. According to the literature, these glasses contain 96% SiO_2, 3% B_2O_3 (weight), small amounts of Na_2O, Al_2O_3, and other oxides, and thus their composition lies between vitreous silica and the Pyrexes which contain about 80% SiO_2. Electron-microscope studies[10,11] have indicated that the porous glasses with pore sizes less than 200 Å can be roughly described as a collection of highly interconnected silica particles of 100–300 Å in diameter.

The surface area, pore size, and pore-size distribution of glasses were investigated by nitrogen adsorption and desorption near the condensation point and by mercury porosimetry on these samples.[9] The nitrogen adsorption isotherms analyzed with the Brunauer-Emmett-Teller (BET) equation[12] yield the volume of the gas required to form a complete monolayer. Multiplying the number of molecules in a monolayer by the average area occupied by each molecule (estimated from the density of solidified gas) gives the surface area of the adsorbent. The Kelvin equation[13] which relates the vapor pressure over a curved surface to its radius of curvature was employed for the pore-diameter determination. The diameter of the pores was also determined by measuring the pressure required to force mercury into capillaries, the diameter being inversely proportional to the pressure necessary to overcome the forces due to the surface tension.[14] The characteristics of the samples are summarized in Table I. The pore diameter determined from nitrogen adsorption with the assumption of cylindrical pores is almost twice as large as values from the desorption and mercury porosimetry which are controlled by capillary constrictions.

Infrared work[15] indicates that a porous glass surface is heterogeneous and consists primarily of free and hydrogen-bonded hydroxyl groups which are attached to both silicon and boron with OH group density of approximately one per 20 Å^2.

TABLE I. Solid and porous glass sample characteristics.

Glass	Density (g/cm^3)	Surface (m^2/g)	Porosity (%)	Pore distribution at halfwidth (Å)
Solid	2.17 ± 0.005			
22 Å	1.70 ± 0.01	126	16–17	
37.5 Å	1.45 ± 0.01	123	24	34–40
60 Å	1.61 ± 0.01	53	21	50–73
140 Å	1.51 ± 0.01	28	25	130–152

It has been suggested[16] that silica contained in the boron-rich phase precipitates during the leaching process carried out with HCl, and part of this precipitate may remain in the pores. Such a product would give a high surface area insensitive to the actual surface area of the pores because of the colloidal silica contribution. This type of behavior has not been observed in our samples. Even if our porous glass happens to contain a silica precipitate, this will not effect the comparison with theoretical specific heat which is expressed in terms of total measured surface and volume of the sample.

Specific-heat measurements in the temperature region 1.5–15 K were performed by the discontinuous heating method. The experimental system and data handling were described elsewhere,[17] and thus we will concentrate only on the aspects pertinent to the measurements on porous glasses. Considerable care was taken in sample preparation for the measurements with porous glasses because they are highly hygroscopic and adsorbed water would contribute appreciably to the heat capacity. With a typical amount of adsorbed water of 0.02 g per gram of glass, the errors in the specific heat could amount to 25%. For this reason, the samples were baked in oxygen and then in vacuo at 500 °C in a Pyrex tube, weighed, and transferred to the cryostat in a dry box. It was assumed that the glass samples were also annealed during this heating, although temperatures around 1000 °C are usually chosen to anneal glasses. We did not attempt heating to higher temperatures since the porous glass structure collapses around 900 °C. The sample space was pumped down to pressures in the 10^{-7}-Torr range before starting the experiment. With a cryostat at 4.2 K, the calorimeter was heated to around 70 °C, which is the highest temperature allowable for the thermometer. No change in the pressure was observed upon this heating, indicating that most of the gases were desorbed. The performance of the system including thermometry was tested by measuring an ASARCO copper sample.[18] The agreement with other published data[18] for the specific heat was within 0.4%. The accuracy of the total heat capacity was estimated to be ± 1%.

Typically, the samples weighed about 2 g and were in the form of several rectangular slabs with a thermal conduction path of 1.6 mm. Both solid and porous glasses exhibited thermal nonequilibrium after heating. The corrections for these nonequilibrium and heat-leak effects were evaluated using a numerical procedure.[17] Heat capacity of the samples accounted for at least 50% of the total, and thus the accuracy of the measurement on the glasses is better than ± 2%.

III. RESULTS AND DISCUSSION

The results for 22 Å, 140 Å, and solid glasses are plotted as C/T vs T^2 in Fig. 1 from 1.5 to 5 K, as C/T^2 vs T from 1.5 to 15 K in Fig. 2 and listed in Table II. For clarity, the specific heat of the 60 Å glass is not shown on the graphs; it differs by less than 10% from the 22 Å glass over the whole temperature region from 1.5 to 15 K. The specific heat of the 37 Å glass also agrees with the previous two glasses above 5 K but deviates at lower temperatures where it is up to 40% higher at the lowest temperature. Since the 37 Å glass had a slightly different composition, a direct comparison with the other glasses cannot be made; so in Table II, we only listed the results on 22 Å, 60 Å, and 140 Å, and solid glasses. Higher iron content in the commercially available 37 Å glass was probably responsible for the excess specific heat.

Two interesting aspects of the data concern the close agreement of the specific heat of our solid glass with the measurements on vitreous silica and other glasses with different compositions, and the existence of the enhancements in the specific heats of porous glasses. It has long been known that the thermodynamic properties of amorphous materials are not sensitive to composition. Noncrystalline solids with completely different compositions such as vitreous silica, SiO_2, silica- and germania-based glasses containing large amounts of other oxides, polymers, varnishes, selenium, and GeO_2 all have very similar specific heats and thermal conductivities.[19] It has also been observed that the low-temperature specific heat of the same substance in the amorphous state is larger than that in the crystalline state. The measured specific heats of these crystalline solids agree very well with the calculations in the Debye model using data from the elastic measurements, whereas a large disagreement is found for amorphous solids.

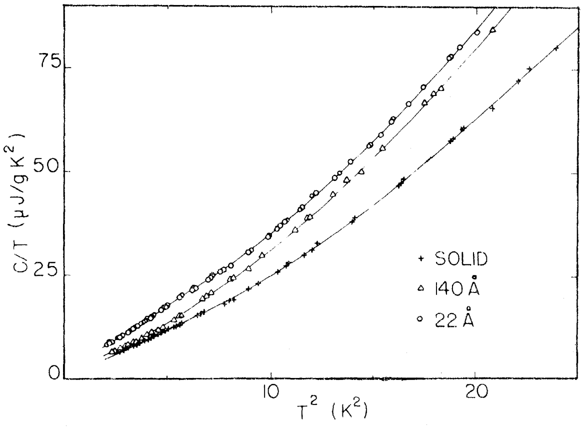

FIG. 1. Specific heat C of solid, 140- and 22-Å porous glasses between 1.5 and 5 K plotted as C/T vs T^2.

The plot in Fig. 1 indicates that the specific heat of solid glass below 5 K cannot be represented by a cubic term only or by a combination of a linear and a cubic term. The least-squares polynomial analysis yields the adequate representation below 5.5 K in the form $C = (1.15 \pm 0.15)T + (1.79 \pm 0.05)T^3 + (0.063 \pm 0.0025)T^5$ μJ/gK, the error limits being the sums of the systematic error and the 95 % confidence limits. Because of the failure of the Debye model to account for the low-temperature vibrational properties of glasses, coefficients may not have physical meaning. However, it may be of interest to point out that the value of the linear coefficient agrees reasonably well with that reported for vitreous silica in the region below 1 K.[19] The presence of a linear-temperature term has been reported in many other amorphous solids and appears to be characteristic of the amorphous state. Excitations responsible for this contribution could be phonon-assisted tunneling,[20] resonant tunneling, or other localized phonon excitations.[21] The presence of the linear term indicates that any attempted comparison of Debye temperatures calculated from the total specific heat and those computed from the elastic measurements is not possible because of the existence of other types of excitations contributing to the specific heat of noncrystalline solids.

Pyrex glasses having very similar composition to our glass showed another anomaly with a shape suggestive of a Schottky behavior in the specific heat.[22] In magnetic fields, the maximum of the anomaly shifted to higher temperatures and it was suggested that the excess specific heat was caused by the spins of iron impurities. On the basis of the composition, one would expect the specific heat of our solid glass to be quite similar to the specific heat of vitreous silica or Pyrex. In comparison with the iron-free vitreous silica, our solid glass has a specific heat higher by about 10% over most of the temperature range, while Pyrex specific heat is up to 90% higher at 1.5 K, due to the contribution from iron impurities. The iron content of our solid glass and 22, 60, and 140 Å glasses was determined to be below 20 wt ppm by atomic-absorption spectroscopy. The excess specific heat of 37 Å glass above that of 22 or 60 Å glass appears to be due to higher iron content (130 wt ppm).

The significant enhancements of the specific heat of porous glass (up to 75%) above the heat capacity of the solid glass are suggestive of the

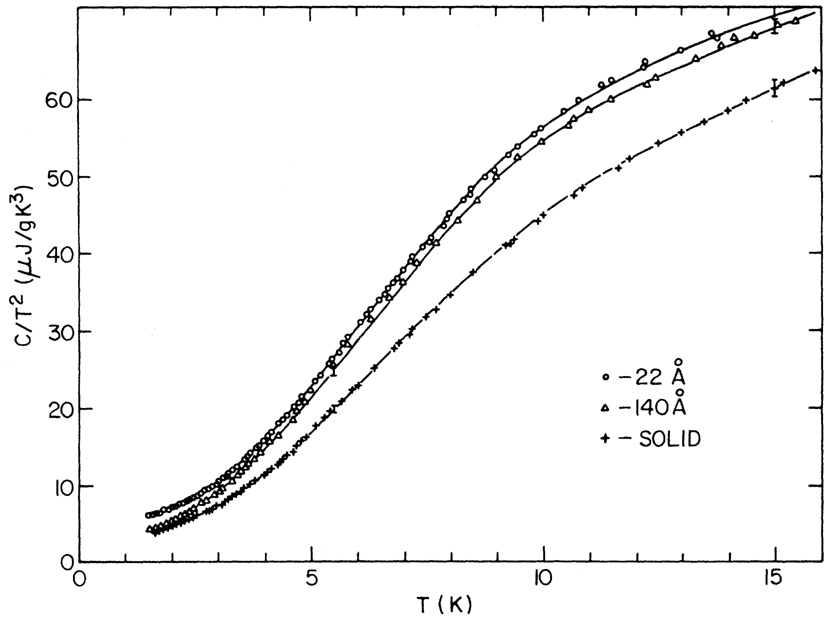

FIG. 2. Specific heat C of solid, 22, and 140 Å porous glasses between 1.5 and 15 K plotted as C/T^2 vs T. The enhancements above the specific heat of solid glass are more significant at low temperatures where they are up to 75%, while at 15 K they are only ≃15%.

presence of lower-frequency phonon modes existing in these samples with large surface area. The average number of neighbors of the surface atoms is lower than in the bulk, and thus the atoms at or near the surface move with greater displacements and lower frequencies than bulk atoms in any solid. Figures 1 and 2 demonstrate that the simple description of the specific heat of porous glasses with a polynomial having T and T^3 terms or T^2 and T^3 terms, respectively, is not possible even below 5 K. Because the representation of the specific heat of solid glass requires T and T^5 terms in addition to usual T^3 term, the analysis for the porous glass in the form given by Eq. (1) does not have to hold. However, it is possible to fit roughly the enhancements to the sum of T^2 and T^4 terms below 7 K. The surface enhancement constant B from (2) was calculated using the transverse and longitudinal room-temperature sound velocities in Pyrex glass[23] which are $v_t = 3.28\times10^5$ cm/sec and $v_l = 5.64\times10^5$ cm/sec (the low-temperature values might be somewhat higher but for the estimate of B, the eventual differences were neglected), and we obtained $B = 2.1\times10^{-5}$ mJ/K³ m²; B is expected to be almost independent of temperature within the present temperature range. The calculated BS products are compared with the coefficients of the quadratic temperature terms in Table III. Although the coefficients agree within a factor of 2–3 with the BS products, they do not scale with surface area.

TABLE II. Specific heat of solid glass, 22-, 60-, and 140-Å porous glass μJ/gK vs temperature.

T (K)	C^s	C^{22}	C^{66}	C^{140}
		μJ/gK		
1.50	8.24	13.24	14.46	9.31
1.75	12.63	19.67	21.54	14.17
2.00	18.64	28.19	30.69	21.22
2.25	26.61	39.44	42.50	30.83
2.50	37.00	53.83	57.61	44.67
2.75	50.29	72.21	76.47	61.58
3.00	67.09	94.78	99.96	83.08
3.50	113.8	158.2	164.2	144.2
4.00	183.7	252.0	256.7	236.6
4.50	284.5	381.9	385.2	366.5
5.00	426.4	562.5	557.8	538.9
6.00	835.0	1098	1092	1038
7.00	1430	1862	1849	1773
8.00	2227	2870	2849	2763
9.00	3256	4163	4095	4008
10.00	4490	5640	5540	5461
12.00	7589	9158	9060	8880
15.00	13 810	15 830	15 680	15 650

It is highly unlikely that the semi-infinite model would provide an adequate description of the be-

TABLE III. Comparison of the products BS (B is the surface enhancement constant and S is the surface area) with the coefficients D of the T^2 term determined from the measured specific-heat enhancements.

Pore size Å	BS	D
	μJ/gK³	
22	2.65	1.85 ± 0.1
60	1.11	2.45 ± 0.2
140	0.59	0.2 ± 0.2

havior of the very complex porous structure. If the degree of interconnectivity is low, the structure might be more appropriately described by isolated particles, and size effects would be important at low temperatures. Calculations[24,25] indicate that the specific heat of small clusters does not take the form given in (1) and does not have to be a monotonic function of cluster size. The finite size of clusters results in size quantization of phonon frequencies and in the low-frequency cutoff, leading to a rapid decrease of the specific heat as the temperature is lowered. A simple estimate[8] of the cutoff temperature θ_c corresponding to the low-frequency cutoff for particles of characteristic dimension d is given in the isotropic-continuum approximation by $\theta_c = \hbar\pi v_t / k_B d$. Although the cutoff temperature is between 8 and 2.7 K for isolated glass particles of diameter between 100 and 300 Å, θ_c will be significantly reduced for the highly interconnected structure. Thus the size effects on the specific heat of porous glasses may not be of importance in the present temperature range. Moreover, the theoretical estimates based on the semi-infinite model relate only to the glass surface, while the experimental surface enhancements reflect the combined effect of vibrations of OH groups (with heat treatment at 500 °C, there is roughly one OH group per 35 Å^2), boron rich regions at the surface,[15] as well as silica.

The question whether the adsorbed solidified gases or water vapor do not make a significant contribution to the observed enhancements should be carefully examined. In order to investigate this possibility, a table with the specific-heat enhancements of the 22 Å glass, the specific heats of ice, nitrogen, oxygen, and helium is included. The values listed in the temperature range from 1 to 15 K are approximate only, since they will serve for simple estimates. It is anticipated that the specific heats of the adsorbed layers of solid gases or liquids will perhaps substantially differ from the listed values of bulk specific heats, being substrate and coverage dependent, but no attempt has been made to estimate the changes in the specific heats of adsorbed solid gases. Table IV shows that about 0.1 g of ice or 2×10^{-2} g of oxygen, or 10^{-2} g of nitrogen, or 10^{-5} g of helium per 1 g of glass would be required to account for the observed porous-glass enhancements between 2 and 4 K. It is unlikely to have in our experimental conditions even the fraction of the above amounts. With typical pore volume of 0.1 cm^3 per 1 g of glass, the pores would have to be filled completely with water to enhance the specific heat by the required amount. As it was measured, the equilibrium amount of water vapor contained in 1 g of glass after long adsorption or desorption was about 0.02 g. This amount reduced substantially by baking and pumping could not effect significantly the enhancements. The nitrogen adsorption isotherms near the normal boiling point yielded the monolayer capacity of 35 cm^3 STP per 1 g of 22 Å glass by the BET method, while helium monolayer capacities were estimated to be 53 cm^3 STP.[26] Near the boiling point of nitrogen or rare gases (except helium), one monolayer is typically adsorbed at $p/p_0 \simeq 0.1$, where p_0 is the saturation pressure. The sample pressure at helium tem-

TABLE IV. Enhancements in the specific heat of 22-Å porous glass and the specific heat of solid oxygen, nitrogen, ice, and liquid helium.

T	C^{22}_{glass}	$\Delta C^{22}_{\text{glass}}$	C_{ice} [a]	C_{O_2} [b,c]	C_{N_2} [b,d]	C_{He} liquid at sat. press. [e]	C_{He} 1 monolayer on Vycor [f]
			mJ/gK				
1.5	0.013	0.005	0.05	0.19	0.41		
2.0	0.028	0.0095	0.12	0.43	0.98	5200	250
3.0	0.095	0.028	0.41	1.5	3.2	2500	620
4.0	0.25	0.068	0.98	3.6	7.7	400	1000
5.0	0.56	0.14	1.9	7.4		11 500	
6.0	1.10	0.26	3.3	13.4			
8.0	2.87	0.64	7.8	35			
10.0	5.64	1.15	15.2	72	200		
15.0	15.8	2.0	50.0	220	450		

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perature is likely around 10^{-10} Torr, and if it is assumed for simplicity that the coverage is proportional to the pressure, the negligible amounts of nitrogen or oxygen are adsorbed. Unfortunately, the estimates of the relative pressure p/p_0 at which a monolayer of helium is created near 4.2 K vary substantially from[26] 4×10^{-4} for Vycor glass, through[27] 10^{-6} for argon-plated copper to 10^{-12} for plain Pyrex,[28] and we cannot eliminate completely the possibility that helium does not contribute to the enhancements on this basis. For this reason, we examined the effect of heating the sample to 300 K while the surroundings remained at 4.2 K or 1.2 K and then remeasured the heat capacity. The latent heat of vaporization for bulk helium is about 90 J/mole, but the heat of adsorption of helium in submonolayer quantities might be as high as 1000 J/mole.[29] Even in this case, it is probable that a certain part of the helium would desorb by heating the sample up to 300 K, and then the heat capacity would be lower in the subsequent measurement. Within the precision of the measurement (± 1%), no such change was observed in any specific-heat measurement on porous glasses.

The accuracy of these measurements could be improved, since the samples were small and the calorimeter was designed for the measurements on samples of small metal particles embedded in these porous glasses. It would be definitely advantageous to bake the samples directly in the calorimeter and prevent contamination and adsorption of gases during the transfer. In order to ensure that there are no contributions from adsorbed solid gases, helium or other contaminations, the measurements would have to be performed in an ultrahigh vacuum system. In any case, these preliminary results yield the first indication of the surface effects on the specific heat of amorphous systems. The thermal conductivity of porous glasses as determined from thermal nonequilibrium was observed to be lower compared with solid glass, suggesting that the additional scattering of phonons by the pore boundaries is quite important at low temperatures.

IV. CONCLUSION

The low-temperature specific heat of solid unleached glass agrees quite closely with that of "iron-free" Pyrexes or vitreous silica and thus supports the lack of sensitivity of the thermodynamic properties of the amorphous materials to the composition. Enhancements up to 75% in porous glasses above the specific heat of solid glass suggest the evidence for the softening of the phonon density of states due to low-frequency surface modes. These enhancements do not scale simply with the surface area and cannot be described by a quadratic temperature dependence. This is most likely due to the complexity of porous structure or to the heterogenerity of the glass surface resulting from hydroxyl groups and boron. If the different contributions to the surface specific heat are nonadditive, nonquadratic temperature dependence may arise even at the lowest temperature. The vibrational contribution of hydroxyl groups to the surface specific heat could be separated by studying the porous glasses degassed at different temperatures, since the number of OH groups decreases as the heating temperature increases. Owing to the insensitivity of the specific heat to the glass composition, alkali-borosilicate glasses could be a desirable system for investigating the interfacial effects on the vibrational properties of amorphous solids. Measurements of the specific heat of solid glasses prepared at different development temperatures and with varying development time which alter the area of the interface between silica-rich and boron-rich phases could yield the information about the vibrational behavior of the interface.

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