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Transition Temperature of Superconducting Indium, Thallium, and Lead Grains

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Experimental results on the transition temperature of indium, thallium, and lead grains of various sizes, together with preliminary measurements on other metals, can be interpreted in terms of changes in the phonon spectrum which alter the electron-phonon coupling constant, although some anomalies exist.

In this paper, measurements of the superconducting transition temperature of indium and thallium in porous glass are presented. The samples are produced by forcing molten metal into the porous structure, as described in the literature.[1,2] The pore diameter d was determined by mercury porosimetry,[2,3] and the values obtained were in agreement with those obtained from electron microscope pictures of the structure. The metal in the porous glass has been described as being in the form of spherical grains of closely equal size.[4]

The critical fields of metals in porous glass behave like granular superconductors.[2,5,6] In such a system the electron mean free path l is of the form $l = d\tau$, where d is the grain diameter and τ is the transmission probability of the electron between grains. For indium in normally prepared porous glass, $\tau \sim 0.03$.[2] The metal grains produced in this way are highly crystalline, as shown by the sharpness of the x-ray diffraction lines. This indicates that in these samples surface or size effects dominate, as distinct from the films evaporated at low temperature, where amorphousness of the metal lattice is an extra complication.

The transition temperature T_c was located by a mutual inductance technique as the temperature at which the imaginary part χ'' of the complex susceptibility $\chi(=\chi' + i\chi'')$ begins to change.[1] Measured in this way, T_c is independent of the amplitude of the ac field up to 20 Oe. The value used here was 1 Oe. The transition width ΔT_c was about 0.05 °K wide. Hake[7] has recently shown that fluctuation effects in samples with small values of $\xi_0 l$ can produce changes in resistivity above T_c. In view of this, the values of T_c obtained here could be lower by an amount of order ΔT_c.

Recently, McMillan[8] showed that the transition temperature of simple metals could be increased by a reduction of Θ_D, the Debye temperature. It has been suggested[9–11] and confirmed experimentally[12] that in small crystallites the phonon spectrum is appreciably altered by a greater proportion of low-frequency surface phonons, and it has been suggested that this is the cause of the shifts in T_c in granular or disordered materials.

Garland *et al.*[9] have derived the following equation for T_c:

$$\ln \frac{\langle\omega^2\rangle^{1/2}\omega_{0b}}{1.26T_c\langle\omega_b^2\rangle^{1/2}} = \frac{1+\lambda}{A(1-0.5\mu^*)\lambda - \mu^*} , \qquad (1)$$

where $\langle\omega^2\rangle$ is the average of the square of the phonon frequencies, λ is the electron-phonon coupling constant, and it is the phonon contribution to the electron mass renormalization[7];

$$\lambda = 2\int_0^\infty \alpha^2(\omega)\,F(\omega)\,d\omega/\omega \quad , \tag{2}$$

where $\alpha^2(\omega)$ is the electron-phonon interaction strength and $F(\omega)$ is the phonon spectrum.

λ is inversely proportional to $\langle\omega^2\rangle$.[8] A is a constant of order unity, depending on the crystal structure, and, in general, is reduced by disorder; μ^* is the reduced Coulomb pseudopotential. The subscript b refers to the bulk material, and ω_{0b} denotes the highest phonon frequency.

The decrease in $\langle\omega^2\rangle$ results in the equation[9]

$$\ln\frac{T_c}{T_{cb}} = \frac{1}{2}\ln\left(1+\frac{\delta\lambda}{\lambda}\right) + \frac{1+\lambda}{A(1-0.5\mu^*)\lambda-\mu^*} - \frac{1+\lambda(1+\delta\lambda/\lambda)}{A(1-0.5\mu^*)\lambda(1+\delta\lambda/\lambda)^{1-\beta/2}-\mu^*} \quad , \tag{3}$$

assuming that $\delta\ln\lambda = 2\delta\ln\langle\omega\rangle$, and that $\delta\ln A = \beta\delta\ln\langle\omega\rangle$. By assuming that the degree of disorder was similar in each of several films produced by Buckel and Hilsch,[13] Garland *et al.*[9] find that β is roughly constant $\simeq 0.52$.

Recently, Watton[14] has extended Garland's result to situations where the grain size changes, i.e., granular films with different average grain sizes, or metal in porous glasses with different pore size. Watton assumes that, in a thin surface layer of thickness W, the coupling constant has a larger value. This gives

$$\delta\lambda/\lambda = 2K/d \quad , \tag{4}$$

where

$$K = [\lambda(\text{surface}) - \lambda(\text{bulk})]3W/\lambda(\text{bulk}) \ .$$

Equation (3) can be derived from a simple model in which surface modes and bulk modes are combined in the ratio of surface atoms to bulk atoms in a grain. The phonon spectrum $F_r(\omega)$ for a spherical grain of radius r is then

$$F_r(\omega) = (3a/r)f_s(\omega) + (1-3a/r)f_b(\omega) \quad , \tag{5}$$

where $f_s(\omega)$ and $f_b(\omega)$ are the phonon spectra of the surface modes and the bulk modes, respectively, and a is the interatomic spacing. If the expression for $F_r(\omega)$ is substituted into Eq. (2), then Eq. (4) follows, if $W = a$ the interatomic spacing. (See Appendix.)

The observation of McMillan[8] that $\lambda\langle\omega^2\rangle$ is constant in a particular system leads to the conclusion that (see Appendix)

$$\int_0^\infty \omega\alpha_s^2 f_s(\omega)\,d\omega = \int_0^\infty \omega\alpha_b^2 f_b(\omega)\,d\omega \quad , \tag{6}$$

where α_s^2 and α_b^2 are the electron-phonon interaction strengths for surface and bulk phonons, respectively. This can be verified by a tunneling measurement. With Eq. (4), Garland's expression becomes

$$\ln\frac{T_c}{T_{cb}} = -\frac{1}{2}\ln(1+2Kd) + \frac{1+\lambda}{A(1-0.5\mu^*)\lambda-\mu^*} - \frac{1+\lambda(1+2K/d)}{A(1-0.5\mu^*)\lambda(1+2K/d)^{1-\beta/2}\mu^*} \ . \tag{7}$$

The values of A, λ, and μ^* are determined from the bulk properties of the metal and have been tabulated by Garland *et al.* Once these bulk values have been fixed, Eq. (7) contains two adjustable parameters, namely, β and K. As mentioned above, Garland *et al.* find that β is roughly equal to 0.52 for many metals. Equation (7) has been calculated for indium using the bulk values given by Garland *et al.* of $A = 0.85$, $\lambda = 0.84$, and $\mu^* = 0.09$. The calculated curve is plotted with the experimental points in Fig. 1. As shown, the values of $\beta = 0.48 \pm 0.01$ and $K = 10 \pm 1$ Å yield a good fit. The uncertainty limits were obtained as the change in the parameters required to shift the value of α outside the envelope of the experimental points at the maximum of the curve.

The interatomic spacing, about 3 Å for indium, gives a value of $\lambda_s = 1.79$ and $\lambda + \delta\lambda = 1.35$ for $d = 22$ Å where the maximum value of T_c occurs. For sizes smaller than $d = 22$ Å, the model predicts

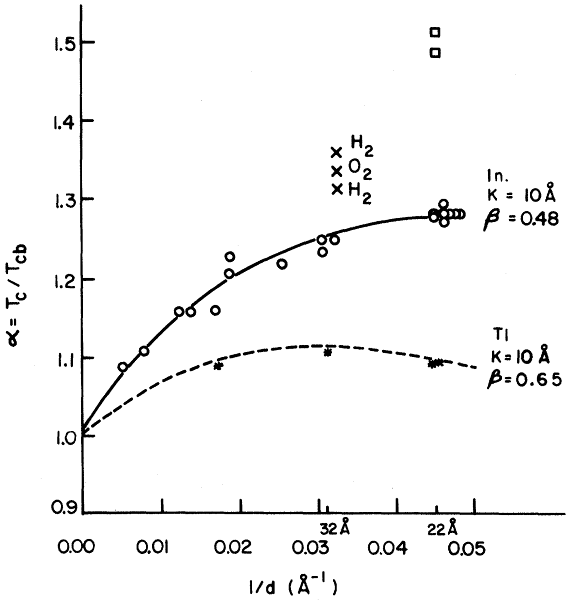

FIG. 1. Ratio of the transition temperature to the bulk transition temperature is plotted versus the reciprocal of the pore diameter. The solid line is calculated from Eq. (7) for indium, and the broken line is calculated for thallium.

that T_c will be reduced, and for a grain of 10 Å diam, this model gives $T_c \sim 4.1$ °K.

Most of the points for indium lie on or near the calculated curve; however, there are some curious exceptions that are as yet unexplained. In one particular batch of small-pored glass, the transition temperature for samples impregnated with indium is anomalously high, as shown in Fig. 1. The effect is large, and the resulting values of T_c are ~1 °K higher than the maximum of the fitted curve. It is not possible, therefore, to explain this behavior in terms of the surface phonon model, and it suggests that some other mechanism is operating.

Values of T_c, again higher than those corresponding to the maximum of the fitted curve, can the obtained by bubbling oxygen or hydrogen through the indium prior to impregnation. The same result can be achieved by the addition of In_2O_3 powder to metal. The shift in T_c is accompanied by a reduction of Hc_2, which can be explained in terms of an increase of 30–50% in the tunneling parameter τ. No satisfactory explanation exists for the observed shifts in T_c; however, the results again suggest the operation of another mechanism in addition to the surface phonon mechanism.

The results obtained for indium are qualitatively similar to the results obtained by Watton in films deposited at low temperatures and progressively annealed. The value of β obtained by Watton is 0.52 compared with the value 0.48 used here. Watton suggests a value of $K = 20$ Å might be reasonable, whereas the value obtained here is 10 Å. This value of K is based on the values of d obtained by mercury porosimetry, and these appear to be in reasonable agreement with electron microscope pictures of the structure.[4]

For thallium with $A = 0.85$, $\lambda = 0.81$, and $\mu^* = 0.08$, a good fit is obtained with $K = 10 \pm 1$ Å and $\beta = 0.65 \pm 0.01$. The lattice parameter for thallium is 3.1 Å so that $\lambda_s = 1.79$, and at the maximum value of T_c, which occurs at 32 Å, $\lambda + \delta\lambda = 1.32$. This is similar to indium, but the value of β is considerably higher. For a 10-Å grain of thallium the predicted value of T_c is 2.2 °K, which is less than the bulk value of 2.39 °K.

The data for tin and gallium are incomplete; however, it appears that tin is similar in behavior to indium and thallium. The data for lead are shown in Fig. 2. Curve A is for measurements made in this study, and curve B is that made by Strongin and Kammerer[15] on thin films deposited at low temperatures. Suppressed values of T_c have also been observed by Zavaritsky.[16] Using the values of $A = 0.90$, $\lambda = 1.22$, and $\mu^* = 0.09$[9] the best fit to the data occurs with $K = -4$ and $\beta = 0.50 \pm 0.05$. A good fit to the Strongin and Kammerer data is obtained with $K = 30 \pm 2$, $\beta = 0.50 \pm 0.05$, and this fit indicates that superconductivity is completely quenched at grain diameters of 30 Å. The negative values of K indicate that for lead, according to this model, the value of $\langle\omega^2\rangle$ increases with decreasing grain size.

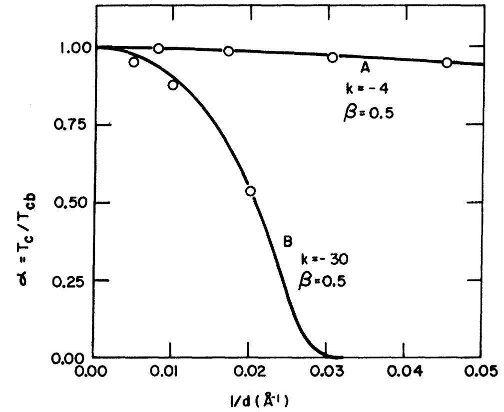

FIG. 2. Ratio of the transition temperature to the bulk transition temperature is plotted versus the reciprocal of the pore diameter. Curve A shows the results of this work and curve B shows the results of Strongin and Kammerer (Ref. 15). The solid lines are calculated from Eq. (7).

Tunneling measurements have been made on films deposited at low temperature[17] and on bulk lead.[18] For the films, assuming that $\alpha_s = \alpha_b$, Leslie finds $\langle\omega^2\rangle = 21.9$ (meV)^2, whereas McMillan and Rowell find a value of $\langle\omega^2\rangle = 24$ (meV)^2 for bulk lead. In the measurements of McMillan and Rowell the frequency cutoff at the very high value of 11 meV was suggested as being due to the surface of the sample, which makes the comparison of the two measurements somewhat doubtful. Leslie also finds that μ^* has the large value of $\mu^* = 0.19$. Although there are uncertainties in the values of $\langle\omega^2\rangle$ derived for tunneling, it is clear that the Strongin and Kammerer[15] results cannot be explained by this surface phonon model as the results require for grains of 60 Å that $\langle\omega^2\rangle$ be two times the bulk value.

From the results presented here, the effect of grain size on T_c being much weaker, it may still be possible to explain the results by a slight increase of $\langle\omega^2\rangle$. For grains of 22 Å diam a fractional increase $\delta\langle\omega^2\rangle/\langle\omega^2\rangle = 0.25$ is needed which is about the uncertainty of the tunneling measurement. Again, the present result may be altered if α_s is appreciably different from α_b.

Using an unrealistic but simple model (a phonon spectrum of a δ function of frequency ω_s for the surface phonons and a Debye spectrum for the bulk spectrum with a cutoff of ω_D), it is found that if $\alpha_s^2\omega_s/\alpha_b^2\omega_D \gtrsim 0.7$, the $\langle\omega^2\rangle$ increases with decreasing size, as discussed in the Appendix.

The gallium results are interesting in that for $d = 22$ Å, $T_c = 7.090$ °K, and for $d = 32$ Å, $T_c = 7.135$ °K, and T_c does not change with cycling to room temperature, in contrast with the amorphous gallium films produced at low temperature,[19] whose values of T_c drop irreversibly to the bulk value of 1.09 °K when the temperature is taken above 50–60 °K. X-ray diffraction shows that the gallium grains in porous glass are amorphous.[20]

When the metal is in such close contact with the silica it might be expected that the electronic and acoustic properties of the glass affect the superconducting state. However, these are probably second-order effects as the following arguments indicate. The surface of the silica is covered with OH – groups, with a density of 5 per 100 (Å)^2. When these OH – groups are removed from the glass surface and replaced with Cl – groups or CH_3O – groups, prior to impregnation, although the dielectric properties of the glass and the chemistry of the surface is changed, the shift in the transition temperature is less than 0.05 °K, whereas the total shift from the bulk value at that pore size is 0.6 °K. This work has been described previously.[21]

Samples of porous ZrO_2 were constructed from powders resulting in a structure similar to the porous glass and these were impregnated with indium. A sample with a pore size of 22 Å has a transition temperature of 4.32 °K, whereas a porous glass sample with the same pore size had a transition temperature of 4.37 °K. The surface of ZrO_2 is appreciably different from the silica surface both chemically and electrically.

The low-frequency acoustic modes due to the silica should propagate through the grains, as will be discussed below; however, this effect is not likely to be pore size dependent. It might be expected also that the presence of the silica affects the surface phonon frequency; again, this effect probably will be pore size independent. Also, the fact that the Cl-treated and the CH_3O-treated glass and the ZrO_2 sample have values of T_c which seem to depend only on pore size indicates the effect of the matrix is not important. From the above arguments it may seen reasonable to apply this simple phonon model to metals in porous glass as a first approximation to the behavior of T_c as a function of d.

Rothwarf[22] has suggested that the shifts in transition temperature in small grains occur because of a decrease in number of real low-frequency phonons present as the grains become small. These real phonons lead to depairing and, in consequence, T_c is increased. The decrease in number of real phonons is due to a low-frequency cutoff of $q_0 = \hbar/d$ in a grain of diameter d. This leads to a transition temperature that increases monotonically with decreasing grain size. This model, which has no adjustable parameters, explains measurements on tin[23] and aluminum[10,24] very well. This model, however, does not explain the results obtained here for thallium and indium, or suppression of the T_c for lead. These low-frequency phonons will be present in small grains due to their contact with the medium in which they are embedded and this should lead to a dependence of T_c on the Debye temperature of the medium. If the grains were isolated in vacuum or were embedded in a medium of very high Debye temperature, the model would seem more plausible.

A much more detailed calculation of the effect of thermal phonons on pair breaking has been carried out by Appel,[25] who finds that an absence of thermal phonons can cause an increase in T_c. Contrary to the work of Rothwarf, Appel finds that the shift of T_c can only amount to a few percent of T_c even in the complete absence of thermal phonons.

It is a pleasure to thank R. A. Watton for a copy of his paper prior to publication, N.K. Hindley, M. Strongin, and A. Rothwarf for helpful comments, and J.D. Leslie for experimental results prior to publication.

APPENDIX: PHONON SPECTRUM OF A SMALL SPHERICAL GRAIN

The phonon spectrum is calculated with the assumption that it is the sum of a surface spectrum $f_s(\omega)$ and a bulk spectrum $f_b(\omega)$, which do not depend on the grain radius r. It is assumed that the number of surface modes n_s is proportional to the number of surface atoms and the total number of modes n_T is equal to $3N$ where N is the total number of atoms. The frequency distribution $F_r(\omega)$ for a grain of radius r is

$$F_r(\omega) = (n_s/n_T) f_s(\omega) + (1 - n_s/n_T) f_b(\omega) \quad . \qquad \text{(A1)}$$

The McMillan average[8] $\langle\omega_r^2\rangle$ for the grain is

$$\langle\omega_r^2\rangle = \frac{2[(n_s/n_T)\bar{\omega}_s + (1 - n_s/n_T)\bar{\omega}_b]}{(n_s/n_T)\lambda_s + (1 - n_s/n_T)\lambda_b} \quad , \qquad \text{(A2)}$$

where

$$\bar{\omega}_s = \int_0^\infty \alpha_s^2 \omega f_s(\omega)\, d\omega, \quad \bar{\omega}_b = \int_0^\infty \alpha_b^2 \omega f_b(\omega)\, d\omega \quad ,$$

$$\lambda_s = 2\int_0^\infty \alpha_s^2 f_s(\omega)\, d\omega/\omega, \text{ and } \lambda_b = 2\int_0^\infty \alpha_b^2 f_b(\omega)\, d\omega/\omega \quad .$$

The value of λ for the grain is

$$\lambda = 2\int_0^\infty [(n_s/n_T)\alpha_s^2 f_s(\omega) + (1 - n_s/n_T)\alpha_b^2 f_b(\omega)]\, d\omega/\omega$$
$$= (n_s/n_T)\lambda_s + (1 - n_s/n_T)\lambda_b \quad . \qquad \text{(A3)}$$

It has been suggested by McMillan that $\lambda\langle\omega_r\rangle$

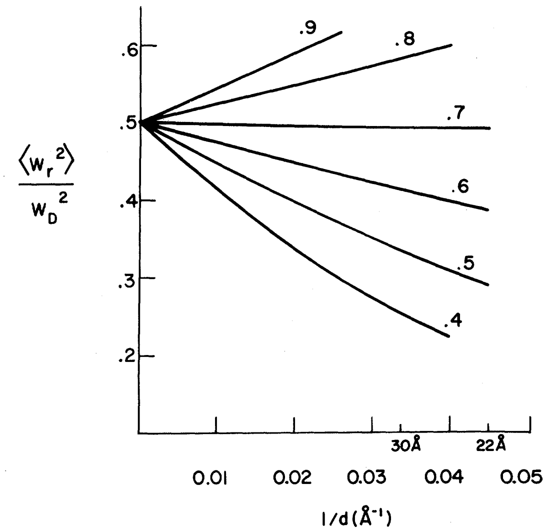

FIG. 3. Ratio of the average phonon frequency and of the Debye frequency is plotted as a function of the reciprocal of the grain diameter for different values of the parameter $\alpha_s^2\omega_s/\alpha_b^2\omega_D$.

= const, from Eqs. (A2) and (A3), the condition for this being that given in Eq. (6).

Rearranging Eq. (A3) gives

$$(\lambda-\lambda_b)/\lambda_b=\delta\lambda/\lambda=(n_s/n_T)(\lambda_s-\lambda_b)/\lambda_b \quad . \qquad \text{(A4)}$$

Taking n_s equal to the number of surface atoms for $a/\kappa \ll 1$, $(n_s/n_T)=3a/r$, where a is the interatomic spacing, then (A4) has the form of Eq. (4) with $W=a$.

It is interesting to evaluate these equations using simple distributions for $f_s(\omega)$ and $f_b(\omega)$. Using

$$f_s(\omega)=\delta(\omega-\omega_s) \quad \text{and} \quad f_b(\omega)=3\omega^2/\omega_D^3 \quad ,$$

where ω_D is the Debye frequency, Eq. (A2) for $\langle\omega_r^2\rangle$ can be evaluated for $a/\kappa \ll 1$,

$$\langle\omega_r^2\rangle=\frac{\omega_D^2[4a\gamma(\omega_s/\omega_D r)+(1-3a/r)]}{4a\gamma(\omega_D/\omega_s r)+2(1-3a/r)} \quad , \qquad \text{(A5)}$$

where $\gamma=\alpha_s^2/\alpha_b^2$. $\langle\omega_r^2\rangle$ versus $1/r$ is plotted in Fig. 3 for various values of the parameter $\alpha_s^2\omega_s/\alpha_b^2\omega_D$. Surprisingly, if $\alpha_s^2\omega_s/\alpha_b^2\omega_D \gtrsim 0.7$, $\langle\omega_r^2\rangle$ increases with decreasing r. Although these phonon spectra are idealized, this calculation serves to demonstrate that, even in a simple model, $\langle\omega_r^2\rangle$ does not always decrease with decreasing r.

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