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LOW TEMPERATURE THERMAL PROPERTIES OF
GRANULAR MATERIALS

by

Richard Haynesworth Tait

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Research Group:
Prof. R. O. Pohl
LASSP

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LOW TEMPERATURE THERMAL PROPERTIES OF GRANULAR MATERIALS

Richard Haynesworth Tait, Ph.D.
Cornell University, 1975

The low temperature ($0.1\text{K} < T < 100\text{K}$) specific heat and thermal conductivity of a variety of structurally disordered materials were measured to determine whether or not the low temperature excess specific heat and anomalous thermal conductivity of glasses are associated with "grainy" structures (on a scale of $50\text{-}500 \text{ \AA}$) that are postulated to exist in glasses. The materials examined (pressed powders, sintered ceramics, glass ceramics, phase separated glasses, and recrystallized glasses) all had granular structures with grain sizes varying from $70 \text{ \AA}$ to 30μ ($3 \times 10^5 \text{ \AA}$).

For the samples studied, no correlation of "glassy" thermal properties with granular structures was found. While the granular structures did significantly affect the thermal conductivity and specific heat of these materials, only those samples with atomic or molecular disorder (i.e. phase separated glasses and solid solution glass ceramics) showed "glassy" behavior at low temperatures, and this glassy behavior was not dependent on the size or existence of the grains composing the sample.

I. INTRODUCTION

While the low temperature thermal properties of non-magnetic, dielectric single crystals are well understood, this is not the case for glasses. The excess specific heat and the particular form of the phonon scattering rate seen in all glasses are not understood at present despite the considerable amount of work that has recently been done on the problem. Because of the broad generality of these "glassy" effects (they are seen in a huge variety of amorphous dielectrics and are of the same order of magnitude in all glasses) a valid model should not depend on the details of the composition of the glass. One concept that is therefore quite appealing is the idea that extended structural features exist in all glasses and that these structures are responsible for the anomalous low temperature properties of glasses. Such a picture does not depend on the molecular nature of the glass but only on the existence of a "glassy" structure. The observed minor variations in the measured properties of amorphous materials from sample to sample could easily be explained by variations in the density and scattering rates of the "structures" in the different samples.

If the above concept has any applicability to glasses, then it should be possible to produce "glassy" behavior (or to enhance "glassy" behavior already present) in a material by introducing a large amount of long range structural

disorder into it. Also, it should be possible to make a "glass" by bringing together a large number of individual structural units to form a solid. For example, by decreasing the characteristic size of such "structures" in a crystalline material from $d \sim 1$ cm (the size of a large single crystal) to $d \sim 50-500 \text{ \AA}$ (a reasonable size for a "structure" in a glass) it should be possible to observe a continuous transition from single crystal behavior to "glassy" behavior. It is this picture of a glass that we set out to examine.

We have studied the low temperature thermal conductivity and specific heat of a wide variety of granular materials with grain sizes varying from $70 \text{ \AA}$ to 3μ in an effort to isolate the effects of granular structures on the properties of crystalline and amorphous materials. In Chapter II we discuss the theoretical and experimental background relevant to this problem. In Chapter III we discuss the preparation and characterization of the granular samples and in Chapter IV we describe our experimental techniques. In Chapter V we give the results of our measurements and discuss their significance. In Chapter VI we summarize our findings and draw conclusions about the validity of the extended structural defect model of the low temperature thermal properties of glasses.

II. BACKGROUND REVIEW

The low temperature thermal properties of nonmagnetic single crystal dielectrics are well understood. The low temperature specific heat of a nonmagnetic pure dielectric single crystal (of volume V) is due to phonons and is given by:¹

$$C_V(T) \equiv \frac{C(T)}{V} = \int_0^\infty d\omega \, g(\omega) \frac{(\hbar\omega)^2}{k_B T^2} \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} . \quad (1)$$

Here $g(\omega)d\omega$ is the number of phonon states per unit volume with angular frequencies in the region between ω and $\omega+d\omega$ and $\beta = 1/k_B T$. Using the Debye elastic continuum approximation for an anisotropic medium¹ (i.e. ignoring the possibility of dispersion) we write:

$$\omega_{\vec{k}\lambda} = v_{\lambda}(\theta_{\vec{k}}, \phi_{\vec{k}}) |\vec{k}| . \quad (2)$$

$v_{\lambda}(\theta_{\vec{k}}, \phi_{\vec{k}})$ is the phase velocity of the phonon with wave-vector $\vec{k}$ and polarization λ . Within this approximation we find¹ that the density of states is given by:

$$g(\omega) = 3 \frac{\omega^2}{2\pi v_{Deb}^3} \quad : \quad \omega \leq \omega_D \quad (3)$$

$$g(\omega) = 0 \quad : \quad \omega > \omega_D$$

where we have

$$\omega_D \equiv \left(\frac{N}{V} 6\pi^2 v_{Deb}^3 \right)^{1/3} . \quad (4)$$

Here N is the number of atoms in the volume V and v_{Deb}^3 is defined by:

$$\frac{1}{v_{\text{Deb}}^3} \equiv \frac{1}{12\pi} \int_{\lambda} d\Omega_{\vec{k}} \frac{1}{v_{\lambda}^3(\theta_{\vec{k}}, \phi_{\vec{k}})} \quad (5)$$

If the medium is isotropic then the phase velocity is independent of direction and we get:

$$\frac{1}{v_{\text{Deb}}^3} = \frac{1}{3} \left(\frac{2}{v_t^3} + \frac{1}{v_l^3} \right) \quad (6)$$

v_t is the speed of transverse phonons and v_l is the speed of longitudinal phonons. With the density of states given by Eq. (3) and the Debye speed of sound, v_{Deb} , given by Eq. (6) we find that for $T/\theta_D < 0.1$ ($\theta_D \equiv \frac{\hbar \omega_D}{k_B}$):

$$C_V(T) = \frac{2\pi^2}{5} \frac{k_B^4}{\hbar^3 v_{\text{Deb}}^3} T^3 \quad (7)$$

$$C_V(T) = c_{\text{Deb}} T^3$$

Eq. (7) was derived with the density of states of Eq. (3) which is based on the assumption that there is no dispersion, i.e. that v_{λ} is independent of $|\vec{k}|$. This assumption has been experimentally found to be correct for most crystals for frequencies that contribute to the specific heat for $T \leq 0.01 \theta_D$.

For single crystals for which the exact density of states $g(\omega)$ (including dispersion) has been accurately measured or

calculated, the agreement between the observed specific heat and the specific heat calculated using Eq. (1) is quite good², i.e. the deviations of the measured specific heat from the T^3 limit of Eq. (7) are well accounted for by dispersion in the function $\omega(\vec{k})$.

Our understanding of the low frequency elementary excitation spectra of dielectric crystals has expanded into the area of crystals containing atomic defects. For example, the observed excess specific heat of single crystals containing low concentrations of heavy impurity atoms^{3,4} have been successfully explained by calculations predicting localized vibrational excitations for this system.⁵ Also, the enhancement of the specific heats of alkali halides containing low concentrations of certain defects (e.g. KCl:OH^{-6} and NaBr:F^{-7}) have been explained by models based upon the existence of low lying atomic tunneling states for the defects.⁸

The low temperature thermal conductivity of dielectric single crystals, like the low temperature specific heat, is well understood. Heat transport is due to phonon flow, and the flow can be calculated satisfactorily⁹ using a Boltzmann equation in the relaxation time approximation and the Debye continuum approximation for the phonon density of states. In the general anisotropic system the thermal conductivity is a tensor quantity for which the $(i,j)^{\text{th}}$ term is given by:⁹

$$K_{ij} = \frac{1}{(2\pi)^3} \int_{\lambda} d^3k \tau_{\lambda}(\vec{k}) \frac{(\hbar\omega_{\lambda})^2}{k_B T^2} \frac{e^{\beta\hbar\omega_{\lambda}}}{(e^{\beta\hbar\omega_{\lambda}} - 1)^2} (s_{\lambda})_i (s_{\lambda})_j. \quad (8)$$

Here $\tau_{\lambda}(\vec{k})$ is the relaxation time of the phonon of wave-vector $\vec{k}$, $\omega = \omega(\vec{k})$, λ is the polarization, $\vec{s}_{\lambda}$ is the group velocity of the phonon wavevector $\vec{k}$ (given by $\vec{s}_{\lambda} = \vec{\nabla}_{\vec{k}} \omega(\vec{k})$), and i and j are Cartesian directions.

Eq. (8) is quite complex and doesn't really give much insight. If we simplify this expression to the isotropic case where $v_{\lambda} = \text{constant}$ (i.e. $\omega_{\lambda} = v_{\lambda} k$) then $\tau_{\lambda} = \tau_{\lambda}(\omega)$ and K becomes a scalar and the integral in $\vec{k}$ space can be transformed into ω space. We find then:

$$K = \frac{1}{3} \sum_{\lambda} \int_0^{\omega_D} d\omega v_{\lambda}^2 \tau_{\lambda}(\omega) \frac{\omega^2}{2\pi^2 v_{\text{Deb}}^3} \frac{(\hbar\omega)^2}{k_B T^2} \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}. \quad (9)$$

If we write $\ell_{\lambda}(\omega) \equiv v_{\lambda} \tau_{\lambda}(\omega)$ then

$$K = \frac{1}{3} \sum_{\lambda} v_{\lambda} \int_0^{\omega_D} d\omega \ell_{\lambda}(\omega) g_{\lambda}(\omega) \frac{(\hbar\omega)^2}{k_B T^2} \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2}. \quad (10)$$

Here $g_{\lambda}(\omega)$ is the Debye density of states for one mode, $\ell_{\lambda}(\omega)$ is the mean free path of the phonon of frequency ω and polarization λ . The prediction of the thermal conductivity of a dielectric crystal thus comes down to predicting the frequency dependent scattering rate $\tau_{\lambda}^{-1}(\omega)$. When a number of scattering mechanisms are operative, then the total scattering rate is the sum of the scattering rates of these

mechanisms⁹, i.e.

$$\tau_{\lambda}^{-1}(\omega) = \sum_n \tau_{\lambda n}^{-1}(\omega) \quad (11)$$

Therefore, we also find that:

$$\ell_{\lambda}^{-1}(\omega) = \sum_n \ell_{\lambda n}^{-1}(\omega) \quad (12)$$

The scattering rates of a number of mechanisms have been calculated.^{9,10} These mechanisms include dislocation scattering ($\tau_{\lambda}^{-1}(\omega) \propto \omega$), isotope or point defect scattering ($\tau_{\lambda}^{-1}(\omega) \propto \omega^4$) and boundary scattering ($\tau_{\lambda}^{-1}(\omega) = \text{constant}$) among others. In general, the integral in Eq. (10) (with the scattering rate of Eq. (11)) has to be solved numerically if a number of different scattering mechanisms are important. In systems for which this has been done, the fit to experimental data is good.^{11,12}

However, the numerical solution of the integral does not throw any added light onto the physics of the scattering problem. We therefore go to the dominant photon approximation to make the interpretation of thermal conductivity measurements more straightforward. We note that the integrand in Eq. (10) is a strongly peaked function of ω . The integrand peaks (if $\ell(\omega) = \text{constant}$)⁸ at ω_{dom} where $\hbar\omega_{\text{dom}} = 4.2/\beta = 4.2 k_B T$. If we assume that $\ell_{\lambda}(\omega)$ is sufficiently slowly varying, then we can pull it out of the integral to find:

$$K \approx \frac{1}{3} \int_{\lambda} v_{\lambda} \ell_{\lambda}(\omega_{\text{dom}}) \int_0^{\omega_D} d\omega g_{\lambda}(\omega) \frac{(\hbar\omega)^2}{k_B T^2} \frac{e^{\beta\hbar\omega}}{(e^{\beta\hbar\omega} - 1)^2} . \quad (12)$$

Ignoring the differences between the speed of sound of the different polarizations and the polarization differences of the mean free path we have $v_{\lambda} = v_{\text{Deb}}$ and $\ell_{\lambda} = \ell(\omega_{\text{dom}})$. We also note that the integral in Eq. (12) is just the Debye specific heat of the polarization λ . Therefore we can write:

$$K = \frac{1}{3} v_{\text{Deb}} \ell(\omega_{\text{dom}}) C_{v_{\text{Deb}}} \quad (13)$$

where

$$\ell^{-1}(\omega_{\text{dom}}) = \sum_n \ell_n^{-1}(\omega_{\text{dom}}) . \quad (14)$$

Although Eq. (13) (with the condition of Eq. (14)) is "at best only [of] qualitative significance",⁹ it is a very useful form of the thermal conductivity expression and will be used.

For many atomic defect systems, the scattering properties are relatively well understood^{8,13} just as are the scattering mechanisms in pure single crystals.

While the low temperature thermal properties of dielectric single crystals and dielectric single crystals with low levels of impurities are well understood, the same cannot be said for the low temperature thermal properties of dielectric glasses. The specific heats of all glasses never approach

the Debye limit even for $T/\theta_D \ll .01$.¹⁴ At low temperatures ($T \lesssim 2K$) the specific heats of glasses have the form:^{15,16}

$$C_v = c_1 T + c_3 T^3, \quad (15)$$

where c_3 is larger than c_{Deb} by 20% to 300% depending on the glass. (We also note that in some glasses a small term quadratic in temperature is found in addition to the two terms of Eq. (15).¹⁵) Also at temperatures such that $T \sim 0.01 \theta_D$, the specific heats of glasses deviates earlier from a high temperature T^3 dependence than do single crystals.¹⁵ This behavior is shown in Figure 1 for vitreous SiO_2 and two of the crystalline forms of SiO_2 : α -quartz and cristobalite.¹⁷ It has been demonstrated that the large specific heat at low temperature is not an impurity effect.¹⁵

Besides this anomalous excess specific heat, dielectric glasses also have a characteristic form of the thermal conductivity at low temperatures. In Figure 2 we show the thermal conductivity of a large number of amorphous dielectrics. All these glasses show a plateau in the thermal conductivity at $T \sim 5-20K$. Also, for $T < 1K$, the thermal conductivity obeys the law,

$$K \propto T^\delta \quad (16)$$

where $\delta = 1.9 \pm .1$ for all glasses.^{15,16} Love¹⁸ has demonstrated (with Brillouin scattering) that phonons with

$\frac{\hbar\omega_{\text{dom}}}{k_B} \leq 0.3\text{K}$ ($\nu_{\text{dom}} \sim 20\text{ GHz}$) are well defined propagating excitations and that up to this frequency there is no observed dispersion in the phonon spectrum. Also, it has been demonstrated (with boundary limited conductivity in glass fibers^{15,19}) that phonons carry the heat in glasses for $T < 1\text{K}$ and that these phonons travel at the speed of sound measured at low frequencies ($\nu \sim 10^7\text{ Hz}$). Therefore, the problem in understanding this characteristic thermal conductivity comes down to explaining the form of the scattering rate, $\tau^{-1}(\omega)$ (see Eq. (9)) that gives rise to this conductivity.

The source of the excess low frequency modes and the characteristic phonon scattering rate found in all glasses is a matter of current debate. The theoretical models that have been proposed to account for these features can be broken down into three basic categories: (1) atomic or molecular defect models²⁰⁻²³ (the tunneling model²⁰⁻²² is the best developed theory in this class), (2) "liquid-like" models that propose the existence of large $\vec{k}$, small ω phonon modes^{24,25}, and (3) extended structural defect models. We will not go into a detailed review of the theories in the first two categories (many aspects of the theories of glassy properties are discussed in Ref. 15). However, since the research discussed in this thesis was carried out in an

Figure 1. Specific heat of three different forms of SiO_2 as a function of reduced temperature. For sources of data for α -quartz see Ref. 15. Data for cristobalite from Ref. 17.

Figure 2. Thermal conductivity of a large number of amorphous materials. Data from Ref. 15 and sources quoted therein.

effort to produce "glassy" behavior (or to enhance "glassy" behavior already present) by introducing a large number of extended structural defects into a material, we will discuss the structural defect models of glasses in some detail.

Baltes et al.^{26,27} have proposed a model for the specific heat of glasses based on the elastic excitations of "grains" that are supposedly present in all glasses. Although Baltes²⁷ was logically inconsistent in his application of the results of these calculations to glasses, his original formulation²⁶ does give a good introduction into the area of the elastic vibrations of small particles.

Baltes et al.²⁶ have calculated the vibrational spectrum of an elastic sphere of radius R and speeds of sound $\{v_\lambda\}$. Since small particles have large surface to volume ratios, we expect that surface vibrations (surface phonons) will constitute a large fraction of the low frequency spectrum for small particles, and this is what Baltes found. For $k_B \theta_D \gg k_B T \gg \hbar \omega_c$ ($\omega_c \equiv 2v_\lambda/R$; the significance of ω_c will be discussed later), Baltes et al.²⁶ found that the specific heat of the sphere exceeds the specific heat of a corresponding volume of bulk elastic material and that the excess specific heat of one polarization with velocity v_λ (there are three polarizations) is given by $(\Delta C_{vib_\lambda} = C_{v \text{ grain}_\lambda} - C_{v \text{ bulk}_\lambda})$:

$$\Delta C_{\text{vib}_\lambda} = \frac{1}{6} \frac{k_B^2}{\hbar v_\lambda} \frac{T}{R^2} + \frac{9\zeta(3)k_B^3}{4\pi\hbar^2 v_\lambda^2} \frac{T^2}{R} \quad (17)$$

For the excess heat capacity due to this one polarization we find:

$$\begin{aligned} \Delta C_{H_\lambda} &\equiv \Delta C_{\text{vib}_\lambda} V = \Delta C_{\text{vib}_\lambda} \left(\frac{4}{3} \pi R^3 \right) \\ \Delta C_{H_\lambda} &= \frac{k_B^2 T}{9\pi\hbar v_\lambda} (2\pi R) + \frac{3\zeta(3)k_B^3}{4\pi\hbar^2 v_\lambda^2} T^2 (A) \end{aligned} \quad (18)$$

Here A is the area of the sphere. The first term on the right of Eq. (18) is a "curvature" term and is only important (for 200 Å particles of Al_2O_3) for $T \leq 5\text{K}$ for which we have $k_B T \sim \hbar \omega_c$. The second term on the right is the "surface phonon" contribution and is proportional to T^2 and to the surface area of the sphere.

A number of people have calculated the excess phonon density of states due to the existence of a surface, and the excess heat capacities calculated from these densities of states are comparable to the "surface phonon" term of Eq. (18). Dupuis et al.²⁸ calculated the heat capacity of a thin slab of an isotropic medium and found a T^2 excess heat capacity (proportional to the area of the slab) with a coefficient equivalent (to within 30%) to that in Eq. (18). Chen et al.²⁹ and Alldredge et al.³⁰ have numerically determined the phonon density of states (using lattice dynamical techniques) for 15 layer slabs of alkali halides using

realistic interparticle potentials. They found excess heat capacities that were comparable (to within 30%) in magnitude to the surface phonon term in Eq. (18), although one of the potentials³⁰ produced a non- T^2 temperature dependence at the lowest temperatures ($T \lesssim 4K$).

Although the surface induced excess heat capacities of these slab models are comparable to the asymptotic ($k_B T \gg \hbar \omega_c$) value calculated by Baltes et al.²⁶, the slabs used in the calculations are infinite in two dimensions while the particles in Baltes'²⁶ calculation are finite in all dimensions. Therefore, the phonon density of states found for a slab model is large even for very long wavelengths, but the phonon density of states for a particle goes to zero for phonon wavelengths greater than the particle size. Consequently, the phonon heat capacity of a particle is "cut off" (i.e. goes exponentially to zero) for temperatures such that $k_B T < \hbar \omega_c = \hbar \left(\frac{2v}{R} \right)$. We thus see the significance of the frequency, ω_c , mentioned earlier. Baltes et al.²⁶ took this "cut off" explicitly into account by using the exact summation form for the specific heat (rather than the integral form) and by using the exact vibrational frequencies of the sphere. When applied to the measured heat capacity of Pb and In grains in porous glass³¹, this "cutoff" calculation²⁶ worked rather well.

Baltes²⁷ attempted to account for the linear temperature

dependent term of the excess specific heat of glasses by postulating that all glasses are composed of small ($d \sim 60 \text{ \AA}$) grains. He then ignored the cutoff effect and simply used Eq. (18) down to low temperatures ($T \sim 0.1\text{K}$). The linear term in Eq. (18) dominates at this temperature so that he was able to reproduce the observed¹⁵ excess specific heat. It is difficult to justify the neglect of the cutoff since the wavelength of phonons in this region is quite large, i.e. $\lambda_{\text{dom}} \sim 5000 \text{ \AA} \gg d$.

Jura and Pitzer³² proposed another mechanism for the excess heat capacity of a collection of small particles at low temperatures ($k_B T \ll \hbar \omega_c$) that is more acceptable. They suggested that while the internal vibrational modes of the particle are cut off below ω_c , the particle as a whole may undergo simple harmonic motion. If the forces between particles are sufficiently weak, then the vibrational frequencies of the oscillations would be low enough so that $\hbar \omega_{\text{particle}} \ll k_B T$ for experimentally accessible temperatures T . The heat capacity of these modes will correspond to the Dulong-Petite limit for these vibrations and there will be a constant heat capacity of k_B per particle per mode. There are 6 possible modes (3 rotational and 3 translational) for each particle so that the heat capacity in this model would be a constant $6 k_B$ per particle.

In Figure 3 we plot the specific heat of $200 \text{ \AA} \text{ Al}_2\text{O}_3$

Figure 3. Theoretical specific heat of $200 \text{ \AA}$ Al_2O_3 spheres calculated by adding the specific heat of the internal elastic vibrations of the sphere (see Ref. 26) to the specific heat of the external harmonic motion of the spheres (see Ref. 32).

spheres calculated by adding the constant heat capacity of $6 k_B$ per particle suggested by Jura and Pitzer³² to the cutoff internal heat capacity (using $v_\lambda = v_{\text{Debye crystal}} = 7.1 \times 10^5$ cm/sec for all three polarizations) suggested by Baltes et al.²⁶ We note that the constant $6 k_B$ per particle is only an upper limit for the heat capacity of these external vibrations since the binding forces may be strong enough to make some of the vibrational frequencies high enough so that $\hbar\omega_{\text{particle}} \sim k_B T$. If this is the case, then the heat capacity of these external oscillations will be less than the upper limit of $6 k_B$ per particle.

While Baltes²⁷ and Jura and Pitzer³² did not attempt to determine the thermal conductivity of their granular systems, a number of people have calculated the thermal conductivity of isotropic materials with speed of sound/density fluctuations. Klemens^{33,34} derived an expression for the scattering of phonons due to variations in the speed of sound as a function of position in an isotropic material. If $v(\vec{x})$ is the speed of sound in the material at point $\vec{x}$, then the deviation of v from the mean speed of sound, $\bar{v}$, is given by $s(\vec{x}) \equiv v(\vec{x}) - \bar{v}$. The correlation function, $f(\vec{r})$, that describes these fluctuations is given by

$$f(\vec{r}) \equiv \frac{1}{V} \frac{1}{s^2} \int_V d^3x s(\vec{x}) s(\vec{x} + \vec{r}) \quad (19)$$

Here V is the volume of the sample and $\overline{s^2}$ is given by

$$\overline{s^2} = \frac{1}{V} \int_V d^3x s^2(x) . \quad (20)$$

For the case of spherically symmetric correlations with a characteristic length a , we use the correlation function $f(\vec{r}) = f(r) = e^{-r/a}$ (the exact form of the correlation function is not as important as the existence of a characteristic length, i.e. we could use any one of a number of expressions³⁵⁾ and we find for the scattering rate for phonons of wavevector k

$$\tau^{-1}(k) = \overline{v} \frac{48\pi}{a} \frac{\overline{s^2}}{\overline{v}^2} \ln(1 + 4k^2 a^2) - \frac{4k^2 a^2}{4k^2 a^2 + 1} . \quad (21)$$

In the limit that the characteristic length of the fluctuations is much smaller than the phonon wavelength (i.e. $a \ll \lambda$ or $ka \ll 1$) we find that (also noting that $\omega = \overline{v}k$):

$$\tau^{-1}(\omega) = 48\pi \frac{\overline{s^2}}{\overline{v}} \frac{\omega^4 a^3}{\overline{v}^3} . \quad (22)$$

This equation has the form of Rayleigh scattering from a collection of mass defects of volume a^3 with the mass mismatch and concentration of defects contained in the term $(\frac{\overline{s^2}}{\overline{v}^2})$. However, the numerical coefficient is off by four orders of magnitude since the mass defect scattering is given by:^{14,34}

$$\tau^{-1}(\omega) = r \frac{\omega^4 V_0}{4\pi v^3} \quad (23)$$

Here V_0 is the volume of the defect and r is the mass mismatch and concentration dependent coefficient given by:¹⁴

$$r = \sum_i f_i \left(1 - \frac{m_i}{m}\right) \quad (24)$$

Here m_i is the mass of the i^{th} defect, f_i is the fraction of the i^{th} defect and m is the average mass. It is not clear why Klemens' simple expression for the scattering rate is so much larger than the straightforward Rayleigh scattering expression. A change in the form of the correlation function will not remedy the problem. In fact, while Eq. (23) (with $r = 1$ and $V_0 =$ the molecular volume) works quite well in describing the plateau in the thermal conductivity of glasses, the same calculation with Eq. (22) gives a value that is three orders of magnitude too small if we choose $\frac{s^2}{v^2} \sim 1/2$.

Morgan and Smith³⁵ have carried out a calculation for the phonon scattering rate due to density fluctuations using a simple, isotropic model³⁶ of a disordered solid that contains only one kind of atom. They numerically solved their equations using a density-like fluctuation correlation function $f(r) = e^{-r/a}$ where

$$f(r) = \frac{1}{V} \frac{1}{\Delta^2} \int_V d^3x \Delta(\vec{x}) \Delta(\vec{x} + \vec{r}) \quad (25)$$

and $\Delta(\vec{x}) = \gamma(\vec{x}) - 1$. $\gamma(\vec{x})$ is roughly proportional to the density of the material ($\gamma(\vec{x}) \equiv 1$ for a material with no density fluctuations) and $\Delta^2 = \frac{1}{V} \int_V d^3x \Delta^2(x)$. They evaluated the scattering as a function of k and found³⁶ a scattering rate with a k dependence very similar to that of Eq. (21).

However, the strength of the scattering was three or four orders of magnitude lower than Eq. (21). Morgan and Smith³⁶ state that the phonon scattering "results from the spatial fluctuations of the local frequency about its average value." This scattering mechanism is identical to that proposed by Klemens^{33,34}, but the three order of magnitude discrepancy in scattering rates predicted by the two calculations indicates differences in the models whose origins are obscure at present. Examination of the curves presented by Morgan and Smith³⁶ indicate that their model predicts a long wavelength scattering rate comparable to Eq. (23), the Rayleigh scattering form.

In order to account for the form of the thermal conductivity of glasses, Morgan and Smith³⁶ require that there be fluctuations with two characteristic lengths: one small ($a \sim 5 \text{ \AA}$) and one large ($a \sim 1000 \text{ \AA}$). The small correlation length fluctuations account for the plateau (as they do in the calculation of Zeller and Pohl¹⁴) at $T \sim 5\text{-}10\text{K}$ while the large correlation length fluctuations account for the low temperature T^2 temperature dependence. The magnitude of

the fluctuations for the short correlation length are described by $\Delta^2 \sim 0.3$ which is in reasonable agreement with the value of $r = 1$ that was used by Zeller and Pohl.¹⁴ However, for the case of the long correlation length ($a \sim 1000 \text{ \AA}$) Morgan and Smith³⁶ require $\Delta^2 \sim 0.01$. This value of Δ^2 implies that $\gamma(\vec{x}) - 1 = \Delta(\vec{x}) \sim 0.1$, i.e. that density fluctuations on the order of 10% exist in glasses for distances on the order of $1000 \text{ \AA}$. Klemens³⁴ fares better in this region since he only requires $\frac{s^2}{v^2} \sim 10^{-5}$ for $a \sim 1000 \text{ \AA}$. However, as we mentioned earlier, Klemens³⁴ cannot hope to fit the high temperature regime with reasonable values of $\frac{s^2}{v^2}$.

Lu and Nelkin³⁷ have proposed an extended linear defect model to explain the low temperature thermal properties of glasses. Noting that the thermal conductivity of a dislocation in a crystal goes like T^2 ^{9,38} and that the specific heat of a linear defect in a crystal has been theoretically shown to be linear in temperature,³⁹ they suggested that such linear defects exist in glasses (although they do not have any physical model for what a "dislocation" in a glass actually is). A more detailed atomic model of dislocations⁴⁰ in crystals lends support to the existence of the excess modes⁴⁰ for dislocations in crystals.

This model of a glass requires that the defect be longer than thermal wavelengths since the excitations responsible for the excess specific heat are essentially long wavelength,

longitudinal vibrations of the linear defect. These excitations have a dispersion relation given by:³⁹

$$\omega^2 = v^2 k_z^2 - \omega_0^2 \exp(-4\pi v^2 / k_z^2 V_0) \quad (26)$$

Here V_0 is the perturbation due to the defect, ω_0 is a constant on the order of ω_D , and v is the velocity of sound of the bulk unperturbed medium. For small k_z , the second term on the right of Eq. (26) is small and we have $\omega \approx vk_z$. This model requires a density of about 4×10^{10} defects/cm² to explain the specific heat of SiO₂. This model has no explanation of the excess T^3 specific heat of glasses and for sufficiently high densities of linear defects they should interact and the linear term should go to zero at a measurable temperature. With a density of 4×10^{10} defects/cm², Lu and Nelkin³⁷ require that the "Burgers vector" of the linear defect be $\sim 5 \text{ \AA}$ if recent calculations⁴¹ of the scattering cross section of dislocations are applicable to "dislocations" in glasses. To date, there has been no observation of linear defects in glasses.

III. SAMPLE PREPARATION AND CHARACTERIZATION

A. Pressed Powders and Sintered Ceramics

The fabrication of a dense polycrystalline ceramic typically follows three steps:⁴² (1) production of a finely divided powder, (2) consolidation of the powder into a porous compact (usually with about 50% open volume) at room temperature, and (3) densification of the compact into a low porosity solid by heat treatment (sintering). Certain variations on this procedure (high pressure hot pressing⁴³ and explosive compaction, for example) will compact and consolidate the powder in a single step. We will discuss the steps of this three-step process (and variations on it) as they pertain to the materials we have studied.*

(1) Powder Production and Characterization

The ceramic materials we were most interested in are the refractory oxides such as SiO_2 , Al_2O_3 and MgO . Ultrafine oxide powders are usually prepared by calcining (heating) an appropriate precursor salt⁴³ (e.g. $\text{MgO}(\text{OH})$ or $\text{Al}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) at temperatures ranging from about 500°C to

* For good discussions of present theoretical concepts concerning these three steps in ceramic forming see articles in Refs. 45-48. For a complete discussion of the problems associated with production of a typical fine grain ($d < 1\mu$) ceramic see Refs. 49 and 50.

1200°C. The thermal decomposition of the salt causes a large change in specific volume so that a large number of oxide nuclei are formed during the decomposition. Small particles are left if these nuclei are not allowed to grow.⁵¹ Particle size is controlled by the temperature and length of time of the calcination⁵¹ as is the crystal phase of the oxide (for oxides with more than one possible crystal phase).

Another technique used for powder manufacture is the hydrolysis and/or oxidation of the appropriate metallic chloride in an oxygen-hydrogen flame.⁵²⁻⁵⁴ For example, we have the reaction $4\text{AlCl}_3 + 3\text{O}_2 \rightarrow 2\text{Al}_2\text{O}_3 + 6\text{Cl}_2$ and the reactions $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ and $3\text{H}_2\text{O} + 2\text{AlCl}_3 \rightarrow \text{Al}_2\text{O}_3 + 6\text{HCl}$. The oxides that are produced in this vapor process form small particle aerosols. The particle size (which can be varied from about 80 Å to about 1500 Å) and crystal structure (for materials with more than one crystal structure) depend upon the temperature of the flame, the density of the reactants in the flame, and the residence time of the reactants in the flame.^{53,55,56} This technique is used on an industrial scale to produce tonnage quantities of SiO_2 , TiO_2 , and Al_2O_3 ,^{52,57} and on a laboratory scale to produce 100 gram size quantities of Fe_2O_3 , GeO_2 , and ZrO_2 .⁵³

The oxide powders used to produce the ceramic samples we have studied were produced by the above two techniques. The Cabosil (SiO_2) and Alon (Al_2O_3) powders were produced by the

hydrogen-oxygen flame process while the rest of the powders were produced by calcining salts. In Table I we list the powders used in our experiments and the characteristics relevant to our work. We note that the bulk density of the powders as received was quite low and that the surface areas of these small particle materials is quite high.

The particle sizes were determined by transmission electron microscopy (by the manufacturers and by K. Pohl). Particle size distributions were not determined, but examination of the electron micrographs indicated that the distribution function is relatively narrow, i.e. a half width of about 50-100 Å in the case of the .02 μ (200 Å) Al₂O₃ powders. The surface areas (measured by the manufacturers) were determined by nitrogen adsorption techniques.⁶⁰ The metallic impurity level was determined by the manufacturers using emission spectrography.

The crystal structure of the particles was determined by x-ray powder techniques by the manufacturers. γ -Al₂O₃ is a transition form of Al₂O₃⁶¹ that exists only as very small particles. γ -Al₂O₃ transforms to α -Al₂O₃ at temperatures greater than about 1100°C.⁶¹⁻⁶³ γ -Al₂O₃ has a cubic crystal⁵⁷⁻⁵⁹ structure while α -Al₂O₃ has a hexagonal crystal structure. The crystal density of γ -Al₂O₃ is about 3.8 gm/cm³ (an uncertainty exists due to the experimental uncertainties in the lattice constants⁶¹) while the density

Table I. Powder Characteristics

Material	Chemical Composition	Particle Size	Surface Area	Crystal System	Metallic Impurity Level (Manufacturer's specifications)	Bulk Density (% of solid density)
Linde B ⁵⁸	Al ₂ O ₃	.02μ	100±20 m ² /gm	γ-Al ₂ O ₃ Cubic	.02%	5%
Gamma-Exal ⁵⁹	Al ₂ O ₃	.02μ	100±20 m ² /gm	γ-Al ₂ O ₃ Cubic	.02%	5%
Alon ⁵⁷	Al ₂ O ₃	.02μ	100±20 m ² /gm	γ-Al ₂ O ₃ Cubic	1%	2%
Linde A ⁵⁸	Al ₂ O ₃	.3μ	15±3 m ² /gm	α-Al ₂ O ₃ Hexagonal	.02%	15%
Linde C ⁵⁸	Al ₂ O ₃	1μ	3±1 m ² /gm	α-Al ₂ O ₃ Hexagonal	.02%	15%
Cabosil ⁵⁷ EH5	SiO ₂	.007μ	390±40 m ² /gm	Amorphous	.05%	2%

of single crystal α - Al_2O_3 is 3.98 gm/cm^3 . Finally, Larch⁶⁴ has shown (with neutron diffraction) that small SiO_2 particles produced by the hydrolysis of SiCl_4 have an amorphous structure that is similar to that of bulk fused quartz but must have certain differences since there are noticeable differences in the diffraction patterns of the two materials.

One characteristic of these powders that we have not discussed is their tendency to agglomerate, i.e. they form aggregates during the powder production process, and these aggregates are difficult to break down. Such aggregates are readily observed in transmission electron micrographs of these powders. For all of the $.02\mu \text{ Al}_2\text{O}_3$ powders, the agglomerates are of the order of $.3\mu$ in diameter. These agglomerates affect the consolidation of the powders into compacts as well as the sinterability of the compacts. These effects will be discussed later.

(2) Powder Consolidation

Oxide powders are usually consolidated at room temperature in two ways:⁴⁹ (1) by the application of pressure-- either unidirectionally (as in die pressing) or hydrostatically (as in pressing on a bag containing the powder in a hydraulic high pressure cell) and (2) by the removal of liquid from a liquid-powder suspension. The samples we have studied were produced by die pressing and pressure slip-casting (one variation of the liquid removal process).

Die Pressing

The die pressing was carried out using a 100-ton hydraulic press (at Bard Hall), a cylindrical 2.54 cm diameter steel die and ram, and a tungsten carbide bottom plate. A schematic drawing of the press is shown in Figure 4a. Figure 4b shows an enlarged view of the die, ram, and bottom plate configuration near the die wall. The following procedure was used to press samples: (1) The surfaces of the steel die, the steel ram, and the tungsten carbide bottom plate were abraded with 600A silicon carbide emery paper before each set of pressings (and whenever powder bonded to the walls of the die) and were then cleaned with acetone. (2) A small amount ($\lesssim 1$ mg) of silicone grease (Dow Corning Stopcock Grease) was rubbed onto the surfaces to act as a lubricant and to prevent powder from binding to the surfaces.⁶⁵ (3) A measured amount of powder (typically .9 gm for Linde B, Alon, and Gamma-Exal powders; .6 gm for Cabosil powder; and 3 gm for Linde A and Linde C powders) was then put into the die and the ram was inserted. (4) 153,000 psi of pressure was then applied to the powder (60 tons of force on a 1-inch diameter ram) building up from 0 pressure to full pressure in about 30 seconds. (5) The sample was left under pressure for about three minutes.⁶⁶ (6) The pressure was then released and allowed to go to 0 psi in about 10 seconds. (7) The ram and die were lifted

Figure 4. Schematic diagram of the steel die, steel ram, and tungsten carbide bottom plate used to prepare pressed samples.

from the bottom plate and the sample was removed. All of the surfaces were then cleaned with acetone and steps (2) through (7) were followed to produce the next sample. The first two samples pressed during a sequence of pressings were always discarded in case any impurities had been left in the die even after cleaning it with emery paper and acetone.

The $.02\mu \text{ Al}_2\text{O}_3$ and the $.007\mu \text{ SiO}_2$ compacts were typically ~ 1 mm thick and typically weighed 1.3 gm and .7 gm respectively. For these materials the sample either dropped out when the die was lifted off of the bottom plate or was only lightly attached to the die walls and could be pulled off with tweezers. The Linde A and Linde C samples were typically 3 mm thick, weighed 3.5 gm, and had to be forced out of the die. This was accomplished by pressing on the ram after the bottom plate had been removed.

The $.02\mu \text{ Al}_2\text{O}_3$ samples and the $.007\mu \text{ SiO}_2$ samples were quite hard and translucent. The SiO_2 samples were somewhat more transparent. The Linde A and Linde C samples were totally opaque and chalky. The density of a sample was determined from the mass of the sample (measured after vacuum outgassing at $T = 600^\circ\text{C}$ to drive off adsorbed water vapor) and the measured dimensions of the sample. The densities are tabulated in Table II.

Table II. Pressed Powders

Material	Chemical Composition	Particle Size	Density	Single Crystal Density
Pressed Linde B	$\gamma\text{-Al}_2\text{O}_3$	.02 μ	.50 ρ_{crys}	3.8 gm/cm ³
Pressed Gamma Exal	$\gamma\text{-Al}_2\text{O}_3$	.02 μ	.51 ρ_{crys}	3.8 gm/cm ³
Pressed Alon	$\gamma\text{-Al}_2\text{O}_3$	.02 μ	.49 ρ_{crys}	3.8 gm/cm ³
Initially Sintered Pressed Linde A	$\alpha\text{-Al}_2\text{O}_3$	.3 μ	.56 ρ_{crys}	3.98 gm/cm ³
Initially Sintered Pressed Linde C	$\alpha\text{-Al}_2\text{O}_3$	1.0 μ	.58 ρ_{crys}	3.98 gm/cm ³
Pressed Cabosil	Amorphous SiO ₂	.007 μ	.53 ρ_{vit}	2.20 gm/cm ³

Die pressing ultrafine ceramic oxide powders presents a number of problems.⁶⁷ First, laminations in the material perpendicular to the direction of applied pressure (i.e. in a plane parallel to the ram face and the surface of the bottom plate) are formed at the high pressures required to produce a solid compact. Second, at these pressures the powder compact adheres to the walls of the die and to the face of the ram even with the silicone grease film applied. It has been proposed⁶⁸ that these defects arise from residual shear elastic stresses, die wall friction and the pressure gradients in the material during pressing.

For thick ($t > 1.5$ mm) samples of the $.02\mu$ Al_2O_3 powders and the $.007\mu$ SiO_2 powder, these two problems combined to cause the compacts to disintegrate when we attempted to remove them from the die. The edges of the compact adhered to the die walls and the compact would not fall out easily. If pressure was applied to the ram to remove the sample, the sample shattered into small plate-like pieces (~ 2 mm across by $\sim .1$ mm thick) combined with a fine powder. Increasing the length of time under pressure from 3 minutes to 8 hours did not alter this behavior.

It has been suggested⁶⁹ that usable thin compacts of these very fine powders could be produced because of the existence of the curved die wall and the imperfect seal at the die-bottom plate interface (see Figure 4b). This poor

seal (a small amount of powder was observed to puff out during the initial rise of pressure for a number of samples) could allow shear stresses to be relieved by expansion of the powder into the interface between the die edge and the bottom plate. This hypothesis is supported by the observation that all good compacts had a powdery rim (≈ 1 mm) around their entire circumference.

A lamellar structure still existed in these samples, however, although the lamellae were bonded together strongly enough to prevent the material from shattering. In Figure 5a we give a sketch of the appearance of one of the $.02\mu$ Al_2O_3 samples. Laminations were obvious at the edge of the disks, but if the disks were broken in the center, they broke cleanly with no laminations apparent. Also, thermal conductivity measurements indicated that the materials were highly anisotropic. In Figure 6 we show the thermal conductivity of pressed Linde B ($.02\mu$) and pressed Cabosil ($.007\mu$) in the direction of the pressure axis and in the direction perpendicular to the pressure axis. As can be seen, the thermal conductivity through the laminations is considerably lower than the conductivity parallel to the laminations.

The Linde A ($.3\mu$) and Linde C (1μ) compacts did not have as serious a problem with laminations and adhesion to the walls as did the finer powder compacts. Thick samples

(a)

(b)

Figure 5. Schematic diagram showing the typical appearance of (a) a pressed Gamma Exal ($.02\mu$), Linde B ($.02\mu$) or Cabosil ($.007\mu$) sample and (b) a pressed Linde A ($.3\mu$) or Linde C (1.0μ) sample.

Figure 6. Thermal conductivity of pressed Linde B ($.02\mu$) and pressed Cabosil ($.007\mu$) samples perpendicular and parallel to the laminations in the samples.

($t \sim 3$ mm) could be pressed out of the die without any trouble, and the edges did not exhibit the powdery rim seen from the finer powder samples. However, the compacts did laminate, but they only laminated into two pieces. We show a sketch of the shape of a typical Linde C (1μ) sample in Figure 5b.

No attempt was made to deagglomerate the materials before pressing. Typical techniques to break down agglomerates (ball milling for example) were thought to offer too much of a chance for the introduction of impurities. The aggregate structure was therefore present in the pressed specimens⁴⁹ and affected the density of the compacts. The higher the degree of agglomeration, the lower the pressed density (a totally deagglomerated powder typically has a compacted density 5 to 10% greater than that of the agglomerated powder⁵⁰).

In Figure 7 we show scanning electron micrographs⁷⁰ of a freshly fractured surface (perpendicular to the plane of the disk sample--parallel to the pressure axis) of a pressed Linde B ($.02\mu$) sample. The grainy agglomerate structure ($d \sim .1-.3\mu$) is clearly visible in Figure 7b. Figure 7a shows some of the lamellar structure.

Pressure Slipcasting

The technique of pressure slipcasting offers a number of advantages over die pressing. The pressure slipcasting

Figure 7. Scanning electron micrographs of freshly fractured surfaces of a pressed Linde B ($.02\mu$) sample.

process consists of the following steps:⁷¹ (1) The powder is first suspended in a solution of water and a deflocculent (an electrolyte). The electrolyte forms an electrical double layer on the surface of the particles causing them to repel each other and to deagglomerate.⁵⁰ Control of the concentration of the deflocculent and the weight percent of powder to water controls the amount of deagglomeration and particle repulsion. Centrifugation of the suspension is used to separate out the remaining agglomerates (which are heavier) to leave a highly deagglomerated material. The centrifuged suspension (or slip) is then placed in a sealed container with a microporous filter at one end. N_2 gas (at a pressure of 50 to 700 psi) is introduced into the container and forces the liquid through the microporous filter. The powder particles are too large to pass through the filter and they form a cake as the water is forced out. The cake is relatively dense but is structurally weak⁷² and must be fired before it can be handled.

The slipcasting of our powders was performed by R. Klug and C. Scott at Alfred University. The deflocculent used was Darvan C⁷³ (an ammonium polyelectrolyte). The suspensions were typically 10-20% by weight solid with the rest water. Slipcast specimens of two of our powders (Linde A ($.3\mu$) and Linde B ($.02\mu$)) were made. A sample of slipcast Y_2O_3

stabilized ZrO_2 (with a particle size of $.06\mu$) was obtained from P. Reith⁴⁹ who has studied the ceramic properties of this material extensively.⁷⁴ In order for these specimens to be handled without breaking they had to be sintered. As received from Alfred University, the ZrO_2 sample had been fired at 1000 C for one hour and the Linde B ($.02\mu$) and Linde A ($.3\mu$) samples had been fired to 900°C for 30 minutes.

The Linde A and ZrO_2 powders produced nice cakes which sintered satisfactorily. However, the Linde B sample was observed to expand about 40% during the firing.⁷⁵ The reason for this expansion is not known. An electron micrograph of this Linde B sample is shown in Figure 12a. As can be seen, an agglomerate structure still existed in this sample and might have been responsible for this anomalous behavior.

The densities of the specimens as received are shown in Table III.

Table III. Slipcast Materials

Material	Chemical Composition	Particle Size	Sample Density	Single Crystal Density
Linde B	Al_2O_3	$.02\mu$	$.21 \rho_{\text{crys}}$	3.8 gm/cm^3
Linde A	Al_2O_3	$.3\mu$	$.41 \rho_{\text{crys}}$	3.98 gm/cm^3
Zyttrite	$\text{ZrO}_2 + 6 \text{ mole } \% \text{ Y}_2\text{O}_3$	$.06\mu$	$.42 \rho_{\text{crys}}$	6.02 gm/cm^3

(3) Compact Sintering

Sintering of a porous powder compact consists of heating it to a sufficiently high temperature that densification, pore shrinkage, and particle grain growth occur. The sintering of a powder compact into a fully dense polycrystalline ceramic at a temperature T has three stages:⁷⁶ (1) An initial stage takes place first in which densification occurs by formation and growth of necks between adjacent particles. Initial stage sintering proceeds with no grain growth and accounts for the first 2-4% shrinkage of the compact. The rate of shrinkage at a given temperature in this initial stage varies roughly as $R^{-3/2}$ ⁷⁶ where R is the radius of the particles. (2) An intermediate stage occurs next during which "pore shape does not change but the structure evolves by pore shrinkage and grain growth".⁷⁶ Intermediate stage sintering accounts for densification of the body to about 85% of the density of single crystals. (3) A final stage of sintering takes place after the transition from a continuous pore phase to a discontinuous pore phase which occurs at a density of around 85% that of the single crystal. Densification occurs by pore shrinkage (as in the intermediate stage). However, the disappearance of pores eliminates their effectiveness in limiting grain growth so that in the final stage of sintering (when $\rho \rightarrow 100\% \rho_{\text{crys}}$) exaggerated grain growth can take place (as can exaggerated

pore growth⁷⁷). Production of a fine grain ($d < 1\mu$), very dense ($\rho > 99\% \rho_{\text{crys}}$) ceramic is therefore a tricky business and usually requires special processing techniques.

While these general features characterize the sintering process of all materials, the kinetics associated with the densification and grain growth of a particular compact and the morphology of the final solid body depend critically on the nature of the particular compact and the nature of the firing schedule. During sintering, five mechanisms are presumed to be operative:⁷⁸ (1) surface diffusion, (2) grain boundary diffusion, (3) lattice diffusion, (4) evaporation and condensation, and (5) plastic flow. The dominant mechanism (or mechanisms) depends on the material being sintered as well as the stage of sintering. Also, the operative mechanisms are strongly influenced by a whole host of parameters⁷⁹ which include the sintering atmosphere, the presence of impurities or dopants, the temperature, the presence of agglomerates, the initial density of the material, etc. In fact, there are so many parameters that can affect the sinterability of a material that predicting the detailed behavior of a given compact from first principles is impossible.

We have sintered a number of our samples to increase their density and strength and (in three cases) to increase their grain size. The sintering was carried out in a

crystal furnace (used by T. McNelly) located in the Cornell Crystal Growing Facility. A schematic diagram of the furnace is shown in Figure 8. All of the sinterings were done in vacuo in alumina or fused quartz beakers. The temperature was monitored using a Pt-Pt + 13% Rh thermocouple that was placed on top of the sample. A Mo shield was placed outside the graphite shield in order to increase the maximum temperature of the furnace.

Initially, all of the samples were heated to 850°C and allowed to remain at that temperature for two hours to outgas--in particular to drive off the monolayer of water vapor present on the surface of the particles. After the samples had outgassed, the temperature was raised at a rate of 600°C/hr to the temperature chosen for sintering of the particular sample in the furnace. After the sintering was completed, the temperature was lowered at a rate of 600°C/hr until a temperature of about 850°C was reached. At this point, the furnace was turned off and allowed to cool at its own rate.

Shrinkage of a sample was determined by measuring the distance between two marks on its surface before and after heat treatment using the Unitron micrometer microscope in the Technical Operations Laboratory. The distance was typically 2.2 cm and the uncertainty in the separation of the marks was ± 0.002 cm. The density of fully sintered

Figure 8. Schematic diagram of crystal furnace used to heat samples.

samples was determined using Archimedes' principle.

The materials selected for sintering were pressed samples of Linde B ($.02\mu$), Linde A ($.3\mu$), Linde C (1μ) and Cabosil ($.007\mu$) and slipcast, prefired samples of Linde A ($.3\mu$) and Linde B ($.02\mu$). Sintering studies have been carried out by other workers for Linde A^{67,80-82} and Linde B⁶⁷ as well as a number of other Al_2O_3 powders including $\gamma-Al_2O_3$ powders.^{56,83-85} Sintering of small glass particles has also been studied previously.⁸⁶

Linde A

Both the pressed and slipcast Linde A ($.3\mu$) samples were sintered only to improve the compact strength and to increase the interparticle bonding. Therefore, the heat treatment only produced initial stage sintering. The Linde A samples were sintered at $1150^\circ C$ for two hours. The shrinkage was 1.6% for the pressed Linde A sample and 2.2% for the slipcast sample. This is somewhat larger than that observed by Cobb.⁸¹ No electron micrographs were taken of these samples.

Linde C

Pressed Linde C (1μ) samples were sintered at $1150^\circ C$ for two hours. The shrinkage was 1.1%. No electron micrographs were taken of these samples.

Pressed Linde B

A number of die pressed Linde B ($.02\mu$) samples were fired into the final stage of sintering in order to produce very

dense, fine grain ceramic bodies. Unfortunately, we were unable to produce a material with both $\rho > 98\% \rho_{\text{crys}}$ and $d < .5\mu$. Very large grain ceramics were readily produced. We sintered pressed Linde B samples at 1800°C in vacuo for four hours in the high temperature Centorr furnace at the Cornell Crystal Growing Facility (after first densifying them at 1450°C in vacuo for two hours in the low temperature furnace). The microstructure consisted of $15\text{-}30\mu$ size grains with $1\text{-}2\mu$ size pores trapped inside the grains and at the grain boundaries. In Figure 9a we show a scanning electron micrograph of a freshly fractured surface of this sample. A sintering at $T = 1500^\circ\text{C}$ for three and a half hours produced a duplex grain structure with $1\text{-}2\mu$ size grains imbedded in a matrix of $10\text{-}20\mu$ size grains. A large number of trapped pores were also present. An electron micrograph of this sample is shown in Figure 9b.

It has been shown that⁸⁶ a heating schedule different from the conventional time-temperature schedule (a linear heating rate to a maximum temperature and then a "soak" period of 1-4 hours at this maximum temperature) can produce relatively dense samples (from pressed compacts) with fine microstructures without a duplex grain structure. Huckabee and Palmour⁸⁶ developed a firing schedule for Al_2O_3 using the concept that the density of the sample (rather than the sample temperature) should be controlled as a function of

(a)

(b)

Figure 9. Scanning electron micrographs of fracture surfaces of: (a) a pressed Linde B sample sintered at 1800°C and (b) a pressed Linde B sample sintered at 1500°C (see text).

time. Even for reasonably smooth density vs. time curves, they found that relatively complex temperature vs. time curves were required. We have used a firing schedule (shown in Figure 10) that is similar to a schedule (labeled "linear-linear-log"⁸⁶) which produced a highly dense, fine grain structure.

For one sample of pressed Linde B we carried out the sintering to a maximum temperature of 1490°C after reaching this point the temperature was reduced at a rate of 600°C/hr. A micrograph of a freshly fractured surface of this sample is shown in Figure 11a. For a second sample of pressed Linde B we followed the schedule of Figure 10 to a maximum temperature of 1395°C after which the temperature was reduced at a rate of 600°C/hr. A micrograph of this sample is shown in Figure 11b. The density of the low temperature sample was $.90 \rho_{\text{crys}}$ and the density of the high temperature sample was $.958 \rho_{\text{crys}}$. These densities are lower than those found by Huckabee and Palmour⁸⁶ for their samples.

Slipcast Linde B

The slipcast Linde B sample was heated from 850°C to 1100°C at a rate of 600°C/hr and then cooled immediately at 600°C/hr. This initial stage sintering was carried out only to improve the strength of the sample and to increase the interparticle bonding. A 1.0% shrinkage was observed. The density of the sample was $.22 \rho_{\text{crys}}$. An electron micrograph

Figure 10. Sintering schedule used to produce the ceramic microstructures shown in Fig. 11. This schedule was derived from the work of Huckabee and Palmour (see Ref. 86).

(a)

(b)

Figure 11. Scanning electron micrographs of fracture surface of sintered Linde B samples produced following the firing schedule of Fig. 10. (a) Sample 1 - maximum temperature 1490°C, (b) Sample 2 - maximum temperature 1400°C.

of this sample is shown in Figure 12b. Comparison of Figure 12b with Figure 12a (the as-received sample) shows that the sintering did not significantly change the microstructure. In particular, the agglomerate structure was still present.

Coors Ceramic

We obtained an Al_2O_3 ceramic (Ad999) from the Coors Porcelain Co.⁸⁷ It had been fabricated from a die pressed compact of a $.2\mu$ powder and organic binder.⁸⁷ Its density was $.998 \rho_{\text{crys}}$. A scanning electron micrograph of this sample is shown in Figure 13. It has a grain size of about 3μ .

Figure 12. Scanning electron micrographs of fracture surfaces of (a) slipcast Linde B ($.07\mu$) as received and (b) slipcast Linde B ($.07\mu$) fired to 1100°C .

Figure 13. Scanning electron micrograph of a fractured surface of the Coors Al₂O₃ ceramic.

(4) High Pressure Hot Pressing

As mentioned earlier, ceramics are often fabricated with a process that combines the steps of consolidation and densification. The most common technique of this type is high pressure hot pressing, i.e. the application of pressure and heat at the same time.⁸⁸ This technique has had the greatest success in maintaining fine grain size while at the same time producing dense specimens.⁸⁹

We have obtained from T. Vasilos⁹⁰ a specimen of high pressure hot pressed (HPHP) MgO that had been pressed at 250,000 psi at 900°C for 10 minutes.⁹¹⁻⁹³ The starting powder had a particle size of about $.04\mu$ ($400 \text{ \AA}$) and the pressed sample had a grain size of about $.06\mu$ ($600 \text{ \AA}$) as determined by transmission electron microscopy⁹³ ($.04\mu$ grain size with X-ray line broadening⁹³). The sample was essentially fully dense.⁹¹ Transmission electron micrographs can be found in Ref. 93.

We looked into the possibility of doing high pressure hot pressing at the high pressure facilities at Battelle Memorial Institute.⁹⁴ However, the cost was quite high (i.e. \$4,449 for up to 30 samples⁹⁵), and there was no conclusive evidence that satisfactory samples would be produced. Therefore, this area was not pursued.

(5) Explosive Compaction

A final technique we considered was explosive compaction, i.e. compressing a powder into a stainless steel can, wrapping an explosive charge around it, and detonating the charge.^{96,97} This process has been used to compact and densify a large variety of materials (such as Be_2O_3 ⁹⁷ and BaTiO_3 ⁴⁴) to densities $\rho > 96\% \rho_{\text{crys}}$. However, no work has been reported on ultrafine ($d < 1\mu$) grain samples. Battelle Memorial Institute⁹⁴ has facilities for carrying out this process, but cost estimates (i.e. \$4,898 for 30 samples⁹⁵) were too high when measured against the uncertainty of the project to make it worthwhile. This program was not carried farther.

B. Recrystallized Glasses

"Glass is metastable with respect to crystal phases at temperatures below its equilibrium liquidus temperature ... Glasses can form because the rate of crystallization is slow."⁹⁸ With proper heat treatment, crystallization can take place in any glass forming system although the observed rate may be quite slow.⁹⁸

The formation of highly crystallized (>95% crystal) materials from glasses has been extensively studied in the past few years.^{98,99} A lot of progress has been made in understanding the dynamics and morphologies of these materials. Crystallization proceeds by nucleation and growth of crystal phases.⁹⁸ Recent advances in the production of very fine grain recrystallized glasses have been made with control of the nucleation stage. Creation of a large density of nucleation sites for the growth of crystal phases allows nearly complete devitrification to take place with the crystallites remaining quite small.

One of the most extensively studied crystallizing glass systems (and one of the most important commercially) is the $(\text{MgO}, \text{LiO}_2)\text{-Al}_2\text{O}_3\text{-SiO}_2$ system with TiO_2 and/or ZrO_2 as nucleating agents.¹⁰⁰⁻¹⁰⁷ The sequence of events (which takes place at temperatures well below the melting point) in the formation of glass-ceramics from the quenched glass is generally believed to be the following:¹⁰⁵ (1) amorphous

phase separation^{106,107}, (2) formation of crystalline nuclei^{106,107} (titanates and/or zirconates), (3) nucleation and growth of a silica based, metastable crystal phase on the titanate or zirconate nuclei¹⁰³, and (4) crystal phase transformation and grain growth of a stable, silica based crystal phase.^{102,103} There is some argument concerning the exact function of the TiO_2 or ZrO_2 nucleating agent in the formation of the silica crystal phase^{98,108} although they are necessary to produce a fine grained sample. Also, the particular metastable and stable silica based crystal phases¹⁰⁹⁻¹¹¹ depend on the composition of a given sample.

We have studied a commercially available glass ceramic (a "Pyroceram" obtained from G. H. Beall of Corning Research Lab¹⁵) with a composition shown in Table IV. (This is "composition 1" in Ref. 103.)

Table IV. Composition of Pyroceram

<u>Component</u>	<u>Wt %</u>
SiO_2	65.0
Al_2O_3	23.0
MgO	1.8
Li_2O	3.8
ZnO	1.5
As_2O_3	0.9
ZrO_2	2.0
TiO_2	2.0

As received the sample had already been heat treated through the first three steps of the crystallization process. The glass had been melted at 1650°C and then quenched. Heat treatment at around 725°C produced amorphous phase separation. Then heat treatment at around 800°C precipitated either a cubic zirconia solid solution or a titanate solid solution crystal phase.^{101,103} Continued treatment at this temperature caused the silica based crystal phase to grow from these precipitated nuclei of ZrO_2-TiO_2 . The hexagonal crystallizing silica based phase has been designated^{101,103} a stuffed β -quartz solid solution where Li, Al, Mg, Zn and As are the solutes in the SiO_2 crystal. Heat treatment at around 900°C produced a sample with >95% crystal (as determined by X-ray diffractometer measurements) and crystallites smaller than $.1\mu$. The sample (which was received from Corning in this form) was amber in color and transparent.

Scanning electron microscopy of a fracture surface could not resolve the microstructure. An electron micrograph is shown in Figure 14. (The structure shown is simply a flaw on the surface which was included to show that the microscope was focussing.) Dark field transmission microscope examination of the material¹⁵ indicated a mean crystallite size of 600 Å. An X-ray diffractometer trace (made using Cu radiation and General Electric diffractometer) for this sample is shown in Figure 15a.

Figure 14. Scanning electron micrograph of the Pyroceram sample as-received.

Figure 15. X-ray diffractometer traces for Pyroceram samples using Cu radiation: (a) Pyroceram as received, (b) Pyroceram heat treated at 1080°C, and (c) Pyroceram heat treated at 1175°C.

Heat treatment at higher temperatures ($T > 950^{\circ}\text{C}$) causes this material to transform to the tetragonal β -spodumene¹⁰⁰⁻¹⁰³ (keatite^{104,111}) solid solution structure. Heat treatment also induces crystallite growth.

Two groups of samples of the as-received material were heat treated to induce crystal growth. One set of samples was heated in vacuo (in the same furnace used to carry out the low temperature ceramic sintering work - Figure 9) in a silica beaker at 1080°C for 1 hour. The heating and cooling rate was 600°C/hr . The second set of samples was heated in vacuo for 1 hour at 1175°C . The samples heated at 1080°C were almost completely opaque but retained a bit of translucency. The samples treated at 1175°C were completely opaque.

As predicted, heat treatment of the as-received material at $T = 1080^{\circ}\text{C}$ produced a crystal phase transformation to the β -spodumene structure. X-ray diffractometer traces for the two heat treated samples are shown in Figure 15b and Figure 15c. The transformation is readily apparent. Heat treatment at $T = 1175^{\circ}\text{C}$ produced the same crystal structure as heat treatment at $T = 1080^{\circ}\text{C}$.

Scanning electron micrographs of the two heat treated samples of Pyrocera[®] are shown in Figure 16. The microstructure of the 1080°C specimen is on a scale of $.3-.5\mu$ while that for the 1175°C is on the scale of $1-2\mu$. This

(a)

(b)

Figure 16. Scanning electron micrographs of fracture surfaces of (a) Pyrocera heat treated at 1080°C and (b) Pyrocera heat treated at 1175°C.

microstructure is comparable to that seen by Chyung¹⁰² on similar materials.

While nucleating agents are needed to produce a very fine grained, highly crystalline recrystallized glass, these nucleating agents are not essential for the nucleation process. A number of materials can be completely devitrified without any nucleating agent. One such material is $\text{CaOMgO}(\text{SiO}_2)_2$ (diopside). We obtained from A. J. Leadbetter¹¹² a sample of diopside that had been formed as a glass (by quenching from a 1550°C melt¹¹³) and the N devitrified (by annealing at 1000°C for 48 hr¹¹³). After devitrification, the sample was quite porous, however. The crystallite size was about $.2\mu$ as shown by X-ray line broadening¹¹³, but scanning electron micrographs of a freshly fractured surface (shown in Figure 17) showed that an agglomerate structure also existed.

GeO_2 is another material that can be completely devitrified without nucleating agents.^{113,114} Recrystallized GeO_2 can be formed with a process comparable to that for $\text{CaOMgO}(\text{SiO}_2)_6$ and, like diopside, it is highly porous after devitrification. We have not studied this material because of its similarity to diopside.

Figure 17. Scanning electron micrographs of recrystallized diopside (CaO-MgO-2SiO_2).

C. Phase Separated Glasses

A number of glass forming systems undergo separation into two distinct phases.⁹⁸ In particular, the existence of a miscibility gap in the phase diagram is a common occurrence for silicate glasses.⁹⁸ The Gibbs free energy of the single phase structure is higher than that of the two phase structure so that the two phase system is energetically favorable. However, the actual process of separation (like crystallization) depends upon the composition of the glass and its thermal history.⁹⁸

One of the most extensively studied glass forming systems that undergoes amorphous phase separation is the $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ system. This system exhibits phase separation over a very wide range of compositions and temperatures (e.g., Pyrex is a member of this glass forming family and it has been shown to be phase separated on a 20 Å scale¹¹⁵). For these materials, the phase separation takes place on a very fine scale (i.e. $d \leq 1\mu$). Usually the two phases take the form of two continuous, interpenetrating networks although a large number of compositions do show one discontinuous phase that is in the form of small droplets dispersed in a continuous matrix of the other phase.^{116,117} One phase is SiO_2 rich while the second phase is $\text{Na}_2\text{O}-\text{B}_2\text{O}_3$ rich. The exact composition of the two phases depends on the composition and thermal history of a given sample.¹¹⁶⁻¹¹⁸

The regions of immiscibility in the phase diagram of this ternary system have been studied by a number of people.¹¹⁶⁻¹¹⁸ The directions of tie lines in this system (i.e. the compositions of the two phases) are a matter of current debate.¹¹⁶⁻¹¹⁸ The microstructure of glasses in this family has been studied by scanning electron microscopy¹¹⁷, transmission electron microscopy¹¹⁹, small-angle X-ray scattering¹²⁰ (SAXS), and small-angle neutron scattering¹²¹ (SANS).

We obtained a sample of a phase separated $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass (from T. E. Elmer of Corning Research Laboratories) of the composition shown in Table V.

Table V. Composition of Phase Separated Glass

<u>Component</u>	<u>Wt %</u>
SiO_2	67.4
B_2O_3	25.7
Na_2O	6.9

The glass had been formed at 1400°C and then quenched. The phase separation had been developed with a three-hour heat treatment at 710°C . Scanning electron micrographs¹¹⁷ of etched surfaces showed that this sample had an interconnected microstructure on a scale of $.2-.3\mu$.

We also obtained from T. E. Elmer some samples of porous Vycor. Porous Vycor is a sodium borosilicate glass (whose

composition is proprietary but which is about 75% SiO_2 , 20% B_2O_3 , and 5% Na_2O) that has been phase separated on a scale of 70 Å into a silica-rich phase (96% silica) and a sodium borate-rich phase (approaching sodium tetraborate)¹²³. The continuous sodium borate-rich phase was removed by leaching with hydrochloric acid to leave an interconnected set of channels of about 70 or 80 Å diameter (as determined by nitrogen adsorption measurement).^{124,125}

D. Summary of Sample Characteristics

In Tables VI-X we summarize the samples we have studied and their relevant characteristics. In Table VI we have the pressed powder samples. In Table VII we have the slipcast materials. In Table VIII we list the sintered and hot pressed ceramic samples. In Table IX we have the recrystallized glasses and in Table X we list the phase separated glasses. In these tables we give the thermal measurements (i.e. $C(T)$, $K(T)$ or both) that we have made on each of these samples and the figure containing the data.

Table VI. Characteristics of Pressed Powder Samples

Material	Chemical Composition	Particle Size	Electron Micrograph	Density	Single Crystal Density	Single Crystal Debye Sound Velocity	Properties Measured
Pressed Linde B	$\gamma\text{-Al}_2\text{O}_3$	.02 μ	Fig. 7	.50 ρ_{crys}	3.8 gm/cm ³	--	$C_v(T)$ Figs. 25 and 27 $K(T)$ Figs. 6 and 41
Pressed Gamma Exal	$\gamma\text{-Al}_2\text{O}_3$	.02 μ	--	.51 ρ_{crys}	3.8 gm/cm ³	--	$C_v(T)$ Figs. 25 and 27
Pressed Alon	$\gamma\text{-Al}_2\text{O}_3$	.02 μ	--	.49 ρ_{crys}	3.8 gm/cm ³	--	$C_v(T)$ Fig. 26
Initially Sintered Pressed Linde A	$\alpha\text{-Al}_2\text{O}_3$	.3 μ	--	.56 ρ_{crys}	3.98 gm/cm ³	7.1x10 ⁵ cm/sec	$C_v(T)$ Fig. 26
Initially Sintered Pressed Linde C	$\alpha\text{-Al}_2\text{O}_3$	1.0 μ	--	.58 ρ_{crys}	3.98 gm/cm ³	7.1x10 ⁵ gm/sec	$C_v(T)$ Fig. 26
Pressed Cabosil	Amorphous SiO_2	.007 μ	--	.53 ρ_{vit}	2.20 gm/cm ³	Ref. 15 4.1x10 ⁵ cm/sec	$C_v(T)$ Figs. 28 and 29 $K(T)$ Fig. 43

Table VII. Characteristics of Slipcast Samples

Material	Chemical Composition	Particle Size	Electron Micrograph	Density	Single Crystal Density	Single Crystal Debye Sound Velocity	Properties Measured
Initially Sintered Slipcast Linde B	$\gamma\text{-Al}_2\text{O}_3$	.02 μ	Fig. 8	.21 ρ_{crys}	3.8 gm/cm ³	---	--
Initially Sintered Slipcast Linde A	$\alpha\text{-Al}_2\text{O}_3$	.3 μ	--	.41 ρ_{crys}	3.98 gm/cm ³	7.1x10 ⁵ cm/sec	Ref. 163 C(T) - not shown
Initially Sintered Slipcast Zyttrite	ZrO ₂ + 6 mole % Y ₂ O ₃	.06 μ	See Ref. 49	.42 ρ_{crys}	6.02 gm/cm ³	---	K(T) Fig. 44

Table VIII. Characteristics of Sintered Ceramics and HPHP Ceramics

Material	Chemical Composition	Particle Size	Electron Micrograph	Density	Single Crystal Density	Single Crystal Debye Sound	Properties Measured
Sintered Linde B (T=1395°C)	$\alpha\text{-Al}_2\text{O}_3$	.3 μ	Fig. 11	.90 ρ_{crys}	3.98 gm/cm ³	7.1x10 ⁵ cm/sec	K(T) Fig. 41
Sintered Linde B (T=1495°C)	$\alpha\text{-Al}_2\text{O}_3$	1-2 μ	Fig. 11	.958 ρ_{crys}	3.98 gm/cm ³	7.1x10 ⁵ cm/sec	C _V (T) Fig. 25
Sintered Linde B (T=1800°C)	$\alpha\text{-Al}_2\text{O}_3$	15-30 μ	Fig. 9	.985 ρ_{crys}	3.98 gm/cm ³	7.1x10 ⁵ cm/sec	C _V (T) Fig. 25
Coors Ceramic	$\alpha\text{-Al}_2\text{O}_3$	2-5 μ	Fig. 13	.998 ρ_{crys}	3.98 gm/cm ³	7.1x10 ⁵ cm/sec	K(T) Fig. 41
HPHP MgO	MgO	.06 μ	See Ref. 93	1.00 ρ_{crys}	3.65 gm/cm ³	6.70x10 ⁵ cm/sec Ref. 162	K(T) Fig. 46
Sintered Pressed Cabosil	SiO ₂	~1mm	--	--	2.20 gm/cm ³	4.1x10 ⁵ cm/sec	C _V (T) Fig. 28 K(T) Fig. 43

Table IX. Characteristics of Recrystallized Glasses

Material	Chemical Composition	Particle Size	Electron Micrograph	Density	Single Crystal Density	Single Crystal Debye Sound Velocity	Properties Measured
Pyroceram (As-Received)	(see Table IV)	.06 μ	Fig. 14	2.42 gm/cm	2.42 gm/cm ³	4.2x10 ⁵ cm/sec Ref. 15	C _v (T) Fig. 35 K(T) Fig. 47
Pyroceram (T=1080°C)	(see Table IV)	.3 μ	Fig. 16	--	--	(4.2x10 ⁵ cm/sec)	C _v (T) Fig. 35
Pyroceram (T=1175°C)	(see Table IV)	1 μ	Fig. 16	--	--	(4.2x10 ⁵ cm/sec)	C _v (T) Fig. 35 K(T) Fig. 47
Diopside	CaOMgO(SiO ₂) ₂	.2 μ	Fig. 17	--	3.3 gm/cm ³	5.1x10 ⁵ cm/sec Ref. 164	C _v (T) Fig. 38 K(T) Fig. 49
GeO ₂	CeO ₂	.3 μ	--	--	--	--	C _v (T) Fig. 38 (from Ref. 114)

Table X. Characteristics of Phase Separated Glasses

Material	Composition	Particle Size	Electron Micrograph	Density	Bulk Density	Bulk Debye Sound Velocity	Properties Measured
Porous Vycor	96% SiO ₂	.007 μ	--	.72 ρ_{vit}	2.20 gm/cm ³	4.1x10 ⁵ gm/sec	C _v (T) Fig. 28 K(T) Fig. 52
Soda Borosilicate Glass	67.4% SiO ₂ 25.7% B ₂ O ₃ 6.9% Na ₂ O	.3 μ	See Ref. 116	--	--	--	K(T) Fig. 50

IV. EXPERIMENTAL APPARATUS AND TECHNIQUES

A. Cryostats

Low temperature measurements were carried out in a number of different cryostats whose design and operation have been discussed in detail elsewhere. The cryostats used and the relevant temperature ranges for which the cryostats were designed are as follows: (1) a cryostat with a dilution refrigerator¹²⁶ (.06-2K), (2) an adiabatic demagnetization cryostat^{15,127} (.05-2K), (3) a ^3He cryostat^{126,128,129} (.3-6K), and a ^4He cryostat^{130,131} (1.2-100K).

Heat capacity measurements (to be discussed in Section E of this chapter) were made in the ^3He and dilution refrigerator cryostats at temperatures up to 20K. Since these temperatures are well outside the normal operating range of these cryostats, some modification of the standard techniques had to be made.

For the ^3He cryostat the temperature range 4.2-20K was reached in the following fashion. After the initial transfer of liquid ^4He into the ^4He dewar, the ^3He gas was allowed into the ^3He chamber but the ^4He bath was not pumped. After 18-20 hours, the samples had cooled from LN_2 temperatures to 4.2K. The ^3He gas was then pumped back into the storage tank. Temperatures higher than 4.2K were reached by putting

in post heat. The cryostat took about 20-30 minutes to come to equilibrium after the post heat was changed and it was quite stable.

After the 4.2-20K region had been covered, the post heat was turned off, the ^3He gas was readmitted to the ^3He chamber, and the liquid helium bath was pumped down. The temperature range $0.3\text{K} < T < 4.2\text{K}$ was covered in the usual way.^{128,129}

The cool down in the ^3He cryostat was speeded up in a few runs by using ^4He exchange gas in the vacuum can during the cool down from LN_2 temperatures to ^4He temperatures. However, some of the samples studied were porous so that ^4He adsorption would have been a problem if exchange gas had been used when these samples were in the cryostat.

For the dilution refrigerator, the following procedure was used to reach the higher temperatures ($T > 4.2\text{K}$). N_2 or ^4He exchange gas was used in the vacuum can in the cool down from room temperature to LN_2 temperature. Because most of the samples were porous, the exchange gas was pumped out before the transfer of liquid ^4He . After liquid helium had been transferred, the cooling ^3He - ^4He mixture was allowed into the refrigerator. The cooldown to $T = 4.2\text{K}$ took about 48 hours. After the samples had reached helium temperatures, the mixture was pumped back into the storage tanks and the appropriate temperature ($T > 4.2\text{K}$) was reached by using post

heat. The dilution refrigerator took about 40-50 minutes to reach equilibrium after the post heat was changed. Once the range 4.2-20K had been covered, the post heat was turned off. The ^3He - ^4He cooling mixture was then readmitted to the refrigerator and the ^4He pot was pumped down.

To cover the range 1.5-4.2K the following procedure was used for the dilution refrigerator. First, the ^3He - ^4He cooling mixture was pumped out again when the post had cooled to about $T = 2.5\text{K}$. (The presence of a condensed ^3He - ^4He mixture in the still and in the mixing chamber of the refrigerator created convective instabilities for $T > 1.5\text{K}$ when post heat was applied.) After the mixture had been removed, the sample was allowed to cool slowly to $T = 1.5\text{K}$ --the temperature of the ^4He pot. Temperatures between 1.5K and 4.2K were attained by putting in post heat.

The temperature range $T < 1.5\text{K}$ was reached in the standard way.¹²⁶

B. Resistance Bridges

All of the low temperature thermometers used in the studies reported here were resistance thermometers. To measure the resistances, three low power, low frequency A.C. resistance bridges were used. For thermal conductivity measurements in all of the cryostats (except for some measurements in the dilution refrigerator cryostat) two bridges were used that utilized tube electronics and an oscilloscope readout. The circuitry of these two bridges has been extensively discussed elsewhere.^{15,128}

However, for all heat capacity measurements and for some thermal conductivity measurements in the dilution refrigerator cryostat a third bridge was used that utilized a 33 Hz PAR 120 Lock-In amplifier. A block diagram of the wiring of this bridge circuit is shown in Figure 18. A simple operational amplifier preamplifier was used to beef up the signal fed into the input side of the PAR 120.

The center grounding of the output side of the transformer insured that when $R_{\text{Bridge}} = R_{\text{Sample}}$ the output signal to the preamp is 0 volts with respect to ground. The capacitive balance portion of the circuit allowed lead capacitances to be balanced out. The off balance (non null) phase detected signal out of the PAR 120 was observed on either the meter on the face of the PAR 120 or on an X-Y recorder being driven by the PAR 120.

Figure 18. Schematic diagram of the Lock-in amplifier bridge circuit.

The wiring of the switches (not shown) that selected the particular resistance bank of the bridge (R_{Bridge}) and the particular thermometer in the cryostat (R_{Sample}) that were put into the circuit of Figure 18 was essentially identical to that of one of the bridges¹²⁸ mentioned earlier.

C. Thermometers

As mentioned before, all of the thermometers used in these experiments were resistance thermometers. The thermometers used as primary temperature standards were encapsulated, doped Ge crystals supplied by Cryo-Cal Corp. and by Honeywell Corp. The calibrations of these thermometers (which were permanently mounted in the various cryostats) are discussed elsewhere: the ^4He cryostat Ge thermometer is discussed in Refs. 126 and 131, the ^3He cryostat Ge thermometer is discussed in Ref. 128, and the demagnetization cryostat Ge thermometer is discussed in Ref. 15. A Ge thermometer calibrated against the standard thermometer in the demagnetization cryostat was used as a temperature standard in the dilution refrigerator. The calibration of this thermometer is discussed in Ref. 15. A new Ge thermometer (#3773) obtained from Cryo-Cal was calibrated against the Ge thermometers in the ^4He cryostat and the Ge thermometer in the ^3He cryostat. This new thermometer (which was removed after use) was used as a temperature standard in the ^3He cryostat and the dilution refrigerator for $T > 2\text{K}$. Calibration data for this thermometer are given in Appendix A.

Speer 220Ω , 1/2 Watt carbon resistors were used as the working thermometers for all of the thermal measurements we made with the exception of thermal conductivity measurements in the ^4He cryostat (T in the range 1.5-100K). For

these high temperatures measurements, Allen Bradley 100 Ω and 1500 Ω , 1/10 Watt carbon resistors were employed.

For specific heat measurements, calibrated small thermal mass thermometers made from Speer 220 Ω resistors were used. The leads and the insulation of the Speer resistors were removed (either with a string saw or a belt sander) to leave only the carbon resistive element (which typically weighed 15 mg.) This element was then mounted on a piece of copper foil and electrical leads were attached (as described in Ref. 15). These specific heat thermometers (which typically weighed 40 mg when completely assembled) were then cycled to helium temperatures at least 10 times before being calibrated.

The R vs. T calibrations of these thermometers were carried out with the thermometers glued (using GE 7031 varnish) directly to the post. For $T < 1.5\text{K}$ these calibrations were spotchecked during the specific heat measurements. With two exceptions, the calibrations were not observed to change to within the experimental uncertainty of $\pm 0.5\%$. The two exceptions were Speer resistors that had been ground on the belt sander to remove the insulation. These resistors were observed to lower their resistances irreversibly by about 10% between two runs. These thermometers were recalibrated after this change and were not observed to change again.

For $T > 1.5\text{K}$ (and particularly for $T > 10\text{K}$) more care had to be taken concerning the calibrations. A fluctuation of $\sim \pm 0.5\%$ was observed in the resistances of the Speer resistors from run to run. This fluctuation gave rise to a negligible ($\leq \pm 0.3\%$) uncertainty for $T \leq 1.5\text{K}$. However, for $T = 20\text{K}$, a 1% change in R corresponded to about a 6% for these thermometers. Therefore, a special effort had to be made during each specific heat run to recalibrate the thermometers for $T > 1.5\text{K}$. In the high temperature range ($T > 15\text{K}$) the uncertainty in temperature was $\sim \pm 1-2\%$.

Speer resistors were used in spite of this large uncertainty at high temperatures so that the entire temperature range 0.1-20K could be covered in a single run with only one sample thermometer.

The thermal conductivity experiments on long samples ($\ell \gtrsim 2.5\text{ cm}$) were carried out using Speer resistors wrapped in Cu foil as described in Ref. 15. For thermal conductivity experiments on short samples ($\ell < 2\text{ cm}$), thermometers identical in design to the specific heat thermometers were used. The thermal conductivity thermometers were calibrated during each run as described in Ref. 128.

D. K(T) Measurements

Thermal conductivity samples that were longer than about 2 cm were mounted in the usual way¹²⁸ for four probe measurements using brass or copper clamps on the sample as mounts for the thermometers and heater. However, for very small sample ($\ell < 2\text{m}$ --and in particular for $\ell \lesssim 1\text{ cm}$) a modified technique had to be used. This modified mounting is shown schematically in Figure 19.

The following procedure was used for these samples. First, a piece of No. 36 (.13 mm diameter) copper wire that was 5 or 10 cm long was stripped of its Formvar insulation. This wire was then wrapped (three times) tightly around the sample at a point about 2 mm from one end. The loose ends were then twisted into a loop. Another length of No. 36 copper wire was then wrapped around the sample at a point about 2 mm from the other end. Specific heat type thermometers were glued to these two pieces of wire with GE 7031 varnish. One end of the sample was secured in a small clamp between two pieces of In. The clamp was attached to the post. The heater (a 1000 Ω metal film resistor) was mounted at the other end of the sample with No. 36 copper wire and GE 7031 varnish as shown in Figure 19.

The thermal conductivity measurements were made with the standard techniques.^{126,128} The thermal conductivity data were analyzed using the data reduction program initially

Figure 19. Schematic diagram of a typical four probe thermal conductivity sample mount using ground Speer resistors as thermometers.

written by Seward¹²⁸ and modified by Stephens.¹⁵

The measurement of the thermal conductivity of the very low thermal conductivity samples was carried out in the demagnetization cryostat with 4 mil diameter cotton-covered Advance leads in addition to the 3 mil diameter Nb leads already present. At $T = 0.1\text{K}$ the thermal resistance of the leads was $R_{Th} \gtrsim 5 \times 10^{11} \text{ watt}^{-1}\text{K}$ and at $T = 0.5\text{K}$ $R_{Th} \gtrsim 5 \times 10^{10} \text{ watt}^{-1}\text{K}$. The thermal resistance of all of our samples was at least two orders of magnitude lower than these values. Therefore, even for the low thermal conductivity samples, the electrical leads did not contribute significantly to the total thermal conductance.

E. C(T) Measurements

(1) Sample Mounting

The pressed powder and sintered pressed powder samples were in the form of thin disks and could not be mounted with the techniques¹⁵ used for large samples. A standard procedure was developed to deal with these samples.

A number of crosses were cut from pure, ultrathin ($t = .0076$ cm) copper foil (as in Figure 20a), and the mass of each cross (typically .008 gm) was measured. A small amount of bonding agent (GE 7031 varnish, Apiezon N grease or Apiezon T grease) was applied to each cross at the six places indicated in Figure 20b. The mass of the bonding agent was determined and was typically .001 gm for each cross. The crosses were placed on the disks as shown in Figure 20c. For the porous materials (i.e. the pressed powders, the initially sintered pressed and slip cast powders, and porous Vycor) a very thin film of Cu was evaporated onto one side of the sample disk before the cross was applied. This copper film prevented the bonding agent from being absorbed by the sample. Finally, the disks were stacked up (as shown in Figure 20d) and the ends of the copper crosses were all bonded to a disk of the thin copper foil which was placed on the top of the stack.

The samples were mounted in the cryostat as shown in Figure 21. A thermal ground composed of 20 cm of 2.2 mil

Figure 20. Schematic drawing of the steps followed in putting together a specific heat sample from a number of pressed disks: (a) cutting out the copper crosses, (b) applying the bonding agent, (c) attaching the cross to a sample disk, and (d) stacking the disks.

Figure 21. Schematic diagram of a typical specific heat sample mounting.

diameter copper wire was attached to the stack of samples and to the post. The heater was a 50 cm piece of Nichrome wire (with a resistance of about 1000Ω) that had been glued to a 1.5 cm x 1.5 cm piece of .0025 cm thick copper foil. The calibrated thermometers used were Speer resistors as discussed earlier.

For small heat capacity samples (in particular the fully sintered Al_2O_3 samples) the heat capacity of the addenda (copper crosses, copper top piece, bonding agent, heater, the electrical leads, and the thermometer) was a sizeable fraction ($\sim 30\text{-}50\%$) of the heat capacity of the sample over the entire temperature range studied. In order to correct for this, the heat capacity of the addenda was determined separately. A 2.5 cm x 2.5 cm piece of thin ($t = .0025$ cm) copper foil was placed in the sample holder and the heater and thermometer were attached to it. The heater was attached with ~ 1 mg of GE 7031 varnish. The heat capacity of this entire assembly (shown in Figure 22) was measured in the temperature range 0.4-20K. The heat capacity of Apiezon T¹³², GE 7031 varnish^{15,133,134}, and copper are known for this temperature range. Therefore, the heat capacity of the thermometer, heat and electrical leads was calculated by simply subtracting the heat capacity of the bonding agents and the copper base. The heat capacity of the addenda for any sample run was determined by adding the heat capacity of

Figure 22. Schematic diagram of the configuration used to determine the heat capacity of the sample addenda: heater, thermometer, and bonding agent.

the heater, thermometer, and electrical leads (which were identical in the sample runs and the addenda run) to the calculated heat capacity of the bonding agent and copper crosses used on the sample. This addenda heat capacity was subtracted from the data for the sample plus addenda to determine the true sample specific heat.

In Figure 24 we show the heat capacity of a typical addenda.

During one run, we measured the specific heat of pressed Alon with adsorbed N_2 on the surface. The exact amount of N_2 adsorbed was unclear since the following procedure was used to adsorb the gas. The sample of Alon was mounted in the usual way in the demagnetization cryostat. An atmosphere of dry N_2 was put into the vacuum chamber before the cryostat was cooled from room temperature to LN_2 temperature. This nitrogen exchange gas was not pumped out when 4He was transferred into the dewar. The transfer was made very slowly so that the cold walls would not cryopump the N_2 out of the sample before it had cooled. The transfer took about two hours. When liquid 4He finally condensed into the dewar, the sample was considerably below 77K. It is not clear how much gas was cryopumped out of the sample after this. As a rough estimate, we say that " $\frac{1}{2}$ Layer" of N_2 remained after the cool down.

Figure 23. Heat capacity of typical sample addenda.

(2) Data Acquisition

The technique for measuring the specific heat of the samples differed from that used by Stephens¹⁵, but was based on the same principle--i.e. determining the change of temperature, ΔT , of the sample immediately after a heat pulse of energy ΔQ had been put in and writing $C = \frac{\Delta Q}{\Delta T}$. The resistance bridge shown in Figure 18 was used for these measurements with the x-y recorder employed to monitor the phase detected off balance signal. A typical trace of the x-y recorder while a point is being taken is shown in Figure 24a. This sample had a relatively short time constant. The change in temperature, ΔT , can be derived from the change in the resistance, ΔR , of the thermometer. ΔR at $t = 0$ can be determined from the off balance signal of the PAR 120 by finding the off balance signal at $t = 0$ (or rather at $t = \frac{\Delta t}{2}$ where Δt is the length of the heat pulse) and then converting this value (see Appendix B) to ΔR . Since the decay of the temperature of the sample is exponential^{14,15} the off balance signal at $t = 0$ can be found by plotting the off balance signal as a function of time on semi-log paper and extending the straight line back to $t = 0$.

In Figure 24b we have the trace of a sample with a long time constant. There was no need to plot the data for this trace on semi-log paper since the decay is so slow--a straight line was sufficient. In Figure 24c we show the

Figure 24. Three typical thermal decay curves seen in specific heat measurements after a 2 sec heat pulse has been applied: (a) a low heat capacity sample (short time constant decay), (b) a high heat capacity sample (long time constant decay) and (c) an intermediate heat capacity sample (medium length time constant decay) with a long (~ 3 sec) internal time constant (overshoot).

trace of a sample that had a long internal equilibrium time. The sharp peak at short times is the sample coming to equilibrium with itself and the slow decay is the loss of heat from the sample to the bath. The true ΔR can be determined from the dotted line extrapolation.

V. EXPERIMENTAL RESULTS AND DISCUSSION

A. Specific Heat

(1) Pressed Powders and Sintered Ceramics

In Figure 25 we plot the specific heat of four Al_2O_3 samples. (See Table VI for a summary of the characteristics of the samples.) We also plot the specific heat of single crystal $\alpha\text{-Al}_2\text{O}_3$ ¹³⁵ (which agrees well with the Debye prediction using measured elastic constants). The two pressed powder samples ($d \sim .02\mu$) have specific heats that are larger than single crystal $\alpha\text{-Al}_2\text{O}_3$ over the entire temperature range studied (.08-20K). The specific heat of pressed Linde B (.02 μ) is a factor of five larger than the single crystal value at $T = 20\text{K}$. It is a factor of 10^3 larger at $T = 0.1\text{K}$ and it varies linearly with temperature for $T < .15\text{K}$.

The specific heats of the two sintered samples of Linde B ($d \sim .8\mu$, $d \sim 20\mu$), however, agree with the specific heat of the single crystal for $T > 3\text{K}$. The low temperature ($T < 3\text{K}$) excess specific heats of these two samples are identical and have roughly the form of Schottky anomalies. Assuming this excess is due to a set of two level systems, then from the total entropy of the anomaly we find that the density of these systems is about $3 \times 10^{17}/\text{cm}^3$.

The origin of the large excess specific heats of the two ultrafine particle pressed Al_2O_3 powder samples is not obvious and any attempt to associate the linear temperature

Figure 25. Specific heat of four Al_2O_3 samples. Single crystal data from Ref. 163.

dependence of the specific heat with "glassy" behavior will have to be justified. One possible origin of the excess modes is bulk impurities. This explanation seems unlikely in view of the fact that the sintered materials do not show the large excess. The metallic oxide impurities in the starting powder should not be volatilized by the heat treatment. Also, the concentration of Fe in the starting powder (~ 15 ppm by weight according to manufacturer specifications) agrees reasonably well with the concentration of two level systems (7 ppm) calculated from the entropy of the Schottky anomalies in the specific heats of the sintered samples. Specific heat anomalies due to magnetic impurities¹⁵ have been seen in a number of materials. Finally, the concentration of impurity modes required to explain the high temperature specific heat excess is ~ 1 -2% of the total number of atoms present. The total bulk impurity level is quoted as $\lesssim .02\%$.^{58,59}

However, bulk impurities do play a definite role in the low temperature specific heat of a number of other Al_2O_3 samples we have examined. In Figure 26 we show the specific heats of pressed Alon ($d \sim .02\mu$), initially sintered Linde A ($d \sim .3\mu$) and initially sintered Linde C ($d \sim 1\mu$). The specific heat of the pressed Alon ($d \sim .02\mu$) is considerably larger than that of the other two ultrafine powder samples for $T < 1.5\text{K}$ (it appears that the difference should be small

Figure 26. Specific heat of a number of Al_2O_3 samples.

for $T \sim 4K$). However, the impurity level of this material is quite high (i.e. $\sim 1\%$). Therefore, a large impurity related specific heat anomaly is quite likely although we cannot prove that such impurity excitations account for the difference in the specific heats of these powders. The concentration of two level systems required to give rise to the observed excess is ~ 800 ppm.

The most convincing evidence against bulk impurities as the source of the excess for Linde B ($.02\mu$) and Gamma Exal ($.02\mu$) comes from an examination of the specific heats of the other two Linde powders. For the Linde A ($.3\mu$) and Linde C (1μ) samples, low temperature Schottky type anomalies are observed as for the sintered Linde B. Again assuming that the impurities are two level systems then we calculate from the total entropy that their densities are $11 \times 10^{17}/\text{cm}^3$ and $8.5 \times 10^{17}/\text{cm}^3$ (28 ppm and 21 ppm) for Linde C (1μ) and Linde A ($.3\mu$) respectively. These concentrations also agree reasonably well with the expected Fe concentration of ~ 15 ppm in these two samples. However, for these two large grain Al_2O_3 materials, the specific heat approaches C_{Deb} for $T \gtrsim 2K$ while the specific heat of Linde B ($.02\mu$) continues to increase.

Linde A ($.3\mu$), Linde C (1μ), and Linde B ($.02\mu$) powders are all made from the same starting material (they are calcined at different temperatures and for different lengths of time) and they therefore should have essentially

the same impurity levels and essentially the same impurity caused excess specific heat. This implies that the Linde B should also have a Schottky anomaly at $T \sim .6K$. In fact, the Linde B ($.02\mu$) sample and the Gamma Exal ($.02\mu$) sample do seem to have Schottky like anomalies at $T \sim .4K$. The magnitude of the excess is almost identical to the magnitude of the Schottky anomaly excess observed in the sintered Linde B ($.8\mu$) at $T \sim 2K$.

In Figure 27 we plot the low temperature ($T < 1.5K$) specific heats of Linde B($.02\mu$) and Gamma Exal ($.02\mu$) in the form C_V/T vs. T^2 as is often done for the specific heats of glasses.¹⁶ We have also included the impurity specific heat of Linde A ($.3\mu$) divided by 3 (i.e. the ratio of the total impurity related entropy of Linde A to that of sintered Linde B). The pile up of points near $T^2 = 0$ for the two ultrafine powders indicates the linear temperature dependence for these materials for $T^2 \leq .02$. We note that for the two $.02\mu$ powders the deviation of the experimental C_V/T curve from the smooth line joining the low temperature ($T \leq .15K$) and the high temperature ($T > 1K$) data points has the same form as the excess specific heat of Linde A. We consider this strong evidence that the "bumps" seen in Figure 27 are all due to the same impurity (i.e. a spin impurity) and that the dashed lines are the intrinsic (i.e. not bulk impurity related) specific heats of the two fine

Figure 27. Specific heat of some pressed Al_2O_3 samples plotted as C/V vs. T^2 .

powders. The shift of this anomaly from $T = .6\text{K}$ for pressed Linde B ($.02\mu$) to $T = 2\text{K}$ for sintered Linde B (20μ) is assumed to be due to a change in the ionization state of the spin impurity or a change in the local field seen by the impurity caused by a shift of the position of the Fe impurity in the Al_2O_3 lattice.

The curvature in the smooth lines drawn through the high temperature and low temperature data points indicates that fitting the curves would require a term quadratic in temperature, i.e.

$$C_{\text{Al}_2\text{O}_3} = c_1 T + c_2 T^2 + c_3 T^3 .$$

For most glasses, the coefficient c_2 is small if it is present at all. In SiO_2 , for example, $c_2 = 0.15$

An excess specific heat comparable to that for the two ultrafine ($.02\mu$) Al_2O_3 pressed powders is observed in the two porous SiO_2 samples we have measured, i.e. pressed Cabosil ($.007\mu$) and porous Vycor glass ($.007\mu$). Despite the different formation techniques, these two samples have almost identical specific heats over the entire temperature range. In Figure 28 we plot the specific heat of these two samples

Figure 28. Specific heat of a number of SiO_2 samples.

as well as the specific heats of sintered Cabosil and vitreous SiO_2 .

Just as for the Al_2O_3 samples, bulk impurities are not expected to be responsible for the large excess specific heat. The sintered Cabosil has a specific heat almost identical to that of bulk vitreous SiO_2 for $T > 1.5\text{K}$. The small differences that exist for $T > 1.5\text{K}$ are comparable to the fluctuations seen in samples of bulk SiO_2 .

In Figure 29 we plot the specific heats of these three materials in the form C_v/T vs. T^2 . From this figure we can see that the specific heat of sintered Cabosil has the form $C_v = c_1T + c_3T^3$ (where $c_1 = 17 \text{ erg gm}^{-1} \text{ K}^{-2}$ and $c_3 = 19 \text{ erg gm}^{-1} \text{ K}^{-4}$) for $.3\text{K} < T < 1.6\text{K}$. However, for $T < .3\text{K}$, an anomaly can be seen which may be due to impurities. For the two porous samples, the excess specific heat is quite large and has the form $C_v = c_1T + c_2T^2 + c_3T^3$ as for the two Al_2O_3 powders.

A second possible origin (as discussed in Chapter II) for the excess specific heat in these porous materials is the combination of surface vibrations of a grain and the very low frequency harmonic oscillations of the grain as a whole. In Figure 30 we show the expected specific heat of a collection

Figure 29. Specific heat of three SiO_2 samples plotted as C/T vs. T^2 .

of 200 Å Al_2O_3 particles calculated using this model. The observed specific heat curve obviously does not have much in common with the theoretical curve, particularly for $T > 3\text{K}$ where the observed specific heat exceeds the theoretical value by more than a factor of 2. The surface phonons increase the expected specific heat only slightly above the single crystal value. For the low temperatures ($T < 1\text{K}$), however, we cannot rule out the possibility that single particle oscillations are present since the constant $6 k_B$ per particle drawn on Figure 30 is only the maximum specific heat of these excitations. The $6 k_B$ per particle is based on the assumption that all of the vibrational frequencies of the grains are very low (i.e. $\hbar\omega_{\text{vib}} \ll k_B T$ for $T \geq .1\text{K}$) so that for $T \geq .1\text{K}$ the Dulong-Petite limit has been reached for these oscillations. This assumption need not be valid. The real distribution of frequencies, $g(\omega_{\text{vib}})$, may have considerable weight for $\hbar\omega_{\text{vib}} \sim k_B T$ where T is in our measured temperature range.

In Figure 31 we plot the specific heat of porous Vycor ($d \sim 0.007\mu$) and pressed Cabosil ($d \sim 0.007\mu$) along with the prediction of this model for Cabosil (it is difficult to consider single grain oscillations in porous Vycor since it is well connected and not formed from small particles). As can be seen, the result is similar to that for the Al_2O_3 samples.

Figure 30. Experimental and theoretical (see text) specific heat of packed Al_2O_3 ($d \sim .02\mu$) powder.

Figure 31. Specific heat of two porous samples of SiO_2 (pressed Cabosil ($.007\mu$) and porous Vycor ($.007\mu$)) compared to bulk vitreous SiO_2 and theoretical predictions (see text).

A more general model description of the low frequency vibrational excitation spectrum of a granular material can be given which can reproduce much of the results of the single grain vibration picture without having to describe the nature of the excitations. For this model we assume that above some cutoff frequency, ω_c (and therefore a cutoff wave vector k_c), the excitation spectrum is that for the single crystal:

$$g(\omega) = g_{\text{crys}}(\omega) = \frac{3\omega^2}{2\pi^2 v_{\text{Deb}}^3 \text{crys}}$$

for $\omega > \omega_c$. A reasonable choice for such a cutoff is $\lambda_c = 2a$ $k_c a = \pi$. Here a is the size of a grain. For frequencies below some low frequency cutoff, ω_L , the long wavelength excitation spectrum will have the Debye form determined by the long wavelength speed of sound,

$v_{\text{Deb}}(\lambda \gg$

$$g(\omega) = \frac{3\omega^2}{2\pi^2 v_{\text{Deb}}^3(\lambda \gg a)}$$

for $\omega < \omega_c \ll \omega_c$.

In the intermediate region ($\omega_L < \omega < \omega_c$), the nature of the excitations (whether localized or propagating) is not clear and should in general depend on the manner in which the material is put together. Also, the excitation spectrum in this intermediate frequency range will depend on the nature of the material. In general, however, the excitation

spectrum is thought to go through some broad resonance at $\omega = \omega_R$.¹³⁶ The composite spectra for the three regions is shown schematically in Figure 32.

The low frequency ($\omega \sim 3 \times 10^4 \text{ sec}^{-1}$) speed of sound in porous ceramics has been experimentally^{137,138} found (at room temperature) to be lower (by a factor of 1.1 to 2.5 for porosities varying from 5% to 50%) than that for non-porous materials. Therefore the Debye density of states for $\omega < \omega_L$ is higher than for $\omega > \omega_c$. The intermediate region has been drawn in arbitrarily. The only condition on the density of states in this region is that the number of modes with $\omega < \omega_c$ is the same for the porous compact as for the single crystal, i.e.:

$$N_{\text{modes}} (\omega < \omega_c) = V \int_0^{\omega_c} g(\omega) d\omega = V \int_0^{\omega_c} g_{\text{crys}}(\omega) d\omega .$$

With the choice $k_c a = \pi$ we find that

$$N_{\text{modes}} (\omega < \omega_c) = \frac{V}{2a^3} = 5 \times \text{total number of particles} .$$

The single grain excitation model can be reproduced with the assumptions that $\hbar\omega_R \ll k_B T$ and that most all of the modes with $\omega < \omega_c$ are in the peak. With these assumptions $C_V = \text{constant} = 5 K_B$ per particle. But again this need not be the case so that the specific heat in general may be less than $5 K_B$ per particle. The location and magnitude of the

Figure 32. Possible phonon density of states for a packed powder exhibiting a "broad resonance" for $\omega \sim \omega_R$ (see text) and having a velocity of sound for long wavelengths that is slower than the velocity of sound for short wavelengths.

"resonance" will determine the exact form of the expected specific heat.

Considerable progress has been made recently in developing a formalism to describe the elastic properties of granular materials in the long wavelength^{139,140} limit. These calculations have demonstrated that long wavelength propagating elastic waves are well defined entities in the limit that $\lambda \gg a$, where a is the mean size of a grain. It seems possible to formally extend some of these formalisms to the case $\lambda \sim a$, but it is expected that the equations will be too cumbersome to be easily solved. Also, the amount of information about the nature of the grain boundaries which would be required to make the calculations possible is probably beyond reasonable description. At present, therefore, it is difficult to reach firm conclusions about the intermediate frequency region.

Nevertheless, the results of thermal conductivity measurements on porous Vycor (which we will discuss in more detail later) given in Figure 52 show that it has a conductivity essentially identical to that of silica based glasses for $T < .3K$. Since glass fiber measurements have demonstrated that the heat flow in glasses is due to phonons, then we must conclude that for $\frac{\hbar\omega_{dom}}{k_B} < (4.2) \times (.3K) = 1.3K$ phonons must be well defined propagating excitations. This puts a lower bound on ω_L (of our simple model), i.e. $\frac{\hbar\omega_L}{k_B} \geq 1.3K$. However,

for $T \lesssim 0.1\text{K}$, the specific heat does not show any indication of altering its form to approach c_{Deb} even if the speed of sound in Vycor is a factor of 2 smaller than in bulk vitreous SiO_2 . Therefore, we can conclude that for porous Vycor, the simple model we have suggested does not describe the observed results for $T < .3\text{K}$. This throws doubt on its application to any of the porous systems since the specific heat of porous Vycor is not significantly different from that of the other materials.

The model we have just presented ignores the possible shift of modes with $\omega > \omega_c$ to lower frequencies. In particular, we have ignored propagating surface phonons. However, the specific heat of these excitations is small compared to single crystal $\alpha\text{-Al}_2\text{O}_3$ in the region $T > 5\text{K}$ and is expected to be cutoff²⁶ for $T < 2\text{K}$. We therefore do not expect this omission to be a serious problem. More importantly, we have ignored possible low frequency localized vibrational modes of atoms or groups of atoms near the surface. Such vibrations could occur because of alterations of the perfect crystalline potential (due to surface defects). No predictions can be made, however, without further information concerning the structure of the grains.

Besides bulk impurities, surface phonons, and elastic vibrations with $\lambda \sim a$, another possible source for the observed excess low energy modes is adsorbed surface impurities.

The surface areas of these porous, granular materials are quite large. (Pressed Linde B (.02 μ) and pressed Gamma Exal (.02 μ) have surface areas $\sim 100 \text{ m}^2/\text{gm}$. Porous Vycor has a surface area $\sim 130 \text{ m}^2/\text{gm}$ and pressed Cabosil (.007 μ) has a surface area $\sim 400 \text{ m}^2/\text{gm}$.) Therefore the number of adsorbed molecules can be quite large. If we assume an average molecular area of $15 \text{ \AA}^2$ (N_2 is assumed to have a molecular area of $16.2 \text{ \AA}^2$ and H_2O is assumed to have a molecular area of $10.5 \text{ \AA}^2$) then for a sample with $100 \text{ m}^2/\text{gm}$ there are 7×10^{20} impurities/gm with a complete monomolecular layer.

The most likely adsorbed molecule is H_2O (since it has such a large concentration in air), but adsorbed organic molecules are also likely to be present. It has been shown¹⁴¹ that Linde B (.02 μ) which has been exposed to air for some time is more than 5% by weight of H_2O --a value that corresponds to a little more than one layer. This layer is extremely tenacious. A 12-hour outgassing at $T = 150^\circ\text{C}$ ¹⁴¹ removed only about half of this layer of water. At $T = 1000^\circ\text{C}$ hydroxide ions could still be observed to come off.¹⁴¹ (In fact, hydroxide ions have been observed to come off MgO powders at $T \sim 2000^\circ\text{C}$.)⁷⁸ Therefore the four hour room temperature outgassing of the present samples obviously did not remove this entire layer.

It is not clear what the vibrational excitation spectrum of adsorbed water should be for low frequencies. Room

temperature neutron scattering experiments have been carried out^{141,143} for H_2O adsorbed on $\gamma\text{-Al}_2\text{O}_3$ (Linde B (.02 μ)) and on SiO_2 (silica gel), but the excitation spectrum studied was such that $\hbar\omega_{\text{vib}} \geq 30 \text{ cm}^{-1}$ ($\hbar\omega_{\text{vib}}/k_B = T_{\text{vib}} = 53\text{K}$). These neutron experiments were more aimed at determining the physical surroundings of the H_2O molecules through observation of the intramolecular vibrations whose frequencies should depend on the form and location of the H_2O on the surface.

In Figure 33a we show schematically what the layer of H_2O should look like on the grains of Al_2O_3 . The exact way that the H_2O sits on the surface is a matter of much debate even with the neutron results. In fact, there are arguments concerning what species are actually present on the surface (e.g., does the H_2O exist as water molecules or in the form only of hydroxide ions?). In Figure 33b we show some species that are consistent with the neutron scattering and infrared data for H_2O on Al_2O_3 . In Figure 33c we show some configurations^{141,142} suggested for H_2O on SiO_2 .

Since we do not know what the vibrational spectrum of this layer of water is, it is not obvious what the specific heat is expected to look like. As a first approximation we take the specific heat of the layer to be identical to that of an equivalent amount of bulk H_2O . We show this heat capacity in Figure 34. The observed excess specific heat of Linde B (.02 μ) near $T = 10\text{K}$ can be easily accounted for

Figure 33. (a) A schematic picture of the H_2O layer adsorbed onto the Al_2O_3 particles. (b) Some possible configurations for the adsorbed H_2O on Al_2O_3 (see Refs. 142 and 143). (c) Some possible configurations of adsorbed H_2O on SiO_2 (see Refs. 142 and 143).

by this H_2O heat capacity.

In order to demonstrate that adsorbed gases (other than light atoms such as He or Ne) can have large heat capacities at low temperatures, we measured the specific heat of "1/2 Layer" of N_2 adsorbed on Alon ($.02\mu$). (As explained in Chapter IV, the exact amount of N_2 adsorbed is uncertain, but 1/2 a layer is a reasonable guess.) This heat capacity is also plotted in Figure 34. (We note that Alon ($.02\mu$) and Linde B ($.02\mu$) have the same surface areas--i.e. $100\text{ m}^2/\text{gm}$.) The data for the adsorbed N_2 shows that adsorbed layers can have heat capacities comparable to the bulk heat capacity at $T = 1\text{K}$ since the heat capacity of the "1/2 Layer" at $T = 1\text{K}$ is equal to the heat capacity of an equivalent amount of bulk N_2 at the same temperature.

Therefore we conclude that the magnitude of the excess specific heat of Linde B ($.02\mu$) at high temperatures can be well explained by the heat capacity of a layer of H_2O . The magnitude of the results for porous Vycor ($.007\mu$) and pressed Cabosil ($.007\mu$) can also be explained in this manner. However, one problem we encounter is the factor of 3 difference in the surface areas of these two SiO_2 samples ($400\text{ m}^2/\text{gm}$ and $130\text{ m}^2/\text{gm}$ for Cabosil and porous Vycor respectively) but the equality of their specific heats for $T > 5\text{K}$. The surface configurations of the H_2O may account for this act, or there may be more H_2O in the porous Vycor per unit

Figure 34. Specific heat of "1/2 layer" (see text) of adsorbed N_2 on pressed Alon ($.02\mu$) compared to the specific heat of the measured sample of Linde B ($.02\mu$) and the specific heat of the H_2O adsorbed on the surface of the particles if it were in bulk form (i.e. ice).

area. This mechanism for the excess specific heat can be checked in a straightforward manner by examining the specific heats of two samples of the same material--one sample having been exposed to air for some time and the other one having been outgassed at $T \sim 600-800^\circ\text{C}$ and exposed to air as little as possible. We have not carried out such an experiment.

We also note that the vibrational specific heat of the N_2 layer should be small for low temperatures since the N_2 layer seems to have a specific heat that is going as T^2 for low T . The H_2O layer (which is more strongly bonded than the N_2) should therefore also have a specific heat that drops faster than the observed specific heat of the Linde B. This implies that for $T \lesssim 2\text{K}$, the specific heat is caused by some other mechanism.

More quantitative arguments concerning the properties of the adsorbed film of H_2O cannot be made until more work (both experimental and theoretical) has been done of the problem.

In general, the adsorption problem is so serious that we cannot really say too much about the "intrinsic" properties of these materials until this question is resolved. Infra-red absorption measurements¹⁴⁴ for low temperatures ($T < 4.2\text{K}$) are planned on some of these samples for very low frequencies, $\nu \gtrsim 2\text{ cm}^{-1}$. This may help answer some of our questions, but specific heat measurements on properly outgassed samples

is the most crucial experiment.

The last possible source of the excess excitations we will consider for these porous materials is "glassy" excitations, i.e. the mechanisms invoked to account for the excess specific heat of glasses. One recent theory assumes that low lying atomic or molecular tunneling states exist in all glasses. Such a model could easily be applied to the present sample since it is quite possible that a large fraction of the surface atoms or adsorbed gases could have two equilibrium positions that were very close in energy. The large amount of structural disorder expected to be present at the surface of even the crystalline powders, could easily give rise to a number of tunneling modes. We note that the density of two level tunneling states required to account for the excess specific heat up to $T \sim 2K$ is only $\sim 10^{19}/cm^3$ while we have $\sim 10^{21}$ surface atoms/ cm^3 . Such excitations could well account for the excess specific heat below $T = 2K$.

Another physical model used to account for the "glassy" modes is the linear defect model of Lu and Nelkin³⁷, who postulate extended linear defects in glasses. Such a line defect could be a dislocation, although the nature of a "dislocation" in a glass is not clear. In order to reproduce the constant density of states required to give a linear term in the specific heat this theory has to assume

that the length of these defects is much longer than phonon wavelengths, i.e. $\lambda > \lambda_{\text{dom}}$. In Al_2O_3 , $\lambda_{\text{dom}} = 7.7 \times 10^3 \text{ \AA}$ at $T = .1\text{K}$ while the Linde B particles are only $2 \times 10^2 \text{ \AA}$ in diameter. It is difficult to conceive of such a line defect (i.e. a linearly correlated set of atomic defects) existing in a packed powder with a length much greater than the particle diameter. A long defect of this sort, however, could exist in porous Vycor since it is well connected, but the short range of the defects lateral extent (i.e. $\approx d_{\text{pore}}/2 = 35 \text{ \AA}$) should grossly distort the nature of the excitations of possible linear defects and should effectively wash them out. We therefore conclude that linear defects are not responsible for the excess specific heat we observe in these porous materials.

(2) Recrystallized Glasses.

In Figure 35 we give the measured specific heat of three samples of the recrystallized (>95% crystal) $(\text{MgO}, \text{Li}_2\text{O})\text{-Al}_2\text{O}_3\text{-SiO}_2$ glass (a Pyroceram--a Corning product) that contained TiO_2 and ZrO_2 as nucleating agents. These samples (all of the same composition) had different crystallite sizes and different crystal structures (β -quartz solid solution for the as-received sample and β -spodumene solid solution for the other two--see Table IX) due to their different heat treatments. The specific heats of all three of these samples are almost identical for $T > 2\text{K}$ and are more

Figure 35. Specific heat of a number of Pyroceram samples with a variety of particle sizes.

than a factor of three larger than the Debye specific heat ($\theta_D = 519K$) calculated from speed of sound measurements (by Stephens¹⁵) on the as-received ($.06\mu$) sample. The nearly constant specific heat for $T < 2K$ is due to magnetic impurities (Fe in this case). This conclusion is corroborated by the disappearance of the large excess at low temperatures in the presence of a 33 kG magnetic field. The density of two level systems is ~ 800 ppm which agrees reasonably well with the measured level of Fe impurities in the as-received material, i.e. ~ 2000 ppm. Magnetic anomalies are common in Corning products.¹⁵

Nevertheless, the specific heats of the crystallized glasses have more in common with glasses than with crystals. If it is assumed that all (or almost all) of the spin impurity heat capacity has been eliminated at $T = 0.1K$ by the 33 kG field (an assumption that is reasonable but not proven) then the intrinsic excess specific heat of this material is of the same form as that of glass.

Two other researchers have measured the specific heats of glasses and of recrystallized glasses in the $(MgO, Li_2O)-Al_2O_3-SiO_2$ family (with TiO_2 and/or ZrO_2 as nucleating agents) for $T > 1.5K$. Their results are consistent with ours. In Figure 36 we plot the specific heats of these samples along with our results for the as-received Pyroceram ($.06\mu$). Wycherly¹⁴⁵ measured the specific heat of glassy

Figure 36. Specific heat (plotted as C_v/T^3) of a number of glass samples and the corresponding glass ceramic. Also included is the specific heat of the as-received sample of crystallized Pyroceram and two forms of crystalline SiO_2 . The data for the Cervits are from Ref. 145. The data for the $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-6\text{SiO}_2$ glass and glass ceramic are from Ref. 146. The data for cristobalite are from Ref. 17.

and crystalline Cervit (a transparent crystallized glass with the β -quartz solid solution structure) and Bohn¹⁴⁶ measured the specific heats of a number of glasses and corresponding crystallized glasses (most with the β -spodumene solid solution crystal structure). As can be seen, the specific heats of the crystallized materials are all larger than the corresponding glass and have the same form as that of glass.

What is most disturbing about these materials, however, is the observation that this glassy behavior is not dependent on the existence of small crystals.¹⁴⁶ The β -spodumene crystals were all $\gtrsim 1\mu$.¹⁰⁴ For the Al_2O_3 ceramics we measured $C_v = C_{v \text{ Deb}}$ for $d \sim .8\mu$. It is not impossible that all the excess specific heat seen in these materials is due to "dirt", but that seems highly unlikely in view of the fact that Bohn's crystallized samples were cut from the same slab as the glass samples and yet the crystalline specific heat was invariably larger (by a factor of 2 or more). If this excess is intrinsic, then this leads immediately to the conclusion that "structural" defects on the scale $\sim 600 \text{ \AA} - 1\mu$ are not responsible for the excess specific heat in these crystallized samples.

The obvious source of excitations is the complicated solid solution nature of the crystals. Just as in some alkali halide solutions, there may be low lying modes (on the atomic

scale) due to the atomic disorder associated with the solute ions. In other words, given a sufficiently atomically disordered crystal, then the properties should be "glassy". This conclusion is tentative at present, but it should be verifiable in the case of the $(\text{MgO}, \text{Li}_2\text{O})\text{-Al}_2\text{O}_3\text{-SiO}_2$ materials by the study of single crystals (which can be grown) of the solid solution crystal structure. And it could be even more strongly tested by the study of one member of this glass family ($2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$) which forms a stoichiometric crystal (cordierite)^{109,110} rather than a solid solution.

Since we have associated the excess specific heats of the recrystallized glass ceramics with the solid solution nature of the crystallites, a large grain size recrystallized glass that is not a solid solution (i.e. is stoichiometric) should have a specific heat that is not glassy. Jeapes et al.¹¹⁴ have measured the specific heats of vitreous and crystalline GeO_2 ($d \sim .3\mu$) and Jeapes¹¹³ has measured the specific heats of vitreous and crystalline ($d \sim .2\mu$) diopside (CaO-MgO-2SiO_2). The results of their measurements for these two samples are shown in Figures 37 and 38. The results for these samples are quite similar. For $T > 2\text{K}$, the vitreous samples show the typical "glassy" hump and for $T < 2\text{K}$ the vitreous samples show the first signs of a linear term. Unlike the glass ceramics previously mentioned, the

Figure 37. Specific heat (plotted as C_v/T^3) of vitreous and recrystallized GeO_2 (from Ref. 114).

Figure 38. Specific heat of vitreous and recrystallized diopside (from Ref. 113).

recrystallized samples of these materials have specific heats that are lower (by as much as a factor of five) than the specific heats of the corresponding glasses. These crystallized samples for $T > 6\text{K}$ look very much like Debye solids with little dispersion. However, the crystalline specific heats of both samples rise sharply above that of the Debye limit for $T < 5\text{K}$.

The authors^{113,114} claim that this excess is a "glassy" effect, but we have a simpler explanation of the anomaly: namely adsorbed helium. Both the diopside and GeO_2 become porous when they devitrify.^{113,114} There have been no estimates of the surface areas of these porous samples, but a conservative estimate would be $A \sim 1 \text{ m}^2/\text{gm}$. (Linde C (1 μ) has a surface area of $3 \text{ m}^2/\text{gm}$.) ^4He exchange gas was used during the cooldown of their samples from $T = 77\text{K}$ to $T = 4.2\text{K}$.¹⁴⁷ The vapor pressure of an adsorbed ^4He film is extremely low at $T = 4.2\text{K}$ (e.g. 1/2 a monolayer has a vapor pressure $P \sim 10^{-9} \text{ mm}$ ¹⁴⁸). Therefore, no reasonable pumping of the sample chamber would eliminate this film. As has been shown before^{124,125}, the specific heat at $T = 1\text{K}$ of 1/2 layer of ^4He on porous glass is $C \sim 1.6 \times 10^2 \text{ erg/K m}^2$, and it has the form $C = AT + BT^2$. The magnitude of this specific heat for a $1 \text{ m}^2/\text{gm}$ sample is identical to that seen for both the recrystallized diopside and recrystallized GeO_2 . Also, we note that the temperature variation of the helium

specific heat is also comparable to that observed for the two crystallized glasses (although they are not identical). We therefore tentatively conclude that adsorbed ^4He is the cause of the deviation of these samples from Debye behavior at low temperatures. However, without an accurate measure of the surface area of the samples and/or a measurement of the specific heat without exchange gas, this conclusion will remain tentative.

B. Thermal Conductivity

(1) Pressed Powders and Sintered Ceramics

The thermal conductivities of large grain, polycrystalline ceramics have been measured by a number of people for $T > 1K$. In Figure 39 we show the results of DeGoer et al.¹⁴⁹ (which are typical) for the thermal conductivity of BeO ceramics. (The single crystal value is an estimate from the data for other high θ_D materials.¹⁵⁰) The thermal conductivities of the ceramics are less than the expected thermal conductivity of the single crystal for $T < 200K$. Phonon scattering in these ceramics is attributed to four different scattering mechanisms:¹⁴⁹ (1) phonon-phonon scattering (important for high T and assumed identical in the ceramics and the single crystal), (2) point defect (mass defect) scattering, (3) dislocation scattering, and (4) grain boundary scattering. The data for large grain ceramics can be well fit^{149,151} for $T > 1K$ using the densities of these scatterers (except for phonon-phonon scattering) as adjustable parameters.

For $T < 10K$, boundary scattering becomes the dominant mechanism and the conductivities approach the limiting T^3 temperature dependence characteristic of "geometric" (i.e. frequency independent) scattering. An examination of Figure 39 indicates, however, that the low temperature thermal conductivities do not scale with the particle size. In order

Figure 39. Measured thermal conductivity of a number of polycrystalline BeO samples (from Ref. 149) and the expected thermal conductivity of single crystal BeO (see Ref. 150).

to account for the fact that the phonon mean free path, ℓ_{ph} , did not correlate with d (the grain size), frequency independent scattering by pores trapped in the material was invoked.¹⁴⁹ Sample II had considerably more pores than Sample I. Sample I had a density $\rho_I = .992 \rho_{crys}$ while $\rho_{II} = .921 \rho_{crys}$. DeGoer et al.¹⁴⁹ found that for their porous samples, $\ell_{ph} \approx d$ at low T while $\ell_{ph} \approx 10 d$ for their non-porous sample. Similar observations have been made for non-porous polycrystalline CdS ,¹⁵¹ MgF_2 ,¹⁵¹ and KCl .¹⁵²

In Figure 40 we give the thermal conductivity of some Al_2O_3 samples. As can be seen, the behavior of these large grain Al_2O_3 ceramics for $T > 1K$ is similar to the behavior of the BeO samples we have just discussed. The larger grain ($d \sim 5-30\mu$) sample measured by Berman¹⁵³ must have considerable porosity (no data is given) since its boundary limited mean free path ($\ell_{ph} = 12\mu$ --calculated using the dominant phonon approximation) is comparable to the grain size. For the Coors Al_2O_3 ceramic we have measured ($d \sim 2-5\mu$) we find that the boundary limited mean free path ($\ell_{ph} = 31\mu$) is a factor of 10 greater than the particle size. The density of the Coors ceramic is $\rho = .998 \rho_{crys}$.

While the conductivity of the Coors ceramic (3μ) is boundary limited for $.2K < T \lesssim 10K$, the conductivity deviates from this limiting T^3 temperature dependence toward higher conductivities for $T \lesssim .2K$. In Figure 41 we show the low

Figure 40. Thermal conductivity of two polycrystalline α - Al_2O_3 ceramic samples and one single crystal α - Al_2O_3 sample. Data for the single crystal from Ref. 150 and the data for the larger grain ($d \sim 10 \mu$) ceramic sample from Ref. 153.

Figure 41. Thermal conductivity of three polycrystalline Al_2O_3 samples.

temperature thermal conductivity of the Coors ceramic (3μ) as well as the thermal conductivities of two Linde B samples: (1) pressed Linde B ($.02\mu$) and (2) sintered pressed Linde B ($.3\mu$). The sintered Linde B ($.3\mu$) is porous ($\rho = .90 \rho_{\text{crys}}$) as is the pressed Linde B ($.02\mu$) ($\rho = .50 \rho_{\text{crys}}$). For all of these samples, the conductivity differs markedly from the boundary limited value at low temperatures. In fact, the pressed Linde B ($.02\mu$) shows no region for which the conductivity is boundary limited.

In Figure 42 we plot the average mean free path for phonons in these materials using the Debye velocity of sound, v_D , and the Debye specific heat¹³⁵ of single crystal $\alpha\text{-Al}_2\text{O}_3$ in the formula $K = 1/3 C_V v_D \lambda$. For the $0.3\mu \text{ Al}_2\text{O}_3$ sample (which has a boundary limited phonon mean free path of $.15\mu$ --i.e. $\lambda_{\text{ph}} \sim d$ since it is porous) and the $3\mu \text{ Al}_2\text{O}_3$ sample the phonon mean free path increases well above the boundary limited value at the lowest temperatures. The boundaries are transparent to the phonons at these temperatures. Measurable deviation of the mean free path from the constant value first occurs when $\lambda_{\text{dom}} \approx 1/6 d$ (see the scale for λ_{dom} on the top of Figure 42). The difference between $\lambda_{\text{boundary}}$ and $\lambda_{\text{observed}}$ is a factor of 2 when $\lambda_{\text{dom}} \approx d/2$.

For the pressed Linde B ($.02\mu$) sample, a boundary limited mean free path of 0.02μ is indicated on Figure 42, but the observed value of λ_{ph} never approaches a constant.

Figure 42. Calculated phonon mean free paths for a number of polycrystalline Al_2O_3 samples. The mean free paths were calculated from the formula $K = 1/3 C_V v \lambda$ where v was taken to be the Debye velocity of sound for single crystal $\alpha\text{-Al}_2\text{O}_3$ and C_V was taken to be the Debye specific heat of single crystal $\alpha\text{-Al}_2\text{O}_3$.

The measured mean free path exceeds the particle size ($D \sim 0.02\mu$) at $T = 4K$ and continues to rise roughly as $1/T^2$ (i.e. $K \propto T$ for $T < 4K$). Just as for the larger grain materials, the boundaries are transparent to phonons.

We have also measured the thermal conductivity of a pressed Cabosil ($d \sim 0.007\mu$) sample and a sintered Cabosil sample. These results are shown in Figure 43. Comparison of Figure 40 and Figure 43 shows that the thermal conductivity of the pressed Cabosil ($.007\mu$) sample is essentially the same as that for the pressed Linde B ($.02\mu$) sample except at the lowest temperatures where the conductivity of the Cabosil is slightly higher. This agreement implies that the heat transport mechanism is the same for these two pressed powders and is more dependent on the granular nature of the material than the nature of the grains.

The sintered sample of SiO_2 has the same thermal conductivity as that of bulk vitreous SiO_2 ¹⁵⁴ although it was sintered at a temperature ($1290^\circ C$) that is well below the forming temperature of vitreous SiO_2 ($\sim 1600^\circ C$). (We might have expected that the structure of the sintered powder would be sufficiently different from that of bulk fused

Figure 43. Thermal conductivity of pressed Cabosil (.007μ) and sintered Cabosil.

silica to give a different thermal conductivity.)*

We have also measured the thermal conductivity of a slipcast ultrafine powder: Yttria stabilized ZrO_2 (.06 μ). The results for this sample are shown in Figure 44. The thermal conductivity of this porous material is comparable to that of Cabosil (0.007 μ) and pressed Linde B (.02 μ).

It is not obvious that the heat transport at $T \leq 1\text{K}$ for the porous powder samples is due to phonons. For these granular porous materials it is not clear that phonons with $\lambda_{\text{dom}} \sim d$ are well defined, propagating excitations. As discussed earlier, elastic waves with $kd \ll 1$ and $kd \gg 1$ have been shown to be well defined excitations with lifetimes longer than their periods, but no calculations have been made for the case $\lambda \sim d$. Heat transport in this temperature range could well be due to a diffusion mechanism with heat

* It is interesting to note that while the thermal conductivities of the sintered Cabosil and Spectrosil B fused silica are identical, the linear term of the specific heats of the two materials are different (i.e. C_1 sintered Cabosil = 17 erg/gm K^{-2} and C_1 Spectrosil = 12 erg/gm $^{-1}$ K^{-2}). We have not pursued the matter, but it does seem possible that a systematic study of the thermal properties of samples of Cabosil sintered at different temperatures might throw some light on the connection between structure and thermal properties of silica.

Figure 44. Thermal conductivity of a slipcast zyttrite sample.

propagating by random walk from grain to grain. However, the conductivities are sufficiently high (i.e. $K(d \sim .02\mu) \gtrsim K(d \sim .3\mu)$) in this temperature range that the prospect of such a diffusive mechanism being the dominant mode of transport seems improbable. And, in fact, as mentioned earlier, the thermal conductivity of a well connected porous material (porous Vycor glass ($d \sim .007\mu$), which we will discuss in detail in a later section) is comparable to that of vitreous SiO_2 for $T < .3\text{K}$. This fact strongly implies that propagating modes in porous material do exist and are responsible for the heat transport for $\lambda \sim d$.

Even with the assumption that the heat flow is due to phonon flow in all of these polycrystalline materials, the interpretation of the temperature dependence of the conductivity is not immediately apparent. All of the phonon scattering mechanisms mentioned earlier in relation to ceramics (phonon-phonon scattering, point defects, dislocations, boundary scattering) are either not important in this temperature range (such as point defect Rayleigh scattering) or seem to be inoperative (boundary scattering). The most obvious possible cause of the thermal resistance is phonon scattering by the density fluctuations (porosity)/structural disorder of the material. However, no theoretical work on the scattering problem in porous polycrystalline systems has been done for the case $\lambda \sim d$. It is probable that for these materials

detailed information about the connectivity (i.e. the nature of the grain boundaries) of the material is necessary to develop an accurate, quantitative solution.

A straightforward and simple model can be proposed, nevertheless, which contains the basic concepts and can reproduce much of the observed data (and, in fact, it will be shown later that the model calculation by Morgan and Smith³⁵ for density fluctuation scattering in glasses (which works well for the well connected material porous Vycor) has exactly the form we suggest). The model we propose assumes: (1) that phonons are the carriers of heat, (2) that multiple scattering of phonons is not important and (3) that single phonon scattering can be described by the equations for scattering of sound waves by spherical inclusions of diameter a in an isotropic medium. Such a calculation¹⁵⁵ would predict that if $\lambda_{\text{dom}} \lesssim a/2$ (i.e. $k_{\text{dom}} a \gtrsim 10$, then the scattering is essentially "geometric" and the scattering rate (and so also the mean free path) should vary only slowly with k_{dom} (i.e. ω_{dom} or T). For $\lambda_{\text{dom}} \gtrsim 12a$ (i.e. $k_{\text{dom}} a \lesssim 1/2$) the scattering should be Rayleigh and the scattering rate should be of the form:

$$\tau_{\text{Rayleigh}}^{-1} = \frac{\Omega_0 \Gamma k^4 v}{4\pi}$$

Here v is the velocity of sound, Ω_0 is the volume of the inclusion, and Γ is a constant that is dependent on the

density of inclusions and the mass defect associated with the inclusions. In the intermediate region (i.e. $1/2 < ka < 10$) τ^{-1} should be on the order of the geometric scattering rate and should depend on the nature of the inclusion. In Figure 45 we show schematically two possible forms of the function $\tau^{-1}(ka)$. The theory of Morgan and Smith³⁵ predicts a form like the lower curve.

Due to this strong porosity scattering, we never reach a conductivity in the fine grain materials that is comparable to that of glass. Therefore any hope of seeing glassy conductivity for these materials seems dim.

Considerable improvement in the conductivity of fine grained ceramics can be obtained by removing the porosity. In Figure 46 we show the thermal conductivity of a non-porous high pressure hot pressed (HPHP) MgO ceramic whose grain size is $d \sim .06\mu$ and whose density is $\rho \sim 1.00 \rho_{\text{crys}}$. The thermal conductivity of this sample is an order of magnitude larger than that of pressed Linde B (.02 μ) and sintered slipcast ZrO₂ (.06 μ) for $T < .5K$. In this sample there is no indication of "glassy" conductivity (i.e. $K \propto T^2$).

Like the other samples, this HPHP MgO (.06 μ) sample shows a conductivity that is considerably higher than the grain boundary limited value. In fact, the most surprising observation about this sample is that the phonon scattering is so weak at low temperatures that for $T \lesssim .05K$ the thermal

Figure 45. Two possible forms of the phonon scattering rate as a function of reduced phonon wavevector for a spherical cavity of diameter a in an isotropic medium. The exact shape depends upon the nature of medium.

Figure 46. Thermal conductivity of a fully dense, polycrystalline MgO ceramic ($d \sim .06 \mu$) and a single crystal of MgO (from Ref. 150).

conductivity should be limited by the size of the sample ($\ell_{\text{sample}} \sim .1 \text{ cm}$). Extending measurements for this sample to lower temperatures to look for possible "glassy" conductivity at sufficiently low temperatures would be fruitless as the maximum temperature range such a conductivity would cover would be too small to identify it. The phonon mean free path at $T = 0.1\text{K}$ is $\ell_{\text{ph}} = 200\mu$. In vitreous SiO_2 at $T = 0.1\text{K}$ $\ell_{\text{ph}} = 160\mu$.

The high temperature conductivity ($T > 10\text{K}$) of this sample varies as T^2 . A similar temperature dependence has been observed for a hot pressed CdS^{151} sample ($d \sim 2\mu$) and a hot pressed MgF_2^{151} sample ($d \sim .4\mu$). This temperature dependence is characteristic of the scattering of phonons by dislocations. The strain field scattering of a dislocation has been evaluated by Carruthers⁹ who finds that the scattering rate is:

$$\tau_d^{-1}(\omega) = N_d r_c \omega.$$

Here N_d is the density of dislocation lines per unit area and r_c is a constant that depends upon the material. Using the value of r_c applicable to MgO^{156} ($r_c = 2.11 \times 10^{-15} \text{ cm}^2$) we find that we need a dislocation density $N_d = 9 \times 10^{12} / \text{cm}^2$ to explain our observed mean free path at $T = 10\text{K}$. This density is extremely large (i.e. it requires $\sim 4 \times 10^2$ dislocations per MgO grain). It has been noted¹⁵⁶, however, that for alkali halide samples with known dislocation densities,

the calculated values of r_c predict scattering that is 20 to 400 times lower than that actually observed. If the correct value for the constant r for MgO is around 100 times larger for MgO than the value calculated previously¹⁵⁶ (as has recently been proposed⁹) then the expected dislocation density would only be $N_d \cong 9 \times 10^{10} / \text{cm}^2$ -- i.e. ~ 4 dislocations per MgO grain. This value is physically reasonable. However, we cannot conclude that dislocation scattering is responsible for the observed conductivity without further corroboration.

We note that the mass defect mean free path expected for this sample is much larger than the observed mean free path. For a 0.1% impurity level (manufacturers' specifications for the starting powder) we find $\lambda_{\text{point defect}} \cong 2 \times 10^{-5} \text{ cm}$ at $T = 80\text{K}$, $\lambda_{\text{obs}} = 7 \times 10^{-7} \text{ cm}$ at $T = 80\text{K}$. $\lambda_{\text{point defect}}$ increases as $1/T^4$ at lower temperatures while $1/\lambda_{\text{obs}}$ increases only as $1/T$.

For $T < 10\text{K}$, the thermal conductivity of the HPHP MgO decreases more slowly than T^2 and for $T < 1\text{K}$, $K \propto T$. Like the porous media, we expect that mass density/force constant fluctuations are responsible for this conductivity. We will make no attempt to calculate the mean free path, however, as the lack of porosity makes it difficult to assign quantities in the limiting Rayleigh scattering equation.

We note that just as we expect grain boundary scattering to die out for $\lambda > d$, it has been shown that dislocation

scattering should die out when $\lambda > R^{158}$, where R is the mean separation of dislocations.

In summary, we have seen that for polycrystalline ceramic materials, the grain boundaries become transparent to phonons for $\lambda \lesssim 1/6 d$. Also, for these materials, there is no indication of glassy scattering at any temperature, although for the samples with the finest grain sizes the conductivity was limited by the porosity.

(2) Recrystallized Glasses

In Figure 47 we show the thermal conductivity of two samples of a Pyrocera^m recrystallized glass from the $(\text{MgO}, \text{Li}_2\text{O})\text{-Al}_2\text{O}_3\text{-SiO}_2$ glass family. The as-received sample had a particle size $d \sim 0.06\mu$ and the thermal conductivity was measured by Stephens.¹⁵ The heat treated sample had $d \sim 1\mu$. As can be seen, both samples have conductivities that exceed the grain boundary limit at low temperatures. The most interesting aspect of this data is that the conductivity of the fine grained Pyrocera^m ($.06\mu$) is identical to that of soda silica glass for $T < .15\text{K}$ and in general has the same form as that of soda-silica glass for the entire temperature range. This behavior is in contrast to the behavior of the HPHP MgO (0.06μ) ceramic which shows no glassy behavior at any temperature.

In Figure 48 we plot the thermal conductivities of these two non-porous fine grained materials, i.e. HPHP MgO ($.06\mu$)

Figure 47. Thermal conductivity of two samples of Pyroceram with different grain sizes.

Figure 48. Thermal conductivity of polycrystalline MgO ($d \sim .06\mu$) and the as-received Pyroceram ($d \sim .06\mu$). The curve labelled "Pyroceram Structure" was calculated by subtracting out the glassy scattering (assumed to be identical to that of the $\text{Na}_2\text{O}-3\text{SiO}_2$ glass) from the total scattering using

$$\frac{1}{k_{\text{Pyroceram "Structure"}}} = \frac{1}{k_{\text{obs}}} - \frac{1}{k_{\text{glass}}}$$

and the as-received Pyroceram ($.06\mu$). The particle sizes of the samples are the same and the Debye sound velocities are similar (6.6×10^5 cm/sec for MgO and 4.2×10^5 cm/sec for Pyroceram). Also, the order of magnitude of the conductivities are similar. However, the shape of the two curves are quite different.

The difference in shape implies that the scattering mechanisms are different. For high temperatures ($T > 5K$), the low conductivity of both of the Pyroceram samples is easily understood. The recrystallized glass crystallites have a complex solid solution crystal structure of $(MgO, Li_2O)-Al_2O_3-SiO_2$. The material is not stoichiometric. The short range disorder (mass and force constant changes) should introduce considerable scattering. A stoichiometric recrystallized glass (Corning Code 9606 which has crystallites of $2MgO-2Al_2O_3-5SiO_2$ ⁹⁸ (cordierite) nucleated with TiO_2) has a conductivity which is equal to that of the Pyroceram at $T = 1.5K$ but that does not plateau¹⁵⁹ for $T > 2K$. The conductivity of Corning Code 9606 is more than an order of magnitude greater than that expected for either of the present Pyroceram samples for $T = 80K$.¹⁶⁰

The low temperature "glassy" behavior of the fine grain glass ceramic is not so easily explained however. From our earlier analysis of the specific heats of these Pyroceram samples, we come to the conclusion that the specific heat

was "glassy" for all glass ceramics in the solid solution family of $(\text{MgO}, \text{Li}_2\text{O})\text{-Al}_2\text{O}_3\text{-SiO}_2$ irrespective of crystallite size. We also concluded that likely sources of the excess specific heats observed were low lying modes associated with the solid solution atoms or with the TiO_2 or ZrO_2 nucleating agents. Such low lying modes could also be the "glassy" scattering centers for the as-received Pyroceram. If such were the case, then the mean free path of the sample, ℓ_s , could be written:

$$1/\ell_{\text{sample}} = 1/\ell_{\text{glassy}} + 1/\ell_{\text{structure}}$$

Here $\ell_{\text{structure}}$ is the mean free path due to scattering by the granular "structure" of the material and ℓ_{glassy} is the mean free path due to "glassy" scattering. In Figure 48 we also plot the thermal conductivity of the Pyroceram sample that we would expect if the "glassy" scattering were not present, i.e. we plot $K = 1/3 C_v v \ell_{\text{structure}}$ where we calculate the $\ell_{\text{structure}}$ from the equation:

$$1/\ell_{\text{structure}} = 1/\ell_{\text{observed}} - 1/\ell_{\text{glassy}}$$

and $\ell_{\text{glassy}} = \ell_{\text{Na}_2\text{O-3SiO}_2}$. As can be seen, the shape of this curve has more in common with the curve of the HPHP MgO than does the experimental curve. The large grain Pyroceram sample should not show "glassy" conductivity if this model is correct, since for the large crystallite case $\ell_{\text{structure}} < \ell_{\text{glassy}}$.

The above explanation of the observed scattering for Pyroceram can be tested in a straightforward manner as can the earlier explanation of the specific heat. As mentioned earlier, solid solution single crystals can be grown from compositions in this family of glasses. For these samples, we would expect to see "glassy" behavior at all temperatures since $\lambda_{\text{structure}} \sim d_{\text{crystal}} \sim 1 \text{ cm}$. Also, single crystals of stoichiometric cordierite can be grown to demonstrate that the observed effects really are due to solid solution effects and not some dirt effect.

A number of glasses can be devitrified without nucleating agents into a fine grain ($d \sim .3\mu$) polycrystalline solid. Diopside (CaO-MgO-2SiO_2) is one such material. The thermal conductivity of vitreous and polycrystalline diopside is shown in Figure 49. Like all of the other polycrystalline systems we have studied, the thermal conductivity of this sample deviated from the boundary limited value for low temperatures. Unfortunately, when diopside devitrifies it becomes porous (no measure of the porosity is available). This porosity is evidenced in the thermal conductivity since the boundary limited mean free path is such that $\lambda_{\text{ph}} \sim d$.

Because of the porosity, comparison of the thermal conductivities of this sample and the sample of heat treated Pyroceram ($.3\mu$) does not seem warranted. We only note that the thermal conductivity of this sample is comparable in

Figure 49. Thermal conductivity of vitreous and polycrystalline diopside. Data for vitreous diopside and the high temperature data for polycrystalline diopside were from Ref. 113.

form to that of the sintered Linde B ($.3\mu$) sample and does not plateau for $T > 2K$ but continues to rise.

(3) Phase Separated Glasses

As we have seen, the thermal conductivities of the polycrystalline materials that we have discussed are all affected by the presence of the granular structure, but in only one case did we actually observed a glassy conductivity. And in that one case (the as-received Pyroceram ($.06\mu$)) we have argued that the local disorder--not the long range structural disorder--is responsible for the glassy behavior. The crystalline grain boundaries could be messing up the "glassy" scattering so that the observed phonon scattering is not comparable to that for "grains" in glasses. In order to check this possibility, well connected glasses with only mass density fluctuation (speed of sound fluctuations) were needed.

We therefore measured the thermal conductivities of two well-connected, isotropic materials into which only density fluctuations had been produced: namely, phase separating glasses. In Figure 50 we show the thermal conductivity of a sodium borosilicate phase separated glass that had a grain size of 0.3μ . As can be seen, the gross fluctuations in composition and speed of sound that we have introduced seem to have absolutely no effect on the thermal conductivity. A similar observation was made by Krüger¹⁶¹ who studied the

Figure 50. Thermal conductivity of a phase separated soda silica glass.

thermal conductivities of a number of glasses in the $\text{Na}_2\text{O}-\text{SiO}_2$ family (which has a miscibility gap for Na_2O concentrations ≤ 25 mole %⁹⁸) and could not see any effects attributable to the large scale ($d \sim 100-1000 \text{ \AA}$) phase separations in some of the samples. This lack of an observable effect puts quite a strain on the concept of granular scattering in general and the models of Klemens³⁴ and Morgan *et al.*³⁵ in particular.

In order to evaluate the expected phonon scattering rate predicted by Klemens'³⁴ theory for the phase separated sodium borosilicate glass we have studied, we need to know the difference in the speed of sound in the two phases. However the exact compositions of these two phases is not known, although it is known that one is SiO_2 rich and the other is $\text{Na}_2\text{-B}_2\text{O}_3$ rich. Also, for properly heat treated samples of a similar composition, the silica rich phase approaches 96% SiO_2 and the $\text{Na}_2\text{O-B}_2\text{O}_3$ phase approaches sodium tetraborate. With this in mind, we can estimate the difference in the speed of sound in the two phases.

In Figure 51 we show the previously measured¹¹⁶ speed of sound in a number of glasses in this family of glasses. As can be seen, a reasonable guess is

$$\frac{|v_{\text{SiO}_2 \text{ phase}} - v_{\text{Na}_2\text{O-B}_2\text{O}_3 \text{ phase}}|}{\bar{v}} \sim .04$$

Figure 51. Speed of sound in a number of Na_2O containing glasses showing the variation as a function of composition. Graph from Ref. 116.

Therefore, from Eq. (20) in Section II we get: (with

$$s(x) \equiv v(x) - \bar{v})$$

$$\frac{\overline{s^2}}{\bar{v}^2} = 4 \times 10^{-4}$$

If we assume that the fluctuations can be described with the spherically symmetric correlation function $f(r) = e^{-r/a}$ (with a = the grain size = $.3\mu$) then we get Eq. (21) to describe the scattering:

$$\frac{1}{\lambda(k_{\text{dom}})} = \frac{48\pi \overline{s^2}}{\bar{v}^2 a} \ln(1 + 4k_{\text{dom}}^2 a^2) - \frac{4k_{\text{dom}}^2 a^2}{4k_{\text{dom}}^2 a^2 + 1} \quad (21)$$

Evaluating this for the dominant phonon photons at $T = .1\text{K}$ (where $k_{\text{dom}} a = 4.7$) we find that:

$$\lambda(k_{\text{dom}}) = 1\mu$$

However, at $T = 0.1\text{K}$ we find $\lambda_{\text{obs}} = 100\mu$.

For λ_{theory} to equal λ_{obs} would require that

$$\frac{|v_{\text{SiO}_2 \text{ phase}} - v_{\text{Na}_2\text{O-B}_2\text{O}_3 \text{ phase}}|}{\bar{v}} = .004$$

This value is not impossible, but it seems highly unlikely that such a small difference exists. We therefore conclude that the Klemens theory does not work in the case of this phase separated glass.

In Figure 52 we show the thermal conductivity of two samples of porous Vycor glass. The conductivity is almost

Figure 52. Thermal conductivity of two different samples of porous Vycor glass ($d \sim .007 \mu$) and a sample of pressed Cabosil ($d \sim .007 \mu$).

identical to that of SiO_2 below $T = .3\text{K}$ although it deviates from this value for $T > .3\text{K}$. The Klemens theory fails miserably in describing this material. Since $v \equiv 0$ in the pore, then we have $\overline{s^2}/\overline{v}^2 \approx 0.3$ (because 30% of the material is open volume). Therefore, with $a = 70 \text{ \AA}$, Eq. (18) predicts at $T = .5\text{K}$ that:

$$\lambda(k_{\text{dom}}) \approx 1 \text{ \AA} = 10^{-4} \mu.$$

However, $\lambda_{\text{obs}} = 5\mu$.

The theory of fluctuation scattering developed by Morgan and Smith³⁵ works quite well for this case, however, if we assume that the low temperature ($T < .15\text{K}$) scattering is not due to the pores but is due to some other "glassy" effect. We then write:

$$\frac{1}{\lambda_{\text{pores}}} = \frac{1}{\lambda_{\text{observed}}} - \frac{1}{\lambda_{\text{glass}}}$$

or

$$\frac{1}{K_{\text{pores}}} = \frac{1}{K_{\text{observed}}} - \frac{1}{K_{\text{glass}}}$$

If we assume that K_{glass} is given by the dashed line (i.e. $K_{\text{glass}} = .76 K_{\text{SiO}_2}$) in Figure 52, then we find for K_{pores} the curve shown in Figure 53. This curve is of exactly the form predicted by Morgan and Smith³⁵ for density fluctuations with $a \sim 60 \text{ \AA}$ and it is of the right order of magnitude if $\Delta^2 = 0.3$. The differences in conductivity of the two different samples of porous Vycor can be easily accounted for with

Figure 53. Thermal conductivity of porous Vycor "structure" calculated using

$$\frac{1}{K_{\text{Vycor structure}}} = \frac{1}{K_{\text{obs}}} - \frac{1}{K_{\text{glass}}}$$

a difference of $\sim 5-10 \text{ \AA}$ in the mean diameter of the pores in the two samples (such variations are common in different samples of this material). The minimum in the conductivity occurs at $T \sim .4\text{K}$ where $ka \sim 1$ if $a = 60 \text{ \AA}$. Below the minimum, K goes roughly as $1/T$ as is expected for Rayleigh scattering when $ka \ll 1$. While no quantitative comparison of theory and experiment can be made until speed of sound measurements have been carried out on porous Vycor, the excellent qualitative agreement indicates that this analysis should be valid if we accept the assumption that density fluctuations due to the existence of the pores are not responsible for the phonon scattering at the lowest temperatures.

VI. SUMMARY AND CONCLUSIONS

Unfortunately, we conclude that the evidence presented in this thesis does not support the contention that extended structures are responsible for the anomalous thermal properties of glasses. We summarize the thermal properties of granular materials below.

(1) Specific heat: The specific heat of fine grained, porous packed powders were considerably larger than that of the bulk material, but the surface adsorption problem made interpretation of the results in terms of glassy behavior uncertain. However, after the powders were sintered to remove the adsorbing surface (and to let the particles grow) the excess specific heat went away.

For the solid solution recrystallized glasses, an excess specific heat (over that of Debye) has been observed that was larger than the excess in the corresponding glass and that did not decrease with increasing particle size.

For non-solid solution recrystallized glasses, the specific heat of the crystalline phases were lower (by a factor of 5) than the specific heat of the glassy phase except at $T < 2K$ where the observed anomalies are probably due to helium adsorption.

(2) Thermal Conductivity: The presence of a granular structure in polycrystalline ceramics did greatly affect the

form of the low temperature thermal conductivity, but in all the ceramic materials investigated no sign of glassy behavior was observed. The boundaries of the grains became transparent at sufficiently low temperatures, but there was no indication that in the limit $\lambda_{\text{dom}} \gg d$ that the conductivity would go as T^2 .

For the solid solution recrystallized glasses, a T^2 thermal conductivity at low temperatures was observed for the smallest crystallite size. However, because the shape of the thermal conductivity curve was so different from that for an MgO ceramic with the same particle size, we concluded that the granular nature of the material was not causing the observed scattering rate.

For nonporous phase separated glasses, the decomposition of the single phase glass had little or no effect on the observed conductivity, even with the large differences in composition of the two phases. Only removal of one of the phases (by leaching) to produce a porous material had any effect on the conductivity, and even for this material, at sufficiently low temperatures the conductivity was equivalent to that of the bulk, nonporous material. The scattering theories based on spherically symmetric density (or speed of sound) correlation functions cannot account for the observed conductivities of these granular glasses and account for the conductivity of single phase, nonporous

glasses within the same model.

The granular models for glasses do not work on real granular materials. Although a number of the problems we have encountered (water adsorption and Fe impurities for example) make definitive statements impossible, the general conclusion seems to be that atomic or molecular disorder that is present (or not present) determines the existence (or non-existence) of glassy thermal behavior.

As mentioned earlier, the most fruitful areas of work to test this conclusion in relation to the materials we have studied is to examine the specific heat of thoroughly outgassed porous samples and the thermal conductivity and specific heat of Fe free single crystals of the solid solution crystal structure found in the glass ceramics.

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Appendix A

CALIBRATION DATA FOR Ge THERMOMETER (Cryocal #3773)

Tabulated below are the Resistance vs. Temperature data points for the Ge thermometer #3773.

Table XI

R (Ω)	T (K)	R (Ω)	T (K)
33.89	23.30	344.50	4.620
37.34	21.20	390.26	4.251
41.32	19.30	397.25	4.201
45.58	17.61	451.62	3.860
51.05	16.02	521.55	3.510
57.06	14.63	603.20	3.190
64.26	13.28	698.40	2.900
73.38	12.07	809.50	2.640
84.15	11.02	946.50	2.396
96.31	10.05	1034.7	2.270
97.88	9.95	1220.5	2.060
113.76	9.04	1449.4	1.885
132.86	8.23	1768.3	1.696
155.80	7.48	2109.0	1.550
184.50	6.77	2570.0	1.408
217.00	6.15	3030.0	1.302
253.72	5.61	3596.7	1.206
294.80	5.10		
344.50	4.62		

3

Appendix B

The thermal conductivity and specific heat data shown in the figures in the text of this thesis are tabulated in this appendix. In Table XII, we list the materials studied, the properties measured, and the location of the numerical data for these materials.

Table XII

Material	Material Description	Property Measured	Data Table
Pressed Linde B (.02 μ)	p. 70	$C_v(T)$ $K(T)$ $\perp$ to laminations $K(T)$ to laminations	XIII A(1) XIII A(2) XIII A(3)
Pressed Cabosil (.007 μ)	p. 70	$C_v(T)$ $K(T)$ $\perp$ to laminations $K(T)$ II to laminations	XIII B(1) XIII B(2) XIII B(3)
Pressed Gamma Exal (.02 μ)	p. 70	$C_v(T)$	XIII C
Pressed Alon (.02 μ)	p. 70	$C_v(T)$	XIII D
Initially Sintered Pressed Linde C (1 μ)	p. 70	$C_v(T)$	XIII E
Initially Sintered Pressed Linde A (.3 μ)	p. 70	$C_v(T)$	XIII F
Initially Sintered Slipcast Zyttrite (.06 μ)	p. 71	$K(T)$	XIII G
Initially Sintered Slipcast Linde A (1 μ)	p. 71	$C_v(T)$	XIII H
Sintered (1395°C) Pressed Linde B (.3 μ)	p. 72	$K(T)$	XIII I

Material	Material Description	Property Measured	Data Table
Sintered (1495°C) Pressed Linde B (.8μ)	p. 72	$C_V(T)$	XIII J
Sintered (1800°C) Pressed Linde B (20 μ)	p. 72	$C_V(T)$	XIII K
Coors Alumina Ceramic (3 μ)	p. 72	K(T)	XIII L
High Pressure Hot Pressed MgO (.06μ)	p. 72	K(T)	XIII M
Sintered Pressed Cabosil (1mm)	p. 72	$C_V(T)$ K(T)	XIII N(1) XIII N(2)
Pyroceram As- Received (.06μ)	p. 73	$C_V(T)$	XIII P
Pyroceram Treated at 1080°C (.3μ)	p. 73	$C_V(T)$	XIII Q
Pyroceram Treated at 1175°C (1μ)	p. 73	$C_V(T)$ K(T)	XIII R(1) XIII R(2)
Recrystallized Dioposide (.2μ)	p. 73	K(T)	XIII S
Porous Vycor Glass (.007μ)	p. 74	$C_V(T)$ K(T)	XIII T(1) XIII T(2)
Phase-separated Sodium-Borosilicate Glass (.3μ)	p. 74	K(T)	XIII V
" $\frac{1}{2}$ Layer" of N ₂ on Alon (.02μ) ²	p. 92	$C_V(T)$	XIII Y
KBr _{.50} -KI _{.50}	-	$C_V(T)$	XIII Z

Table XIII

A. Pressed Linde B (.02 μ)(1) Pressed Linde B (.02 μ) - Specific Heat Run RT73-M=13.20 gm

T(K)	C_V (erg gm ⁻¹ K ⁻¹)	T(K)	C_V (erg gm ⁻¹ K ⁻¹)
18.76	.300 x 10 ⁵	2.56	.210 x 10 ³
16.82	.234	2.17	.1613
15.09	.1805	1.820	.1306
13.38	.1363	1.658	.1005
12.94	.1187	1.596	.1003
12.73	.1178	1.393	.801 x 10 ²
11.88	.1002	1.339	.719
11.39	.898 x 10 ⁴	1.141	.546
10.06	.665	.914	.416
9.23	.501	.829	.335
8.12	.386	.790	.321
7.63	.345	.728	.294
7.03	.265	.692	.274
6.89	.252	.629	.250
6.38	.202	.556	.209
5.66	.1538	.549	.209
5.14	.1131	.503	.1898
4.73	.938 x 10 ³	.498	.203
4.30	.720	.444	.1672
4.05	.604	.450	.1657
3.80	.511	.417	.1544
3.48	.403	.412	.1483
3.27	.349	.376	.1325
2.99	.291	.372	.1277
2.71	.250	.329	.1091
.329	.1128 x 10 ²	.174	.449 x 10
.322	.1096	.174	.444
.328	.1085	.156	.336
.280	.875 x 10	.156	.329
.277	.814	.132	.277
.270	.864	.136	.282
.230	.645	.132	.278
.226	.685	.125	.213

T(K)	C_v (erg gm ⁻¹ K ⁻¹)
.207	.549 x 10
.208	.592
.189	.517
.188	.470
.177	.418

- (2) Pressed Linde B (.02μ) - Thermal Conductivity I to Laminations.
Run RT 7*- L/A = .101

T(K)	K(Watt cm ⁻¹ K)	T(K)	K(Watt cm ⁻¹ K)
2.56	.1955 x 10 ⁻⁶	.483	.309 x 10 ⁻⁷
2.04	.1760	.458	.290
1.771	.1291	.414	.228
1.547	.1073	.332	.197
1.281	.953 x 10 ⁻⁷	.325	.175
1.100	.832		
1.035	.685		
.836	.605		
.721	.489		
.696	.431		
.611	.352		

- (3) Pressed Linde B (.02μ) - Thermal Conductivity II to Laminations
Run RT 54 - L/A = 1.40

T(K)	K(Watt cm ⁻¹ K ⁻¹)
9.20	.226 x 10 ⁻⁴
7.45	.1585
5.08	.838 x 10 ⁻⁵
4.22	.702
3.11	.393
2.04	.272
1.921	.1833

Run RT55 - L/A = 1.40

T(K)	K(Watt cm ⁻¹ K ⁻¹)	T(K)	K(Watt cm ⁻¹ K ⁻¹)
.845	.1284 x 10 ⁻⁵	.440	.554 x 10 ⁻⁶
.647	.1052	.282	.502
.522	.797 x 10 ⁻⁶	.218	.322
.182	.195	.144	.245
1.352	.232 x 10 ⁻⁵	1.226	.1785 x 10 ⁻⁵

B. Pressed Cabosil (.007 μ)

(1) Pressed Cabosil (.007 μ) - Specific Heat

Run RT 73 - M = 3.92 gm and Run RT 64 - n = 3.92 gm

<u>T(K)</u>	<u>C_V(erg gm⁻¹K⁻¹)</u>	<u>T(K)</u>	<u>C_V(erg gm⁻¹K⁻¹)</u>
19.27	.378 x 10 ⁶	1.070	.265 x 10 ³
17.74	.324	.949	.209
16.05	.259	.742	.1308
13.72	.1696	.651	.1041
12.88	.1435	.570	.821 x 10 ²
11.68	.1061	.510	.692
11.09	.958 x 10 ⁵	.475	.606
10.12	.790	.447	.556
9.26	.606	.423	.507
8.48	.498	.383	.408
7.75	.400	.332	.331
7.11	.306	.301	.302
6.91	.288	.276	.269
6.40	.237	.244	.208
5.68	.1663	.236	.1915
5.13	.1295	.223	.1831
4.75	.1031	.1953	.1540
4.30	.735 x 10 ⁴	.1783	.1341
4.06	.626	.1651	.1200
3.49	.404	.1555	.1085
3.26	.331	.1363	.900 x 10
2.99	.268	.1183	.846
2.72	.202	.1195	.860
2.57	.1709	.1114	.812
2.16	.1180	.1114	.830
1.553	.603 x 10 ³	.1051	.763
1.402	.474	.1047	.761
1.255	.375	.1020	.790
1.104	.282	.1025	.750
1.701	.745		

(2) Pressed Cabosil (.007 μ) - Thermal Conductivity $\perp$ to Laminations
Run RT 51 - L/A .095

T(K)	K(Watt cm ⁻¹ K ⁻¹)
11.71	.592 x 10 ⁻⁵
10.23	.425
7.53	.226
5.48	.1295
4.25	.979 x 10 ⁻⁶
3.22	.527
2.38	.309

Run RT 50 - L/A = 0.95

T(K)	K(Watt cm ⁻¹ K ⁻¹)
2.245	.387 x 10 ⁻⁶
2.039	.333
1.806	.287
1.715	.278
1.588	.246
1.329	.1976
1.149	.1649
1.015	.1582
.938	.1474
.817	.1311

(3) Pressed Cabosil (.007 μ) - Thermal Conductivity $\parallel$ to Laminations
Run RT 53 - L/A = .740

T(K)	K(Watt cm ⁻¹ K ⁻¹)	T(K)	K(Watt cm ⁻¹ K ⁻¹)
1.242	.1367 x 10 ⁻⁵	.215	.553 x 10 ⁻⁶
1.069	.1165	.1772	.518
.962	.1083	.1556	.488
.886	.998 x 10 ⁻⁶	.1441	.459
.794	.998	.1285	.426
.696	.878	.1152	.404
.641	.861	.1055	.357
.561	.828	.0969	.370
.479	.734	.0877	.344
.432	.751	.0807	.332
.389	.701	.0745	.306
.351	.669	.0701	.295
.323	.641	.0659	.291
.287	.620	.0621	.270

(3) cont.

T(K)	K(Watt cm ⁻¹ K ⁻¹)
.271	.595 x 10 ⁻⁶
.252	.604
.225	.555

T(K)	K(Watt cm ⁻¹ K ⁻¹)
.0576	.267 x 10 ⁻⁶
.0544	.273

Run RT 51 - L/A = 6.80

T(K)	K(Watt cm ⁻¹ K ⁻¹)
79.2	.82 x 10 ⁻³
12.69	.515 x 10 ⁻⁴
10.24	.338
7.54	.1843
5.49	.1005
4.27	.647 x 10 ⁻⁵
3.21	.387
2.39	.1821
1.714	.1948

Run RT 50 - L/A = 5.80

T(K)	K(Watt cm ⁻¹ K ⁻¹)
2.270	.244 x 10 ⁻⁵
2.078	.215
1.824	.1873
1.615	.1642
1.342	.1371
1.166	.1245
1.031	.1185
.951	.1157
.827	.1052
.721	.992 x 10 ⁻⁶
.639	.933
.572	.881
.477	.808
.414	.699
.366	.697

C. Pressed Gamma Exal (.02μ) - Specific Heat

Run RT 54 - M=3.77 gm

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
1.965	.1551 x 10 ³	.184	.489 x 10
1.721	.1084	.171	.397
1.581	.1041	.155	.345
1.372	.985 x 10 ²	.144	.321
1.247	.827	.132	.284
1.092	.643	.132	.285
.987	.541	.110	.264
.797	.371	.101	.200
.740	.347	.101	.200
.632	.279	.0943	.173
.576	.257	.0942	.187
.510	.217	.0903	.181
.464	.1772	.0904	.176
.418	.1697	.0837	.150
.384	.1473	.0790	.140
.347	.1378	.0763	.157
.317	.1049	.0737	.140
.289	.1032	.0725	.151
.264	.871 x 10	.0718	.140
.240	.724	.0727	.122
.222	.637	.0724	.124
.222	.681	.0728	.138
.203	.614		

D. Pressed Alon (.02μ) - Specific Heat

Run RT 60 - M = 14.19 gm

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
2.142	.490 x 10 ³	.225	.796 x 10 ²
1.932	.474	.210	.703
1.732	.451	.199	.648
1.600	.442	.187	.578
1.328	.404	.177	.499
1.420	.411	.165	.463
1.249	.397	.159	.428
1.158	.385	.153	.397
1.084	.373	.141	.358
1.012	.369	.130	.312

D. cont.

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
.925	.347 x 10 ³	.132	.298 x 10 ²
.838	.332	.127	.288
.733	.309	.121	.243
.646	.288	.119	.266
.581	.264	.113	.238
.520	.250	.110	.245
.475	.222	.109	.251
.405	.1881	.105	.235
.365	.1633	.101	.232
.328	.1441	.0976	.222
.303	.1257	.0971	.225
.275	.1115	.0928	.238
.251	.946 x 10 ²	.0903	.219
		.0893	.212

E. Initially Sintered Pressed Linde C (1μ) - Specific Heat
Run RT 60-61 - M = 20.73 gm

T(K)	C_v (erg gm ⁻¹ K ⁻¹)
1.515	.1215 x 10 ³
1.362	.1161
1.205	.1118
1.091	.1123
.876	.1182
.738	.1232
.582	.1380
.450	.1501
.301	.1495
.230	.1319
.184	.1174
.165	.992 x 10 ²
.142	.871
.123	.630

F. Initially Sintered Pressed Linde A (.3 μ) - Specific Heat

Run RT 58* - M = 14.28 gm

T(K)	C_v (erg gm ⁻¹ K ⁻¹)
1.561	.1104 x 10 ³
1.424	.1077
1.276	.1050
1.184	.1044
1.037	.1014
.891	.1024
.788	.1081
.691	.1131
.547	.1264
.482	.1262
.432	.1285
.323	.1291
.231	.1101
.203	.1091
.178	.900 x 10 ²
.161	.797
.143	.654
.123	.471
.108	.343
.107	.368
.107	.326

G. Initially Sintered Slipcast Zyttrite (94% ZrO₂ + 6% Y₂O₃)(.06 μ) -

Thermal Conductivity

Run RT 80 - L/A = 2.66

T(K)	K(Watt cm ⁻¹ K ⁻¹)
1.405	.203 x 10 ⁻⁵
1.262	.1632
1.146	.1514
1.043	.1217
.848	.865 x 10 ⁻⁶
.672	.784
.654	.551
.462	.339
.375	.250
.340	.213
.318	.1821

H. Initially Sintered Slipcast Linde A (.3 μ) - Specific Heat

Run RT 74 - M = 11.51 gm

T(K)	C_v (erg gm ⁻¹ K ⁻¹)
4.48	.482 x 10 ³
3.91	.449
3.37	.421
2.66	.378
2.21	.381
1.862	.342
1.602	.324
1.194	.331
.978	.375
.811	.356
.704	.382
.584	.351
.483	.393
.455	.341
.388	.427
.330	.391
.321	.464

I. Sintered (to 1395°C) Linde B (.3 μ) - Thermal Conductivity

Run by L.F. Lou - L/A = 1.56

T(K)	K (Watt cm ⁻¹ K ⁻¹)
1.223	.246 x 10 ⁻⁵
1.052	.1352
.941	.1297
.891	.1021
.846	.865 x 10 ⁻⁶
.797	.742
.735	.621
.624	.426
.531	.284
.460	.281
.451	.236
.341	.177
.292	.101
.269	.123
.242	.931 x 10 ⁻⁷
.221	.681
.163	.818

J. Sintered (to 1495°C) Linde B (.8μ) - Specific Heat

Run RT 84 - M = 16.19 gm

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
21.8	.933 x 10 ⁴	3.91	.631 x 10 ²
19.97	.702	3.50	.407
18.05	.511	3.51	.404
16.82	.410	3.20	.362
15.21	.306	3.19	.358
14.25	.249	2.78	.246
12.66	.173	2.74	.227
11.63	.134	2.59	.188
10.57	.103	2.55	.186
10.46	.102	2.52	.185
9.69	.881 x 10 ³	2.28	.150
8.83	.582	1.961	.126
7.69	.391	1.952	.120
7.28	.326	1.774	.101
6.44	.230	1.783	.961 x 10 ¹
6.24	.203	1.498	.712
5.77	.175	1.513	.721
5.62	.142	1.294	.540
4.92	.107	1.092	.402
4.46	.845 x 10 ²	.948	.295
4.32	.805		

K. Sintered (1800°C) Linde B (20μ) - Specific Heat

Run RT 84 - M = 16.83 gm

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
21.91	.931 x 10 ⁴	3.80	.504 x 10 ²
19.95	.720	3.16	.302
18.18	.539	2.73	.208
16.42	.403	2.16	.1354
15.68	.317	1.913	.1072
14.17	.241	1.584	.804 x 10
12.75	.1716	1.411	.641
11.60	.1286	1.233	.508
10.42	.1004	1.037	.350
9.56	.703 x 10 ³	.901	.254
8.02	.445	.681	.122

K. cont.

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
7.36	.327 x 10 ³	.558	.625 x 10
6.45	.211	.504	.577
6.40	.216	.452	.388
5.27	.1292		
4.59	.853 x 10 ²		
4.42	.801		

L. Coors Al₂O₃ Ceramic (3μ) - Thermal Conductivity
Run RT 59 -L/A = 2.056

T(K)	K(Watt cm ⁻¹ K ⁻¹)	T(K)	K(Watts cm ⁻¹ K ⁻¹)
1.560	.988 x 10 ⁻³	.1627	.1277 x 10 ⁻⁵
1.322	.598	.1463	.961 x 10 ⁻⁶
1.196	.408	.1318	.752
1.071	.296	.1189	.557
1.038	.259	.0999	.375
.965	.218	.0924	.306
.850	.1459	.0886	.230
.772	.1100	.0834	.254
.629	.586 x 10 ⁻⁴	.0793	.220
.398	.1673	.0749	.192
.323	.857 x 10 ⁻⁵	.0718	.205
.277	.559	.0547	.135
.248	.414	.0577	.155
.1827	.1755	.0627	.146

M. High Pressure Hot Pressed MgO (.06μ) - Thermal Conductivity
Run BN-8* - L/A = 5.40

T	K(Watt cm ⁻¹ K ⁻¹)
80.4	.480 x 10 ⁻¹
80.6	.472
60.9	.268
45.1	.1439
30.7	.604 x 10 ⁻²
22.1	.281
6.71	.271 x 10 ⁻³
4.44	.1535

M. cont. Run BN-8 L/A = 5.40

T(K)	K(Watt cm ⁻¹ K ⁻¹)
19.71	.244 x 10 ⁻²
17.77	.1913
16.20	.1505
14.81	.1207
13.47	.1002
12.17	.818 x 10 ⁻³
11.14	.734
10.15	.579
9.19	.461
7.86	.366
7.10	.310
6.53	.326
5.95	.242
5.22	.1932
4.72	.1680
4.39	.1507
1.842	.504 x 10 ⁻⁴
1.661	.437
1.504	.421
1.363	.378
1.246	.357
1.9.69	.258 x 10 ⁻²
16.17	.1668

T(K)	K(Watt cm ⁻¹ K ⁻¹)
14.81	.1228 x 10 ⁻²
13.45	.1084
12.15	.850 x 10 ⁻³
11.141	.738
10.11	.657
9.20	.435
7.86	.375
7.11	.306
6.72	.311
5.95	.259
5.22	.1998
5.19	.1818
4.72	.1771
4.70	.1658
4.38	.1553
4.27	.1457
3.97	.1321
3.61	.1148
3.27	.1014
2.96	.891 x 10 ⁻⁴
2.69	.782
2.45	.692
2.24	.625
2.03	.557

Run RT 79 - L/A = 5.40

T(K)	K(Watt cm ⁻¹ K ⁻¹)
1.604	.370 x 10 ⁻⁴
1.416	.316
1.312	.263
1.205	.247
1.115	.221
.991	.1935
.794	.1468
.707	.1201
.627	.1255
.558	.900 x 10 ⁻⁵
.446	.813
.398	.733
.363	.705

T(K)	K(Watt cm ⁻¹ K ⁻¹)
.306	.570 x 10 ⁻⁵
.269	.446
.226	.351
.182	.309

M. cont.

Run RT 81 - L/A = 5.40

T(K)	K(Watt cm ⁻¹ K ⁻¹)	T(K)	K(Watt cm ⁻¹ K ⁻¹)
.331	.612 x 10 ⁻⁵	.161	.287 x 10 ⁻⁵
.284	.529	.154	.277
.247	.453	.142	.269
.219	.403	.144	.263
.206	.383	.137	.260
.191	.347	.131	.234
.177	.319	.118	.180
.171	.306	.106	.215
		.102	.192

N. Sintered Cabosil (1mm)

(1) Sintered Cabosil - Specific Heat

Run RT 73 - M = 6.64 gm

T(K)	C _v (erg gm ⁻¹ K ⁻¹)	T(K)	C _v (erg gm ⁻¹ K ⁻¹)
18.26	.246 x 10 ⁶	1.171	.539 x 10 ²
16.65	.1955	1.174	.529
14.96	.1516	1.123	.472
13.26	.1022	1.058	.412
12.35	.819 x 10 ⁵	1.024	.378
11.78	.764	9.76	.340
11.02	.635	.918	.295
9.77	.441	.860	.265
9.08	.360	.810	.245
8.18	.264	.726	.1971
7.47	.200	.654	.1658
6.96	.1584	.584	.1503
6.89	.1500	.527	.1205
6.31	.1113	.473	.1051
5.56	.700 x 10 ⁴	.431	.933
5.09	.500	.396	.881
4.72	.372	.363	.770
4.28	.256	.344	.716
4.02	.200	.331	.690
3.76	.1564	.309	.649
3.47	.1121	.288	.576
3.24	.841 x 10 ³	.276	.557
2.94	.621	.250	.541
2.70	.485	.244	.500

N. cont.

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
2.32	.310 x 10 ³	.229	.460 x 10 ²
1.800	.1502	.219	.452
1.633	.1251	.207	.452
1.540	.1022	.193	.409
1.478	.1018	.187	.455
1.390	.790 x 10 ²	.179	.425
1.204	.558	.158	.363

(2) Sintered Cabosil - Thermal Conductivity
Run RT 79 - L/A = 6.75

T(K)	K(Watt cm ⁻¹ K ⁻¹)	T(K)	K(Watt cm ⁻¹ K ⁻¹)
1.504	.426 x 10 ⁻³	.448	.436 x 10 ⁻⁴
1.457	.336	.418	.389
1.335	.298	.352	.284
1.218	.257	.341	.267
1.171	.240	.319	.241
1.121	.218	.285	.1934
.955	.1621	.255	.1563
.878	.1428	.229	.1245
.806	.1202	.216	.1295
.716	.971 x 10 ⁻⁴	.204	.993 x 10 ⁻⁵
.604	.742	.192	.888
.551	.682	.181	.791
.497	.548		

P. Pyroceram As-Received (.06μ)

(1) Pyroceram as-received - Specific Heat
Run RT 76 - M=42.08 gm

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
19.77	.233 x 10 ⁶	4.65	.1776 x 10 ⁴
17.89	.1772	4.36	.1450
16.75	.1430	4.15	.1272
15.69	.1191	3.39	.753 x 10 ³
15.03	.1053	3.06	.664
14.26	.908 x 10 ⁵	2.68	.495
13.46	.842	2.75	.551
13.07	.665	2.49	.447
11.99	.524	2.36	.415
11.28	.421	2.17	.387
10.48	.334	2.04	.369

P. cont.

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
9.94	.272 x 10 ⁵	1.781	.333 x 10 ³
9.53	.243	1.561	.318
8.90	.1818	1.331	.299
8.53	.1618	1.280	.294
7.93	.1218	1.119	.271
7.50	.1376	1.008	.257
6.89	.732 x 10 ⁴	.899	.243
6.37	.552	.813	.232
5.85	.388	.749	.228
5.32	.279	.688	.226
5.24	.263	.641	.212
5.14	.251	.578	.208
4.87	.209	.510	.204
		.446	.1897

Q. Pyroceram Treated at 1080°C (.3μ) - Specific Heat

Run RT 76 - M = 40.67 gm

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
19.75	.226 x 10 ⁶	4.61	.203 x 10 ⁴
18.74	.1951	4.30	.1628
17.41	.1629	4.15	.1467
16.60	.1404	3.77	.1113
16.00	.1286	3.40	.842 x 10 ³
15.32	.1155	3.06	.655
14.54	.995 x 10 ⁵	2.78	.549
14.07	.902	2.52	.453
12.90	.693	2.40	.406
12.14	.587	2.17	.383
11.36	.475	2.04	.341
10.69	.371	1.734	.291
10.15	.339	1.616	.273
9.37	.275	1.375	.249
8.18	.1930	1.332	.244
7.95	.1392	1.144	.233
7.29	.1021	1.037	.225
6.80	.814 x 10 ⁴	.917	.223
6.36	.623	.849	.222
6.05	.525	.778	.220
5.77	.440	.623	.222
5.45	.362	.589	.226

Q. cont.

T(K)	C_v (erg gm ⁻¹ K ⁻¹)
5.25	.317 x 10 ⁴
5.12	.288
4.85	.244

T(K)	C_v (erg gm ⁻¹ K ⁻¹)
.527	.225 x 10 ³
.487	.225

R. Pyroceram Treated at 1175°C

(1) Pyroceram Treated at 1175°C - Specific Heat

Run RT 77* - M = 34.25 gm

T(K)	C_v (erg gm ⁻¹ K ⁻¹)
19.77	.236 x 10 ⁶
17.57	.1783
16.21	.1445
15.54	.1284
13.57	.871 x 10 ⁵
12.52	.688
11.28	.490
10.31	.362
9.36	.264
8.71	.203
8.07	.1580
6.97	.772 x 10 ⁴
6.42	.672
5.77	.457
5.20	.212
4.90	.247
4.44	.1839
3.91	.1295
3.58	.943 x 10 ³
3.21	.792

T(K)	C_v (erg gm ⁻¹ K ⁻¹)
2.88	.635 x 10 ³
2.64	.530
2.38	.443
2.15	.405
1.845	.316
1.600	.281
1.337	.265
1.216	.251
1.044	.237
.967	.226
.886	.224
.813	.223
.753	.220
.658	.224
.597	.222
.571	.224
.521	.229
.491	.228
.438	.231

(2) Pyroceram Treated at 1175°C - Thermal Conduction

Run RT 78 - L/A = 4.70

T(K)	K(Watt cm ⁻¹ K ⁻¹)	T(K)	K(Watt cm ⁻¹ K ⁻¹)
1.708	.1291 x 10 ⁻³	.420	.545 x 10 ⁻⁵
1.548	.986 x 10 ⁻⁴	.392	.462
1.437	.832	.361	.401
1.337	.700	.332	.343
1.214	.547	.312	.294
1.152	.475	.293	.259
1.084	.424	.274	.232
1.052	.392	.256	.205
.948	.313	.235	.1804
.874	.254	.215	.1579
.805	.208	.201	.1363
.748	.1831	.189	.1276
.707	.1594	.180	.1121
.655	.1356	.159	.919 x 10 ⁻⁶
.611	.1208	.145	.873
.539	.905 x 10 ⁻⁵	.128	.611
.495	.757	.121	.637
.448	.607		

Run RT 78* L/A = 1.68

T(K)	K(Watt cm ⁻¹ K ⁻¹)
.274	.223 x 10 ⁻⁵
.215	.1882
.184	.1086
.156	.838 x 10 ⁻⁶
.144	.743
.136	.653
.128	.559
.115	.517
.105	.459
.0962	.372
.0903	.308
.0887	.310
.0756	.260

R(a) cont.

Run BN-6 - L/A = 3.36

T(K)	K(Watt cm ⁻¹ K ⁻¹)
21.83	.261 x 10 ⁻²
19.56	.237
17.41	.214
15.55	.1973
13.97	.1812
12.55	.1672
11.17	.1552
10.01	.1428
8.96	.1317
8.03	.1219
7.20	.1098
6.51	.976 x 10 ⁻³
5.84	.869
5.17	.749
4.70	.613
4.33	.587
3.93	.509
3.58	.441
21.87	.253 x 10 ⁻²
19.57	.233
17.41	.214
15.54	.1982
13.95	.1832
12.54	.1706
11.17	.1574
10.00	.1445
8.96	.1329
8.03	.1211

T(K)	K(Watt cm ⁻¹ K ⁻¹)
7.19	.1076 x 10 ⁻²
6.51	.981 x 10 ⁻³
5.84	.871
5.17	.738
4.70	.620
4.33	.583
3.93	.501
3.58	.458
2.96	.331
2.69	.295
4.70	.605
4.33	.583
3.93	.510
3.58	.443
3.25	.380
2.96	.297
2.70	.231
2.45	.1750
2.22	.1219
2.18	.1964
1.953	.1568
1.756	.1238
1.668	.1142
1.511	.913 x 10 ⁻⁴
1.377	.765
1.252	.849
3.25	.386 x 10 ⁻³

S. Diopside (CaO-MgO-2SiO₂) (d~.2μ)-Thermal Conductivity

Run RT 66 - RT 66* L/A = 1.870

T(K)	K(Watt cm ⁻¹ K ⁻¹)
2.240	.8552 x 10 ⁻⁴
2.051	.6467
1.807	.4322
1.631	.3026
1.482	.2256
1.357	.1741

T(K)	K(Watts cm ⁻¹ K ⁻¹)
.338	.5505 x 10 ⁻⁶
.309	.4396
.278	.3690
.269	.3253
.249	.2727
.218	.2045

S. cont.

T(K)	K(Watt cm ⁻¹ K ⁻¹)	T(K)	K(Watt cm ⁻¹ K ⁻¹)
1.252	.1353 x 10 ⁻⁴	.191	.1524 x 10 ⁻⁶
1.153	.1093	.171	.1248
1.045	.8094 x 10 ⁻⁵	.159	.1028
.936	.6148	.140	.8223 x 10 ⁻⁷
.853	.4724	.130	.7685
.784	.3822	.115	.6025
.744	.3392	.111	.4750
.704	.2927	.0985	.4325
.642	.2375	.0926	.4856
.576	.1861	.0894	.4282
.563	.1842	.0864	.3162
.487	.1239	.0833	.3983
.458	.1247	.0789	.4138
.424	.9043 x 10 ⁻⁶	.0676	.3752
.397	.7765	.0692	.3349

T. Porous Vycor Glass (.007μ) - Thermal Conductivity

(1) Porous Vycor Glass (.007μ) - Specific Heat

Run RT 72 - M = 17.99

T(K)	C _v (erg gm ⁻¹ K ⁻¹)	T(K)	C _v (erg gm ⁻¹ K ⁻¹)
19.01	.352 x 10 ⁶	.906	.1300 x 10 ³
18.74	.343	.859	.1152
16.64	.258	.706	.841 x 10 ²
15.03	.211	.674	.792
13.43	.1603	.602	.660
12.21	.1305	.526	.550
11.43	.1112	.460	.442
10.84	.978 x 10 ⁵	.419	.396
9.69	.736	.383	.358
8.95	.561	.341	.307
8.04	.450	.302	.269
7.46	.350	.272	.228
7.53	.362	.260	.1920
5.05	.1091	.230	.1648
4.98	.1068	.222	.1648
4.47	.715 x 10 ⁴	.195	.1321
3.72	.383	.171	.1071
3.32	.263	.163	.1030
2.99	.1812	.152	.1038
		.144	.1010

T. cont.

T(K)	C_v (erg gm ⁻¹ K ⁻¹)	T(K)	C_v (erg gm ⁻¹ K ⁻¹)
2.61	.1228 x 10 ⁴	.142	.860 x 10
2.483	.1064	.132	.837
2.03	.631 x 10 ³	.125	.781
1.844	.500	.118	.741
2.29	.815	.113	.711
1.720	.470	.110	.663
1.570	.380	.105	.662
1.465	.330	.106	.661
1.359	.287 x 10 ³	.102	.626
1.215	.240	.100	.600
.976	.1490		

(2) Porous Vycor Glass (.007μ) - Thermal Conductivity
Run RT 5 - L/A = 18.40

T(K)	K(Watt cm ⁻¹ K ⁻¹)
1.423	.215 x 10 ⁻⁴
.599	.234
1.122	.1885
1.015	.1798
.894	.1813
.765	.1645
.659	.1518
.455	.1148
.405	.997 x 10 ⁻⁵
.349	.900
.321	.974
.321	.894

T. cont. (2)

Run BN-8* - L/A = 5.120

T(K)	K(Watt cm ⁻¹ K ⁻¹)	T(K)	K(Watt cm ⁻¹ K ⁻¹)
98.00	.566 x 10 ⁻²	13.02	.315 x 10 ⁻³
82.88	.407	9.29	.203
91.26	.399	7.58	.1979
92.39	.552	6.38	.1015
35.06	.1323	5.37	.842 x 10 ⁻⁴
23.60	.819 x 10 ⁻³	5.15	.899
16.76	.421	4.44	.804
13.01	.319	3.75	.580
9.27	.220	3.16	.398
7.59	.1878	2.64	.355

T. cont:

T(K)	K(Watt cm ⁻¹ K ⁻¹)
.635	.1267 x 10 ⁻³
5.37	.840 x 10 ⁻⁴
5.14	.958
4.45	.752
3.75	.588
3.15	.425

T(K)	K(Watt cm ⁻¹ K ⁻¹)
2.20	.283 x 10 ⁻⁴
1.800	.250
1.484	.252

V. Phase Separated Sodium Borosilicate Glass (.3μ) - Thermal Conductivity
Run RT 70 - L/A = 3.50

T(K)	K(Watt cm ⁻¹ K ⁻¹)
4.451	.931 x 10 ⁻³
3.635	.772
2.966	.652
2.665	.610
2.131	.441
1.313	.215
1.186	.1891
.997	.1392
.862	.1011
.746	.751 x 10 ⁻⁴
.690	.691
.606	.526
.572	.507
.491	.395
.445	.345
.395	.1774
.337	.217

Run RT 75 - L/A = 3.50

T(K)	K(Watt cm ⁻¹ K ⁻¹)
.320	.1305 x 10 ⁻⁴
.236	.801 x 10 ⁻⁵
.1612	.625
.1205	.205

Y. " $\frac{1}{2}$ Layer" of N₂ on Pressed Alon (.02 μ) - Specific Heat
Run RT 61

T(K)	C _v (erg gm ⁻¹ K ⁻¹)
1.565	.305 x 10 ³
1.461	.258
1.380	.212
1.315	.1920
1.272	.1604
1.173	.1437
1.083	.1213
.977	.965 x 10 ²
.818	.792
.802	.653
.769	.541
.581	.381
.584	.337
.497	.261
.460	.150
.461	.185
.438	.201
.411	.163
.402	.194

Z. KBr_{.50} - KI_{.50} - Specific Heat

M = 25.02 gm - Run RT 58*

T(K)	C _v (erg gm ⁻¹ K ⁻¹)
1.864	.629 x 10 ³
1.625	.474
1.521	.363
1.417	.289
1.162	.1413
1.139	.1324
.963	.771 x 10 ²
.807	.447
.734	.327
.704	.286
.626	.205
.567	.1593
.549	.1402
.548	.1388
.547	.1368

T(K)	C _v (erg gm ⁻¹ K ⁻¹)
.307	.246 x 10
.308	.254
.295	.204
.267	.1609
.260	.1484
.249	.1354
.241	.1176
.244	.1193
.244	.1212
.237	.1140
.239	.1149
.207	.818
.167	.319
.167	.422
.168	.373

Z. cont.

T(K)	C_v (erg gm ⁻¹ K ⁻¹)
.536	.1311 x 10 ⁻²
.463	.836 x 10
.427	.662
.419	.633
.353	.369
.350	.358
.327	.295

T(K)	C_v (erg gm ⁻¹ K ⁻¹)
.172	.425 x 10
.120	.148
.119	.131
.117	.127
.116	.131
.133	.115