Ultrasonic study of the vibrational modes of sintered metal powders

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(Received 20 March 1985; revised manuscript received 3 July 1985)

The propagation of (1—20)-MHz ultrasound in sintered metal powder discs with powder diameter $d \sim 1$, 10, and 300 μm and occupied volume fractions $0.3 < f < 0.55$, together with static elastic-modulus measurements, has been used to study the vibrational modes that would be thermally excited in submicrometer sinter heat exchangers at millikelvin temperatures. In a low-frequency regime where the ultrasonic wavelength $\lambda \gg d$, the sound propagates with a velocity that agrees well with that expected for continuous medium phonons in a percolation system above threshold. The elasticity exponent $\tau \sim 3.6 \pm 0.5$ is in agreement with the recent Kantor-Webman limit $\tau > 3.55$. By increasing the frequency, it was shown that a band edge exists, at $\lambda \sim 10d$, beyond which sound does not propagate. This edge is associated with a transition from propagating to localized modes of the sinter and is analogous with the fracton edge discussed by Derrida, Orbach, and Yu for a percolation system.

I. INTRODUCTION

This study of the vibrational modes of sintered metal powders began with the realization that new information on the vibrational spectrum might be essential for understanding the anomalous thermal boundary (or Kapitza) resistance between liquid helium and sintered metal heat exchangers at millikelvin temperatures. The Kapitza resistance between a solid and liquid helium is defined by

$$R_K = \Delta T / \dot{Q} \ ,$$

where ΔT is the temperature difference across the interface between the solid and liquid helium when a heat current $\dot{Q}$ flows through the interface. Below 100 mK this resistance is large in comparison to the thermal resistance of centimeter lengths of either the solid or the liquid helium with the same cross section as the interface, and is the limiting factor in the cooling of liquid helium by a solid refrigerant or conversely the cooling of a solid by a helium refrigerant. The practical method of overcoming the high resistance is to enhance the interface area by the use of sintered metal powder. For instance, it is possible to enhance the interface area between helium and a metal chamber by 4 orders of magnitude by packing the cell with submicrometer copper or silver powder. Sintering at about 200 °C under helium, vacuum, or hydrogen allows surface diffusion and the formation of a conducting metal "sponge" in the chamber.

A decade ago it was found that below 20 mK the Kapitza resistance to pure ^{3}He was reduced by more than the area enhancement ratio and that the temperature dependence of the Kapitza resistance changed from the T^{-3} dependence found above 20 mK, and expected from acoustic wave theory,[1,2] to a T^{-1} dependence. The experiments from many laboratories showing the T^{-1} dependence have been summarized in Ref. 3. This behavior, which has been most important for experimental low-temperature physics, has been attributed to a modification of the acoustic heat-transfer process due to the finite size of the metal powder particles, and also to magnetic coupling, an alternate heat transfer process between the solid and liquid helium. The purpose of the work presented in this paper was to study some of the ultrasonic properties of sintered metal powder in order to learn about the vibrational modes that will be excited in the temperature range below 20 mK, and how they might modify heat transfer across the interface.

In Sec. II a model for the vibrational modes of a packed powder will be reviewed. The experiments made to investigate the model will be described in Sec. III, and the results will be presented and discussed in Sec. IV. A feature which emerges from the results is that in addition to the new information on sintered metal heat exchangers, the experiments address the more general subject of porous media, which is of considerable current interest.[4] A brief preliminary report of this work has been published elsewhere.[5]

II. VIBRATIONAL MODES OF A SINTERED POWDER

A. The postulated vibrational spectrum

As part of a study of glasses, Pohl and Tait[6] measured the specific heat and thermal conductivity of several packed-powder samples. The intention was to determine whether the anomalous thermal properties of glasses could be associated with "grainy" structure. These authors pointed out that there is a low-frequency cutoff in the Debye spectrum where $\lambda \sim d$, the powder particle size, and that the missing modes must appear in some other form. They further described a very-low-frequency regime, where the packed powder again appears as an effective continuum solid, and an intermediate frequency regime, where the nature of the modes is not clear. In the very-low-frequency regime the sound velocity is smaller than that of the bulk material, and therefore the density of phonon states is larger than for the bulk metal.

By means of Young's modulus and sound-velocity measurements, Frisken *et al.*[7] determined the very-low-frequency behavior of the sintered metal powders commonly used for ultralow-temperature heat exchangers and Kapitza resistance measurements. The intention was to determine the normal modes of the powder that would be excited below 20 mK and that could provide heat transfer between liquid helium in the pores and the sintered powder. The result was that if all of the bulk modes below the $\lambda \sim d$ cutoff were to reappear as continuous medium phonons, these phonons would typically have a "Debye temperature" of about 20 mK and a density of states 50 times larger than that of the bulk metal below 20 mK. As part of a systematic characterization of sintered metal powder, Robertson *et al.*[8] made further Young's-modulus measurements and confirmed the above behavior. Nishiguchi and Nakayama[9] approximated these low-frequency modes by Einstein oscillators and calculated the heat transfer between these modes and zero-sound phonons in liquid ^{3}He in the pores. The calculation demonstrated that the mechanism was sufficient to explain the magnitude of the heat transfer.

Electron-microscope pictures of sintered metal powder showed that the sinter is quite inhomogeneous and far from the orderly arrangement of powder particles that would be required for a pseudo-Debye-solid. Clusters of clusters would be a better description. Rutherford *et al.*[10] postulated that the continuous medium phonons would in fact only exist for wavelengths larger than about 20 powder diameter at which scale the sinter is reasonably homogeneous. They further supposed that, in the frequency band between the upper limit of the continuous medium phonons and the lower limit of the bulk metal Debye phonons, there exist localized modes involving one or a few powder particles, and that the average density of states for these modes is a constant. The three distinct frequency bands are shown schematically in Fig. 1. Rutherford *et al.* calculated the heat transfer between these localized modes and liquid helium in the pores by means of a "shaking box" model: Each pore was treated as an oscillating cubic box containing ^{3}He quasiparticles behaving as quantum particles in a box. The resulting heat transfer was within a factor of 2 or 3 of experimental measurements and the temperature dependence was correct. The localized-mode model was supported by reasonable numerical agreement with the measured specific heat of packed insulating powders, porous Vycor glass, and liquid ^{3}He in small pores.[6,11] However, there was no direct evidence for the localized modes of the packed powder.

Recent theoretical work, based on percolation and fractal models of disordered media, has produced some theoretical justification for the existence of regions 1 and 2 in Fig. 1. Orbach *et al.*[12–14] have used scaling arguments and effective-medium-approximation calculations for a percolating network to predict a crossover from propagating to localized modes at a length scale below which the network has the self-similarity of a fractal system. In the fractal region they conjecture that the average density of states varies as $\omega^{1/3}$, although more recent arguments by Webman and Grest,[15] based on a microscopic

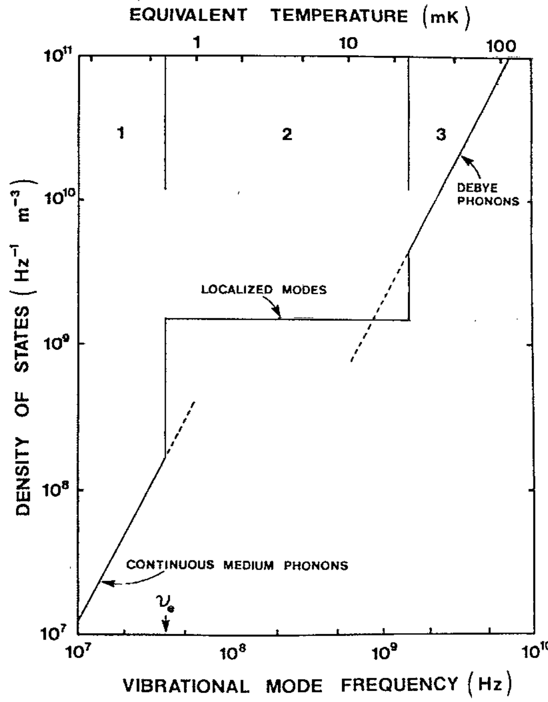

FIG. 1. Density of states of vibrational modes of sintered 1-μm-diam metal powder ($f=0.35$) as postulated by Rutherford *et al.* The continuous medium curve is based upon a "Debye" velocity of 500 m s^{-1} as expected for $f \sim 0.35$. The band-edge frequency ν_e was determined by the condition $\lambda_e \sim 10d$. The upper scale is a measure of the temperature at which modes with frequency along the lower scale dominate in the excitation spectrum.

elasticity model that appears to describe correctly the elastic properties of sinter (see Sec. IV A), predict a $\omega^{-0.1}$ dependence. The latter prediction is very close to the ω^0 dependence of the density of states assumed by Rutherford *et al.* However, the question of to what extent a packed powder, and in particular the sintered metal powders of interest to low-temperature physicists, can be described by fractal geometry remains unanswered as yet.

B. Tests of the model

In region 1 (Fig. 1) for a sinter, it is known that longitudinal waves do propagate, both from static elasticity and ultrasonic experiments. However, in a bulk solid at low temperatures it is transverse waves that dominate in the energy density of thermally excited vibrational modes. Our first question then concerned the characterization of propagating transverse waves in sintered metal powder and was addressed by measurements of ultrasonic wave propagation and of shear modulus. There has been a great deal of work on the application of effective medium and other theories to the elasticity of heterogeneous and percolating systems. We were interested in learning whether sinter was a good example of such systems, and conversely, whether these theories could give more information on the vibrational modes of sinter, and in particular on how the vibrational modes might be tailored for optimization of a low-temperature heat exchanger.

The existence of localized modes in region 2 can be inferred from the specific heat of packed powders, but there are objections.[6] It is difficult to eliminate the possibility that the linear specific heat arose from molecular impurities physisorbed on the very large surface area of the powder samples. In the present work an indirect test was made by measuring the attenuation of ultrasonic waves as a function of frequency. If there is a band edge as suggested in Fig. 1, then there should be a sharp decrease in propagated signal strength as the frequency crosses from region 1 to region 2. Furthermore, the increased inhomogeneity that should occur in a lower occupied volume fraction sinter should cause the band edge to shift to lower frequency.

In region 3 the phonon wavelengths are smaller than the powder particle diameter, and therefore bulk phonons should propagate, but with considerable scattering. Although this behavior is perhaps self-evident, an attempt was made to propagate acoustic waves with $\lambda \leq d$ through sinter.

III. THE EXPERIMENTS

The present work is in three parts corresponding to the three regions illustrated in Fig. 1, for which $\lambda \gg d$, $\lambda \geq d$, and $\lambda \leq d$, respectively. Propagating acoustic modes were expected in the first and third regions, but not in the second where the existence of localized excitations was postulated. The vibrational modes were studied by ultrasonic experiments in the frequency range from 1 to 20 MHz, and the three regions of Fig. 1 were brought into this range by working with ~1-, 10-, and 300-μm-diameter copper powders. In addition to the ultrasonic measurements, a measure of the shear modulus was obtained by twisting sintered copper and silver powder beams.

A. Ultrasonic velocity and attenuation

Ultrasonic velocity and attenuation were measured in thin disc-shaped samples which were dry-polished flat and parallel to better than 10% of the ultrasonic wavelength using fine silicon carbide paper. The sinter samples were sandwiched between two cylindrical fused quartz delay rods, on the opposite ends of which piezoelectric ceramic transducers were mounted. A thin layer of Nonaq stopcock grease was used as the ultrasonic couplant between the sinter and delay rods. Nonaq was selected because it is sufficiently viscous that there was negligible penetration of grease into the porous sinter, so that it was not necessary to insert a protective membrane between the bonding layer and the sinter as was done in some early experiments.[7] Lead metaniobate and PZT-4 transducers were used for longitudinal and shear wave experiments, respectively.

The ultrasonic velocity was determined from the time taken for a short pulse (typically ~2 μs) generated and detected by a MATEC 6600 system to propagate through the sinter sample. For the delay rod setup described above, this was conveniently measured from the time delay between a reflected ultrasonic pulse, which had traveled up and down the delay rod only, and a transmitted pulse, which had passed through the specimen and each delay rod. (The attenuation in the sinter was sufficiently large that multiple reflections of ultrasound in the sinter were negligibly small.) This time delay was measured by superposing the reflected and transmitted radio-frequency pulses on a Hewlett-Packard model No. 1725A oscilloscope using the Δ time mode. To obtain an accurate measurement of the velocity, it was necessary to correct the measured time delay for phase shifts both in the electronics and in the reflected ultrasonic wave from the delay rod/sinter interface (for a recent review, see Ref. 16). For the thin sinter samples used in the experiments, diffraction corrections to the travel time, as computed by Papadakis,[17] are negligible.

Changes in ultrasonic attenuation were determined as a function of frequency from the variation of the transmitted signal amplitude with respect to the reference pulse reflected from the delay rod/sinter interface. The changes in attenuation were measured with calibrated attenuators inserted before the receiver to avoid errors from nonlinearities in the amplifiers. For the large variation in attenuation observed, errors due to frequency-dependent losses in the ultrasonic bonds were negligible. While the main contribution to the measured attenuation appeared to be sound absorption in the sinter, there could also be a contribution from scattering of the ultrasonic wave which can cause phase cancellation in the piezoelectric transducer and thus further reduce the detected signal amplitude. Work is currently in progress using a new phase-insensitive transducer to eliminate these interference effects and hence make more accurate measurements of the attenuation.[18]

B. Static shear modulus

The shear modulus of a series of copper and silver sinter beams was measured by applying a known torque about the major axis of a beam and measuring the twist angle. The beams, mounted vertically in the apparatus, were clamped at each end. The lower clamp was rigidly attached to the frame while the upper clamp was attached to a horizontal pulley to which a torque could be applied by a string, pulley, weight system. A mirror mounted on the horizontal pulley was part of an optical level that enabled the measurement of the small angular deformations. The apparatus was tested on a series of solid beams with equal cross-sectional areas but varying "aspect ratios." Whereas the derivation of shear modulus from the torsion constant for a cylindrical rod is a standard undergraduate problem, that is not the case for the rectangular bar. The problem has been treated by several authors[19] and the result is summarized in Fig. 2.[20] This figure is a plot of the geometrical factor K_2 as a function of the ratio a/b, where

$$(\phi/L)=\frac{K_2 M}{a^3 b G} .$$

a and b ($a \leq b$) are the dimensions perpendicular to the major axis, L is the length of the bar between the clamps, G is the shear modulus, and ϕ is the twist angle due to the applied torque M. The data points are the results ob-

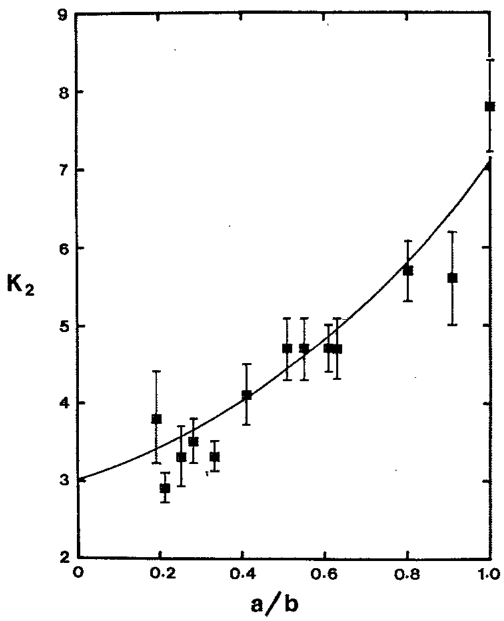

FIG. 2. Plot of the rectangular beam torsion constant parameter K_2 as a function of the ratio of the rectangle dimensions. The curve is the theoretical result, and the points are results obtained for a series of bulk copper beams.

tained with the series of solid copper bars. These bars had small cross sections (4 mm^2) so that the torsion constants would be comparable to those of the sinter beams. The error bars and scatter of the data are a measure of the accuracy of this torsion constant method for measuring G.

C. Sintered metal powder samples

(a) *1-μm sinter.* The samples used to study the shear modulus of the sinter and acoustic propagation in the regime $\lambda \gg d$ were the samples prepared by Robertson *et al.*[8] for Young's modulus and conductivity measurements. The copper had been prepared by presintering "700-Å" powder at 200 °C in a hydrogen atmosphere for 15 min, packing the powder into a mold, and sintering at 200 °C in a hydrogen atmosphere for 15 min. The silver was prepared without the presintering. In addition to providing a continuous structure, this treatment caused the mean diameter of the as-received powder (nominally 70 nm, but measured to be ~200 nm) to grow to ~700 nm by assimilation of small particles into larger particles.[8,21]

(b) *10-μm sinter.* The 10-μm copper powder, from Alfa Products (Danvers, Mass.) was cleaned in trichloroethylene, and then in acetone, and presintered in flowing hydrogen gas at 350 °C for 20 min. The powder was poured into a mold and distributed as evenly as possible by shaking the powder in an ultrasonic cleaner. The powder was then pressed to the desired occupied volume fraction and sintered in flowing hydrogen at 500 °C for one hour. The samples prepared in this way were 17 mm diameter by about 3 mm thickness. It proved difficult to make discs with occupied volume fractions much less than 0.5.

(c) *300-μm sinter.* The −40, +100 mesh copper powder, also from Alfa Products, was first sieved through a 60 mesh to yield a −40, +60 powder with diameters in the range 250—425 μm. The cleaning, presintering, and sintering were as for the 10-μm powder, except that the sintering was done at 650 °C.

IV. RESULTS AND DISCUSSION

The results will be presented and discussed in three sections corresponding to the three regions of Fig. 1.

A. Long wavelength, $\lambda \gg d$

The long-wavelength regime, where the ultrasonic wavelength λ is much greater than the particle size d, was studied using the 1-μm copper and silver sinters. Occupied volume fractions f in the range 0.3—0.6 were selected so as to encompass the range usually used for sintered metal heat exchangers. The longitudinal and transverse velocities are shown in Fig. 3, together with the bulk metal velocities. The straight lines are guides to the eye, indicating that the velocity extrapolates to zero at $f \sim 0.1$. The three elastic moduli, Young's (Y), shear (G), and bulk (B) were derived from the velocities by means of

$$Y = \rho v_t^2 \frac{3v_l^2 - 4v_t^2}{v_l^2 - v_t^2} ,$$

$$G = \rho v_t^2 ,$$

$$B = \rho (v_l^2 - \tfrac{4}{3} v_t^2) ,$$

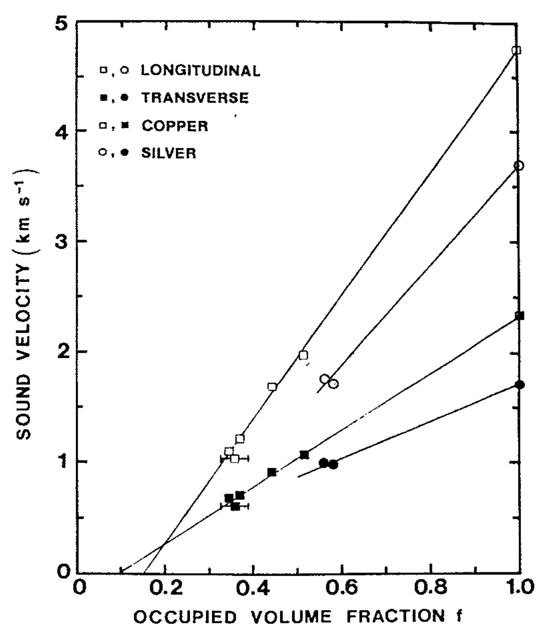

FIG. 3. Velocity of longitudinal and transverse sound in a set of sintered submicrometer copper and silver powder discs as a function of the occupied volume fraction. The bulk velocities are from standard tables [G. W. C. Kaye and T. H. Laby, *Tables of Physical and Chemical Constants,* 14th ed. (Longman, London, 1973)].

where $\rho = f\rho_b$ and ρ_b is the bulk metal density. The Young's and shear moduli are shown in Figs. 4 and 5, where they are compared with the values obtained from the beam bending[8] and twisting experiments. The uncertainty in the Young's moduli derived from the velocity data is relatively large because of the difference-of-squares operation. Nonetheless, it does appear in both figures that the moduli obtained from the ultrasonic measurements are systematically larger than those derived from static beam measurements. This will be brought out more clearly in Figs. 7 and 8 as described below. A test of the self-consistency of the moduli measurements is that Poisson's ratio

$$\nu = (Y - 2G)/2G = \tfrac{1}{2}(v_l^2 - 2v_t^2)/(v_l^2 - v_t^2)$$

should lie between 0 and 0.5. The Poisson's ratios for the copper and silver sinters are shown in Fig. 6. The ultrasonic results have relatively little scatter, are consistent with a gradual decrease in ν with f, and show reasonable values of Poisson's ratio of order 0.25. The beam results, with an average ~ 0, seem to be too small, indicating perhaps that the Young's modulus has been understimated by the beam-bending measurement.

There are a few possible reasons for the differences between the beam and ultrasonic elastic-moduli measurements. The beam-bending and twisting experiments were made two years and one year, respectively, before the ultrasonic experiments, and it is possible that self-sintering at room temperature caused a gradual increase in the strength of the sinters. On the other hand, for one of the silver sinter discs it is known that any change in the longitudinal ultrasonic velocity was less than 2% over the two-year period. Another possibility is that the discs and beams did not receive identical sintering because of the different geometries of the sinter and of the molds; this could explain the difference between the sound and beam moduli measurements, but not the difference between the Poisson's-ratio measurements. It could also be that large scale inhomogeneities in the sinters are responsible for the differences. For instance, the beam-bending and twisting measurements could overemphasize weak regions where the deformation is largest.

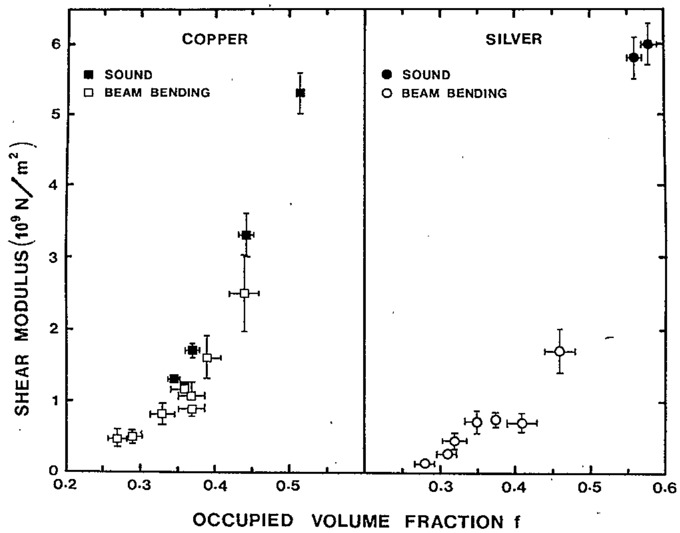

FIG. 5. Shear modulus of elasticity determined from sound velocities in, and beam twisting of, sintered submicrometer copper and silver powder.

There has been a great deal of interest in the propagation of acoustic waves in disordered and porous media, both one component, such as porous rocks, and two components, such as fluid-saturated packed powders. Reference 4 contains many theoretical and experimental results. Most of that work, however, is not of direct relevance to the present experiment which involves the elasticity of a solid structure relatively close to the percolation limit, a regime that has attracted little attention until recently. The new theoretical work[22–25] has been concerned with the question of whether the elasticity and conductivity of a percolating system belong to the same universality class, as originally conjectured by de Gennes[26] for gels near the percolation threshold. That is, if the elastic modulus and the conductivity scale with $p - p_c$ as $K \propto (p - p_c)^{\tau}$ and

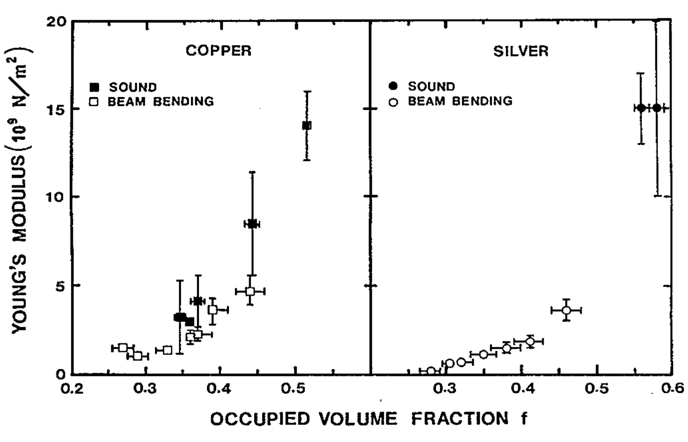

FIG. 4. Young's modulus of elasticity, determined from sound velocities in, and beam bending of, sintered submicrometer copper and silver powder.

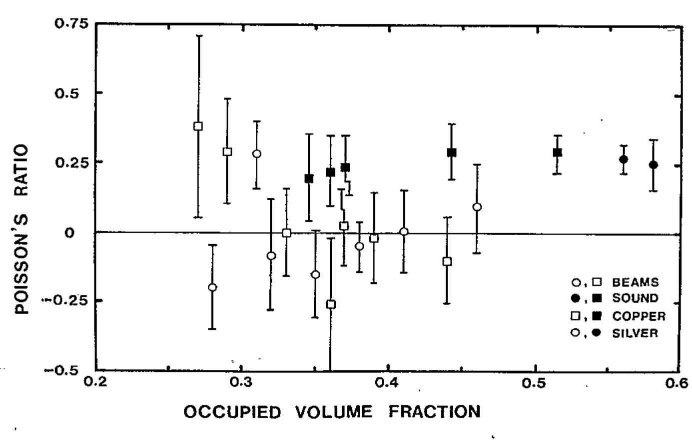

FIG. 6. Poisson's ratio determined from the sound velocity and beam deformation experiments.

$\sigma \propto (p - p_c)^t$, then is $\tau = t$?[27] A model for the elasticity of a percolating system that took account of the bending forces in the backbone structure of the infinite cluster was studied by Kantor and Webman.[23] In three dimensions they found $\tau > t$; their lower limit for τ of 3.55 should be compared with the best estimates for t that are in the range 1.9—2.0.[28] Feng *et al.*,[22,25] by carrying out numerical simulations on lattices with central and bending forces, and Bergman and Kantor,[24] by using solvable fractal models of percolating systems, have similarly found $\tau > t$. Deptuck *et al.*[29] have confirmed these three-dimensional (3D) theoretical results by measuring the Young's modulus and conductivity of sintered submicrometer silver powder beams as a function of f down to $f \sim 0.1$. They found $f_c = 0.06 \pm 0.01$, $\tau = 3.8 \pm 0.5$, and $t = 2.15 \pm 0.25$.

The value of f_c for sintered metal powder appears to be low in comparison with values obtained from computer simulations and theoretical estimates. For instance, for site percolation for the simple-cubic lattice, $p_c^{\text{site}} = 0.31$, corresponding to an occupied volume fraction $f_c = 0.16$;[30,31] for continuum percolation, Cohen *et al.* derive $f_c = 0.15$.[32] However, low values have been obtained in other experimental studies. The closest analogy with sintered metal powder is perhaps sintered perlite.[33] Longitudinal and transverse sound velocities were measured for a range of occupied volume fractions from 0.17 to 0.9 with the velocities extrapolating to zero at $f = 0.04 \pm 0.02$ and $f = 0.07 \pm 0.02$, respectively. For both sintered metal powder and sintered perlite, only the infinite cluster exists since isolated clusters would be unsupported and would fall onto the infinite cluster. In any case, as pointed out by Landauer,[31] the percolation limit depends upon the geometry of the constituents. Other systems have shown percolation limits varying from ~ 0 for fluid in the open pores of rocks[34] or fused glass spheres,[35] 0.02 for an unsymmetrical heterogeneous mixture of metallic and glass particles,[36] ~ 0.15 for various metal-insulator mixtures,[37] and 0.15—0.25 for Pd-KCl mixtures.[38]

The present elastic-modulus measurements do not approach sufficiently close to f_c to determine f_c. Therefore we have assumed $f_c = 0.06$ as found by Deptuck *et al.* Figures 7—9 show log-log plots of the Young's, shear, and bulk moduli plotted as a function of $f - f_c$. The straight lines through the data are best fits and have slopes in the range 3.2 to 4.0 with uncertainties $\sim \pm 0.3$. These values of the elasticity exponents are in reasonable agreement with the lower limit of the Kantor-Webman theory of 3.55; thus it appears that these theoretical predictions are obeyed experimentally in sintered powders over a surprisingly large range of values of $(f - f_c)/f_c$, from a lower value of about 0.6 in the results of Deptuck *et al.* to an upper limit of about 10 in the present experiments. In particular, the Young's-modulus exponent, 3.65 ± 0.3 (Fig. 7) compares very well with the result 3.8 ± 0.5 obtained by Deptuck *et al.* This close agreement for the Young's-modulus exponent is very gratifying, particularly in view of the large values of $f - f_c$ in the present experiments, and gives some credence to the indications from Figs. 8 and 9 that $\tau_B = 4.0 \pm 0.3$ is larger than $\tau_G = 3.35 \pm 0.3$. The difference is, however, at the limit of the experimental uncertainty. The log-log plots also bring out the fact that the moduli derived from the beam measurements are smaller than the acoustic moduli, but for the copper where a comparison can be made there is no significant difference in the dependence upon $f - f_c$.

In their paper on the elasticity of fractal lattices, Bergman and Kantor[24] conjecture that the ratio of bulk modulus B to shear modulus G is equal to the universal

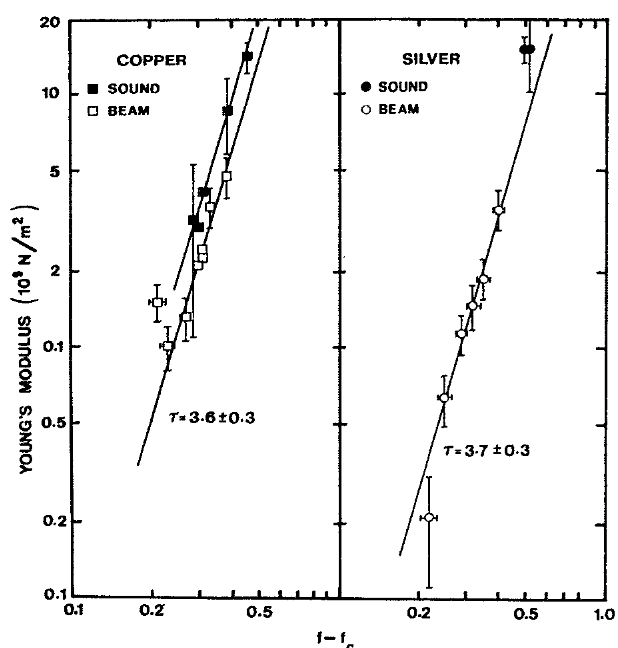

FIG. 7. Log-log plot of Young's modulus versus $f - f_c$ with $f_c = 0.06$ as determined by Deptuck *et al.* The straight lines are best fits to the data.

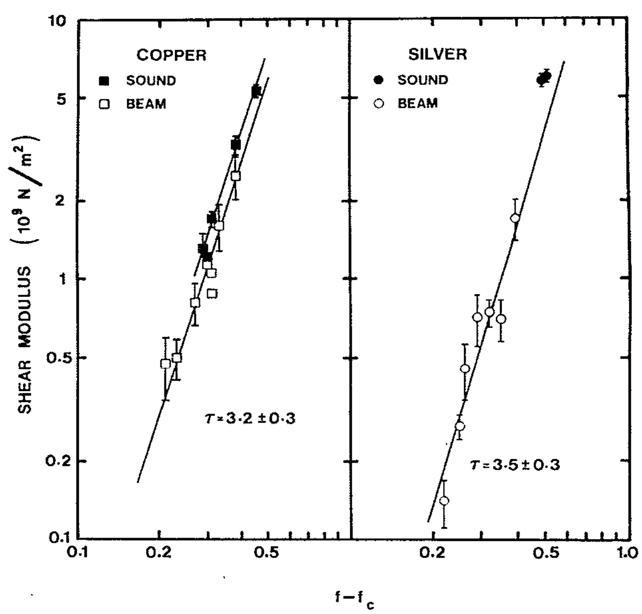

FIG. 8. Log-log plot of shear modulus versus $f - f_c$ with $f_c = 0.06$. The straight lines are best fits to the data.

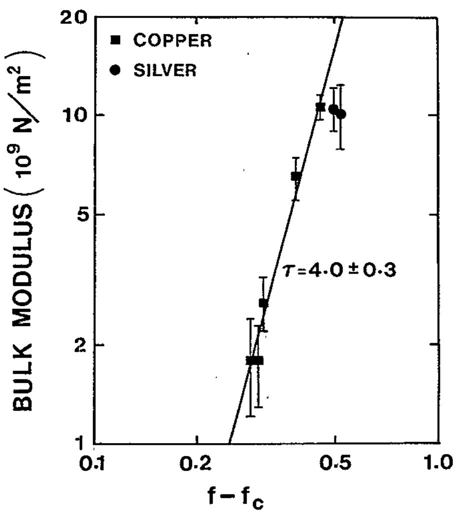

FIG. 9. Log-log plot of bulk modulus determined from sound velocity versus $f - f_c$ with $f_c = 0.06$. The straight line is the best fit.

value $4/d$ for a d-dimensional percolating system near threshold. This ratio can be directly determined for our sinters from the ultrasonic velocity data using

$$\frac{B}{G} = \frac{v_l^2}{v_t^2} - \frac{4}{3} .$$

The results, shown in Fig. 10, indicate that while this ratio for pure Cu is quite large, B/G rapidly approaches the Bergman-Kantor value for a 3D system of $\frac{4}{3}$ at the lowest packing factor studied. In light of their model, it is surprising that the ratio $\frac{4}{3}$ is reached for these data, since the sinters are presumably not fractal-like on length scales of order of the sample dimensions at these packing factors (i.e., the percolation correlation length ξ is almost certainly less than the sample thickness for sinters this far from the percolation threshold). It would be interesting to measure B/G closer to f_c in order to see whether the ratio for sinters conforms to the Bergman-Kantor conjecture over this range or whether B/G continues to decrease with decreasing packing factor as suggested by the data in Fig. 10

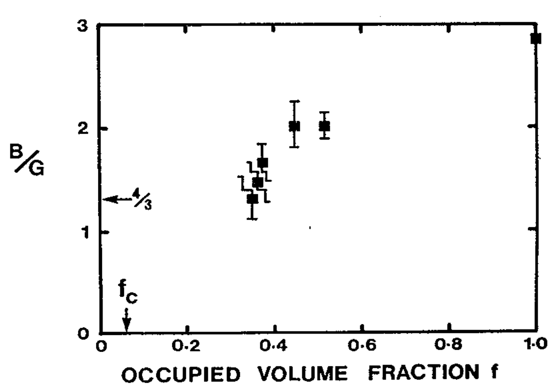

FIG. 10. The ratio of bulk to shear modulus for the sintered copper discs, as determined from sound velocity. The value $\frac{4}{3}$ is the predicted value for the ratio at the percolation threshold f_c.

and by the apparently different critical exponents for B and G seen in Figs. 8 and 9.

While recent percolation theories of elasticity give a very satisfactory description of our results, it is also of interest to examine the extent to which effective-medium theories[13,39] can be used to interpret the data. Calculation of effective elastic moduli for a two-component system where one component is void constitutes a particularly stringent application of such theories, particularly at low occupied volume fractions. In fact, for $f \leq 0.5$, many of the theories become inapplicable since they predict unrealistically high values of the percolation threshold (e.g., $f_c = \frac{1}{2}$ or $\frac{1}{3}$ for spherical or "perfectly disordered" pores and aggregates[39,40]). Recently, Berryman[41] has developed a self-consistent scattering theory in which low values of f_c can be obtained by modeling the shapes of the pores and the interconnected sinter particles as prolate spheroids with small aspect ratios. Figure 11 shows a family of curves for longitudinal and shear velocities of copper sinter calculated from Berryman's model with different values of the aspect ratio. Over the range of occupied volume fractions for which the velocity data was taken, good agreement is obtained between theory and experiment when the aspect ratio is 0.08; however, there does not appear to be a good correspondence between the thin ellipsoids required by the model and the actual shape of the copper sinter "sponge" as observed by electron microscopy.[29] It is necessary to assume even smaller aspect ratios to obtain nonzero values of the velocities down to $f_c = 0.06$, as measured by Deptuck *et al.*, so that as f is reduced the model becomes increasingly difficult to apply with confidence.

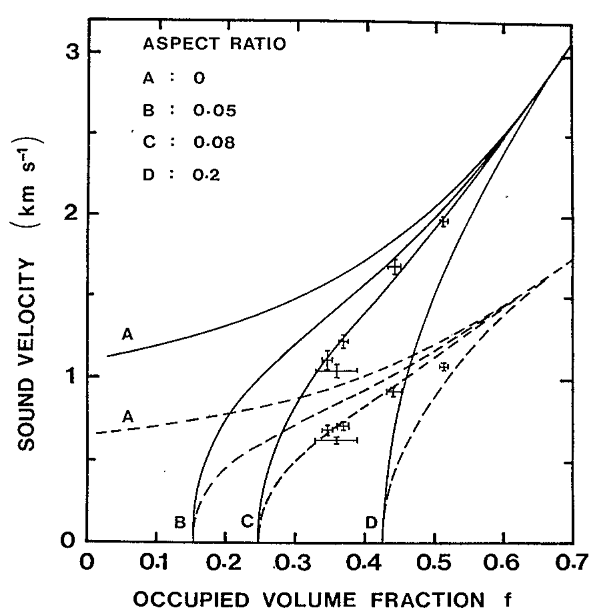

FIG. 11. Longitudinal and shear velocities (solid and dashed curves) of a copper/void composite calculated from Berryman's self-consistent effective-medium theory in which the shapes of the copper clusters and the pores are modeled as prolate spheroids with small aspect ratios. The points are the experimental data of Fig. 3.

B. Localized mode region

The transition from region 1 to region 2 was probed with (1–20)-MHz ultrasonic waves and sintered 10-μm copper powder. As the frequency was increased in this range, the ultrasonic pulses transmitted through the sinter specimens were progressively attenuated and distorted, as illustrated in Fig. 2 of Page *et al.*[5] Figure 12 shows a plot of the transmitted signal for shear waves as a function of λ/d, where λ is the ultrasonic wavelength in the sinter and d is the powder diameter (10 μm), for the samples with $f=0.49$ and 0.56. Note that the transmitted signal has been normalized to dB/cm in order to allow intercomparison between the samples. The very large attenuations observed at $\lambda/d\sim6$ and 8 for the two curves imply an apparent decrease in ultrasonic intensity of 1 order of magnitude per wavelength traveled, indicating that at these values of λ/d there is a crossover to a regime in which sound waves do not propagate. In short, there is a band edge for propagating phonons which shifts to higher frequency (lower wavelength) for the larger occupied volume fraction. Unfortunately the data are not sufficiently accurate to allow these two critical wavelengths to be meaningfully compared with the theoretical variation of the percolation correlation length ξ with $f-f_c$. This correlation length can be taken as the cluster size in a percolation system[42] and, near p_c, varies as $(p-p_c)^{-\nu}$ with $\nu=0.88$.[43] We expect this correlation length to mark the boundary between the propagating and the localized modes so that the crossover wavelengths and frequency are $\lambda_e\sim\xi(f)$ and $\omega_e(f)\sim2\pi v(f)/\xi(f)$, where $v(f)$ is the ultrasonic velocity in the sinter in region 1.

The modified acoustic theory for heat transfer[10] implies that below the temperature (T_e) corresponding to the band-edge frequency, the heat transfer will be markedly decreased. This temperature is given by

$$T_e\sim\hbar\omega_e/3k_B\sim(h/3k_B)v(f)/\xi(f)$$

if we assume that the correlation length does indeed mark the band edge. For $f=0.5$, we have $v\approx10^3$ m s^{-1} (Fig. 3) and $\xi\approx10d$ (Fig. 12),[44] giving $T_e\approx1.5$ mK for $d=1$ μm.

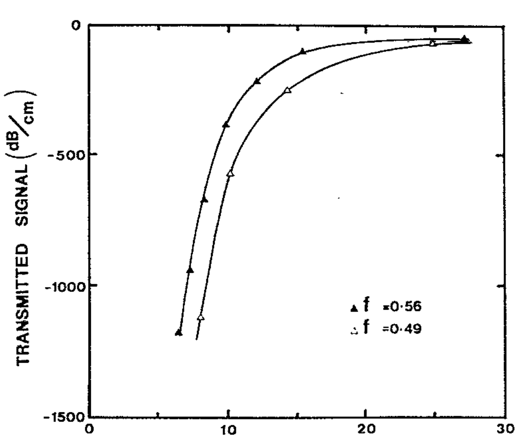

FIG. 12. The variation in transmitted shear wave signal as a function of λ/d for two sintered 10-μm copper powder discs. The wavelength λ was determined from the frequency and the measured sound velocity.

To see how T_e scales with f, we make use of

$$v(f)\propto f^{-1/2}(f-f_c)^{\tau/2}$$

and

$$\xi(f)\propto(f-f_c)^{-\nu}$$

to obtain

$$T_e\propto f^{-1/2}(f-f_c)^{\tau/2+\nu}\ .$$

Thus, with $\tau=3.8$ and $\nu=0.88$,[45] T_e drops to 0.2 mK for $f=0.25$, showing the advantage of using highly porous sinter for heat exchangers in submillikelvin experiments.

The theoretical work of Derrida *et al.*[46] has aroused interest in the question of how the density of states changes across the band edge from phonons to fractons or in our language, because we have not yet determined a fractal dimension for sinter, from phonons to localized modes. In three dimensions, Derrida *et al.* show that

$$D_{\rm fr}(\omega_e)/D_{\rm ph}(\omega_e)\propto(p-p_c)^{-1/2}$$

for an effective-medium-approximation treatment of a bond percolation network with elastic forces described by the scalar Born model. For the sinter phonons, $D_{\rm ph}(\omega)=3\omega^2/2\pi^2v^3$. Rutherford *et al.*[10] argued, from a sum rule for the total number of localized modes, that the localized-mode density of states was $D_{\rm lo}(\omega)=3Nd/2\pi Vv_D$, where N is the number of powder particles, V is the sample volume, and v_D is the bulk metal Debye velocity. With $\omega_e(f)\sim2\pi v(f)/\xi(f)$ and $N/V=f/(\pi d^3/6)$, the ratio of the densities of states at the band edge becomes

$$D_{\rm lo}(\omega_e)/D_{\rm ph}(\omega_e)\sim(3f/2\pi^2)(\xi/d)^2v/v_D\ .$$

For $f=0.5$, as above, $v\sim10^3$ m s^{-1} and $\xi/d\sim10$, so that with $v_D\sim2\times10^3$ m s^{-1},

$$D_{\rm lo}(\omega_e)/D_{\rm ph}(\omega_e)\sim4\ .$$

We can again make use of the occupied volume fraction dependences of v and ξ discussed above to show that the ratio scales with f as

$$D_{\rm lo}(\omega_e)/D_{\rm ph}(\omega_e)\propto f^{1/2}(f-f_c)^{\tau/2-2\nu}\ .$$

Since $\tau/2\sim2\nu$, this argument suggests that as the percolation limit is approached the density-of-states ratio at the band edge varies only weakly with $f-f_c$. While this result does not support the effective-medium-approximation predictions of Derrida *et al.* it is consistent with the findings of more recent scaling arguments by Aharony *et al.*[47] that the density-of-states ratio at crossover is noncritical.

C. Short wavelengths, $\lambda\sim d$

Ultrasonic experiments were performed on 300-μm particle sinters to study the behavior at shorter length scales where the wavelength becomes comparable to the powder particle size. The sinters used had occupied volume fractions of order 0.5. In our frequency range, 1–20 MHz, it was necessary to polish the samples down to a thickness of a few powder diameters in order to obtain measurable transmitted ultrasonic signals. Thus the larger scale inhomogeneities which give rise to the band edge discussed in Sec. IV B were eliminated, although disorder on the scale of the particle diameter was still present. Throughout the frequency range, the transmitted signals were very weak and distorted, the apparent attenuation increasing with frequency as $\lambda/d=1$ was approached. This point corresponds to the crossover from localized modes to bulk metal phonons (i.e., from region 2 to region 3 of Fig. 1). At shorter wavelengths, $\lambda<d$, ultrasonic waves can propagate with relatively low loss within each powder particle; however, the apparent ultrasonic attenuation in the sinter specimen remained very large because of strong scattering at the interfaces between the particles and because of interference effects arising from different ultrasonic paths through the specimen. Therefore this experiment was not able to demonstrate the crossover from localized vibrations of particles to bulk metal phonons within the powder particles, although it did show that in the phonon regime ($\lambda<d$), the phonon scattering at the particle interfaces is very large.

V. CONCLUSION

Sintered metal powder can be described as a percolation system above the percolation threshold. Long-wavelength ultrasonic waves, longitudinal and transverse, propagate as if in a continuous medium with a velocity that varies almost linearly with occupied volume fraction f. The elastic moduli, derived from sound velocity or static deformation, are in good agreement with the scaling relations $K\propto(f-f_c)^\tau$ with $\tau=3.6\pm0.5$. This exponent agrees with the result $\tau>3.55$ derived from a recent theoretical model[23] for the elasticity of percolation structures, and with the result $\tau>t$ derived from several theoretical models[22–25] where t is the conductivity exponent.

The measurement of ultrasonic attenuation as a function of frequency confirmed the existence of a band edge between the low-frequency propagating phonons and what we presume to be localized vibrational modes. The band edge corresponded to a phonon wavelength $\sim 10d$ for the $d=10$-μm particle diameter sinter with a 50% occupied volume fraction. The edge moved to higher frequency for the larger occupied volume fraction, consistent with the correlation length in a percolation system decreasing with increase in $p-p_c$. By scaling the 10-μm result to the submicrometer sinter typically used for low-temperature heat exchangers, it was shown that the temperature below which the dominant vibrational excitations of the sinter change from localized oscillations to propagating phonons varied from 1.5 mK for $f=0.5$ to 0.2 mK for $f=0.25$.

The new results for the variations of the elastic moduli and band edge with $f-f_c$, together with the Rutherford *et al.* postulate that the localized modes have a constant density of states, $D_{\rm lo}(\omega)\sim 3Nd/2\pi V v_D$, imply that the ratio of density of states of localized modes to phonon modes at the band-edge frequency $D_{\rm lo}(\omega_e)/D_{\rm ph}(\omega_e)$ probably has only a very weak dependence upon $f-f_c$. These results are in reasonable agreement with the predictions of recent scaling arguments.[47]

For the modified acoustic theory of heat transfer between liquid ^{3}He and sintered metal powder, the present work has provided indirect support for the existence of localized vibrational modes and has given detailed information on the propagating phonons that will be excited below 1 mK. It has also shown that there is a considerable advantage in decreasing the occupied volume fraction in order to lower the velocity of the propagating phonon modes and to lower the temperature below which only propagating phonons can be excited. This follows from the predictions of Toombs *et al.*,[48] that in the phonon regime the heat transfer between ^{3}He quasiparticles and phonons in the solid varies as v^{-3}, and from the result of Rutherford *et al.*, that heat transfer is larger to localized modes than to phonons, at the same temperature.

Much of the current activity in ultralow-temperature research is focused on liquid ^{3}He and ^{3}He-^{4}He mixtures in the temperature range 0.1–2 mK with increasing emphasis on high magnetic fields because of the interest in spin-polarized Fermi liquids. The implication of a recent measurement[49] of heat transfer between pure ^{3}He and silver sinter as a function of temperature and magnetic field is that for pure ^{3}He in a small field the heat transfer is by some magnetic coupling process that is inhibited by increasing the field. Acoustic coupling therefore probably dominates for pure ^{3}He in large fields and for ^{3}He-^{4}He mixtures in any field. The above temperature range corresponds to the band edge between propagating and localized modes in the submicrometer sinter used to cool the helium, and there is an obvious interest in improving the theory for this region. Scaling arguments for a fractal model of a random structure, coupled with calculations in the effective-medium approximation for a bond percolation model, have now allowed a derivation of the vibrational modes of the structure on either side of the band edge.[13–15,46] The two directions in which we would like to extend work on the modified acoustic theory of Kapitza resistance are to calculate heat transfer between a Fermi liquid in the pores of a random structure with fractal geometry and the vibrational modes of that structure, and to determine to what extent submicrometer sinters have fractal dimensionality.

ACKNOWLEDGMENTS

This research has been supported by the Natural Sciences and Engineering Research Council (NSERC) of Canada and by the School of Graduate Studies and Research of Queen's University. M.C.M. wishes to acknowledge two NSERC Summer Awards and J.P.H. wishes to acknowledge partial support by the Killam Research Foundation. We would also like to acknowledge discussions with T. McMullen, A. R. Rutherford, M. J. Stott, and A. Tyler and assistance from R. D. McCulloch.

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