Size Effect in a Granular Superconductor

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The superconducting energy gap and the transition temperature of a small grain of superconductor are larger than the corresponding quantities for bulk material. This results because the small dimensions cause a discrete, rather than continuous, spectrum of one-electron energy levels. This effect becomes important when the volume of the grain is comparable with, or smaller than, the characteristic volume $\lambda_F^2\xi_0$, where λ_F is the Fermi wavelength and ξ_0 the $T=0$ Pippard coherence distance of the bulk material. As grain size is lowered, the ratio of $T=0$ energy gap to Boltzmann's constant times transition temperature gradually increases from the weak-coupling limit (3.528) to the strong-coupling limit (4.0).

I. INTRODUCTION

IT has been found experimentally[1–5] that certain superconductors, when composed of grains of a suitable size (in the range 50–500 Å), have transition temperatures T_c appreciably higher than that of the corresponding bulk material. One explanation for this has been in terms of Ginzburg's theory[6] of surface-enhanced superconductivity. The Brookhaven group[3] postulated that this was due to oxides at the surfaces of the grains. The RCA group[4] has pointed out that the earlier work[1,2] suggests that oxide is not necessary to get enhancement, only the presence of grain boundaries. The writer[7] has shown that Josephson tunneling[8] between adjacent grains can contribute to the effective electron-electron attraction, and thus may cause enhancement.

In this paper, we wish to consider the contribution of *size of grain* to the enhancement of superconductivity. Thus we shall consider only an individual grain, and answer the question of how the transition temperature and superconducting energy gap change as the size of the grain is lowered. This problem has already been considered by Abeles *et al.*,[4] although no details have been published. In agreement with the present paper, they concluded that the size effect could lead to enhancement of the magnitude observed. Nevertheless, they rejected the size effect, for reasons which do not seem compelling to the writer.[9]

It is instructive to consider the analogous problem of enhancement in a geometrically perfect thin film. Blatt and Thompson[10] have shown that the superconducting energy gap is an oscillatory function of film thickness, the period being the Fermi wavelength λ_F. In addition, there is a steady increase of energy gap with decreasing film thickness. One would expect the oscillatory effect to be washed out as one went to a more realistic model of the film, where the thickness might vary from place to place, over many multiples of λ_F. The steady increase with decreasing mean film thickness would be expected to persist, however. This is just the behavior we will find for the superconducting grain, after having deliberately averaged out the oscillatory behavior associated with changes of grain size by a Fermi wavelength.

Because of the small size of the superconductor, integrals over k space appearing in the BCS theory of superconductivity[11] become discrete sums over k space in the present theory. These sums are evaluated by means of the Poisson sum formula.[12] This replacement of integrals by sums makes the weak-coupling theory of superconductivity tend toward the strong-coupling limit.[13] The quantity $(2\epsilon_0/k_BT_c)$, ratio of the energy gap at $T=0$ to Boltzmann's constant times the transition temperature, increases from the weak-coupling value of 3.528 toward the strong-coupling value of 4. Although we will follow BCS in treating the effective electron-electron interaction as instantaneous and nonlocal, it should be borne in mind that this approximation serves only to simulate what is really a local but time-retarded interaction. For either form of interaction, one ends up with integrations over *energy* (rather than integrations over k space). The size effect in superconductivity manifests itself by converting a

[1] W. Buckel and R. Hilsch, Z. Physik **138**, 109 (1954).
[2] I. S. Khukhareva, Zh. Eksperim. i Teor. Fiz. **43**, 1173 (1962) [English transl.: Soviet Phys.—JETP **16**, 828 (1963)].
[3] O. F. Kammerer and M. Strongin, Phys. Letters **17**, 224 (1965); M. Strongin, A. Paskin, O. F. Kammerer, and M. Garber, Phys. Rev. Letters **14**, 362 (1965).
[4] B. Abeles, R. W. Cohen, and G. W. Cullen, Phys. Rev. Letters **17**, 632 (1966).
[5] R. W. Cohen, B. Abeles, and G. S. Weibarth, Phys. Rev. Letters, **18**, 336 (1967); J. H. P. Watson, Phys. Rev. **148**, 223 (1966).
[6] V. L. Ginzburg, Phys. Letters **13**, 101 (1964).
[7] R. H. Parmenter, Phys. Rev. **154**, 353 (1967).
[8] B. D. Josephson, Advan. Phys. **14**, 419 (1965).
[9] Abeles *et al.* rejected the model since it led to normal-state resistivity three orders of magnitude larger than that observed. In fact, pinholes or bridges in the barriers separating adjacent grains can drastically lower the resistivity without appreciably modifying the isolation of an individual grain (in terms of the quantization of the one-electron levels of the grain, which, as we shall see, is what can cause enhancement of superconductivity in isolated grains).
[10] J. M. Blatt and C. J. Thompson, Phys. Rev. Letters **10**, 332 (1963); C. J. Thompson and J. M. Blatt, Phys. Letters **5**, 6 (1963).
[11] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[12] See, e.g., R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Interscience Publishers, Inc., New York, 1953), Vol. I, p. 77.
[13] D. J. Thouless, Phys. Rev. **117**, 1256 (1960). It should be emphasized that, by "strong-coupling limit," here we mean the case where the one-electron effective mass becomes very large, not the limit where the electron-phonon interaction becomes large (also referred to in the literature by the same phrase).

continuous one-electron energy spectrum into a *discrete* spectrum. This means, however, that the normal-state mean free path for *inelastic* scattering must be large compared with the grain size, otherwise the discrete one-electron spectrum will be broadened until it looks continuous like that of a bulk sample.[14] It is in superconductors with a strong electron-phonon interaction that this restriction will be most severe.

II. MATHEMATICAL ANALYSIS

In the interest of simplicity of exposition, we choose the shape of our superconducting grain to be cubic, with cube edge a. The final results to be obtained are independent of this assumption. We wish to evaluate the free energy of our superconducting grain in a manner analogous to that of the BCS theory. In so doing, we will encounter sums of the form $\sum_k \varphi(\mathbf{k})$. In every case, $\varphi(\mathbf{k})$ will turn out to be a spherically symmetric function of $\mathbf{k}$ that is appreciable in size only in the immediate vicinity of the Fermi surface in k space. The sum is over all values of $\mathbf{k}$ satisfying periodic boundary conditions on the surface of the grain. Thus there is a volume $(2\pi/a)^3$ of k space for each such allowed $\mathbf{k}$ vector. We shall rewrite such sums as

$$\sum_k \varphi(\mathbf{k}) = (a/2\pi)^3 \sum_\nu \int_\infty \varphi(\mathbf{k}) \exp[-i(\boldsymbol{\nu}\cdot\mathbf{k})a] d^3k, \quad (1)$$

where

$$\boldsymbol{\nu} = \mathbf{i}_x\nu_x + \mathbf{i}_y\nu_y + \mathbf{i}_z\nu_z, \quad (2)$$

$\mathbf{i}_p$ being a unit vector along the pth coordinate axis, and ν_p being any integer, positive, negative, or zero. Equation (1) can be considered a threefold application of the Poisson sum formula.[12] Alternatively, it can be thought of as a transformation from a sum over direct-lattice points $\boldsymbol{\nu}a$ to the corresponding sum over reciprocal-lattice points $\mathbf{k}$. (This latter point of view allows us to handle an arbitrarily shaped grain.) In the limit of a macroscopic sized grain ($a\to\infty$), all the terms in the ν sum are negligible except one, that for $\boldsymbol{\nu}=0$. In other words, sums can be replaced by corresponding integrals, as was done in the BCS theory. As grain size is reduced, the finite-$\boldsymbol{\nu}$ terms in Eq. (1) represent the correction to the BCS result.

We have already mentioned the fact that $\varphi(\mathbf{k})$ is appreciable in size only very close to the Fermi surface. This has the following important consequence. Each term on the right-hand side of (1) will be proportional to a sinusoidal function of $\nu k_F a$, where ν is the magnitude of the vector $\boldsymbol{\nu}$. Aside from the $\nu=0$ term, all terms will have sinusoidal phases that change very rapidly as a function of grain size a. For example, for $\nu=1$ the phase changes by 2π as the grain size changes by the Fermi wavelength $\lambda_F=2\pi/k_F$. Since λ_F is a few Angstroms, whereas we shall be concerned with values of a tens or hundreds of Angstroms, it seems reasonable to assume that this very rapid variation with change in size is an artifact of the perfectly geometric (here cubic) grain, and that with a more realistically (and less symmetrically) shaped grain such variations are washed out. We therefore average the various k sums, as they appear in the free energy density associated with the superconducting grain, with respect to this rapid change in phase.

Writing F for this density, we have, following BCS notation,

$$a^3F = 4\sum_{k>k_F} \epsilon_k[f_k + h_k(1-2f_k)] - \sum_{kk'} V_{kk'}[h_k(1-h_k)h_{k'}(1-h_{k'})]^{1/2}(1-2f_k)(1-2f_{k'}) + 2k_BT\sum_k [f_k \ln f_k + (1-f_k)\ln(1-f_k)]. \quad (3)$$

On the left-hand side of (3), we have a^3F, rather than F alone, since we are defining F as a free energy density, while the right-hand side is the free energy of a grain. The first sum on the right-hand side is the one-electron (or kinetic) energy, the second sum is the attractive electron-electron interaction energy, the third sum is the negative of the entropy times temperature.[15] With suitable choices of $\varphi(\mathbf{k})$, the first and third sums take on the form of $\sum_k \varphi(\mathbf{k})$ and therefore can be rewritten as ν sums in the manner of Eq. (1). However, as soon as we average over phases, all terms except $\boldsymbol{\nu}=0$ disappear, and

$$\langle 4\sum_{k>k_F} \epsilon_k[f_k + h_k(1-2f_k)]\rangle_{\text{Av}} = (a/2\pi)^3 \int_{k>k_F} 4\epsilon_k[f_k + h_k(1-2f_k)] d^3k, \quad (4)$$

$$\langle 2k_BT\sum_k [f_k \ln f_k + (1-f_k)\ln(1-f_k)]\rangle_{\text{Av}} = (a/2\pi)^3 2k_BT \int [f_k \ln f_k + (1-f_k)\ln(1-f_k)] d^3k. \quad (5)$$

As far the kinetic energy and entropy are concerned, there is no change from the BCS case (no size effect), the right-hand sides of (4) and (5), when divided by a^3, being exactly what was used in the BCS expression for F.

[14] Note that the mean free path for *elastic* scattering (due to boundary scattering, for example) need not be large, since such scattering doesn't broaden the energy spectrum.

[15] The BCS form of free energy, as given in Eq. (3), relies on many-electron wave functions which are not eigenfunctions of total electron number. This might conceivably lead to difficulties with small systems having few conduction electrons. The above form of free energy can be obtained from a theory using wave functions which are eigenfunctions of electron number [see K. Nakamura, Progr. Theoret. Phys. (Kyoto) **21**, 713 (1959)]. A crucial step in such a theory is the saddle-point method of analytically summing certain cluster expansions. A detailed examination of the assumptions made in carrying out the saddle-point method [see R. H. Parmenter, Phys. Rev. **132**, 2490 (1963)] shows that the method breaks down when there are only a few one-electron energy levels in the energy range over which the pairing interaction operates.

In contrast, there is a size effect in the interaction energy, as a consequence of the fact that here there is a *product* of two $\mathbf{k}$ sums. We invoke the BCS approximation for the interaction constant

$$V_{kk'}=V/a^3, \quad |\epsilon_k|, |\epsilon_{k'}|<\hbar\omega,$$
$$=0, \quad \text{otherwise.} \tag{6}$$

The factor a^{-3} in V/a^3 results from normalization of the one-electron orbitals in the cube of volume a^3. Thus V is the corresponding quantity in a sample of unit volume, in agreement with BCS notation. The interaction energy can now be written

$$-\sum_{kk'}V_{kk'}[h_k(1-h_k)h_{k'}(1-h_{k'})]^{1/2}(1-2f_k)(1-2f_{k'})$$
$$=-a^3V[\sum_{\nu}\chi(a\nu)]^2, \tag{7}$$

where we define

$$\chi(\mathbf{r})=(2\pi)^{-3}\int_{|\epsilon k|<\hbar\omega}[h_k(1-h_k)]^{1/2}(1-2f_k)$$
$$\times\exp(-i\mathbf{k}\cdot\mathbf{r})d^3k. \tag{8}$$

$\chi(\mathbf{r})$ is the antiparallel-spin electron-electron correlation function of the BCS theory. In other words, the joint probability (per unit volume squared) that an electron of spin-up occurs at $\mathbf{r}$ and an electron of spin-down at $\mathbf{r}'$ is[16]

$$n_{\uparrow\downarrow}(\mathbf{r},\mathbf{r}')=(n_0/2)^2+|\chi(\mathbf{r}-\mathbf{r}')|^2, \tag{9}$$

n_0 being the conduction-electron density. Since

$$[h_k(1-h_k)]^{1/2}(1-2f_k)$$

is a spherically symmetric function of $\mathbf{k}$, it follows that $\chi(\mathbf{r})$ is a spherically symmetric function of $\mathbf{r}$.

Since the integrand of (8) is restricted to the region of k space close to the Fermi surface, we can write the one-electron energy ϵ_k, measured with respect to the Fermi energy, as

$$\epsilon_k\cong\hbar v_F(k-k_F), \quad \text{for} \quad |k-k_F|\ll k_F. \tag{10}$$

Integrating, in (8), the factor $(2\pi)^{-3}d^3k\exp(-i\mathbf{k}\cdot\mathbf{r})$ over angles in k space, we get

$$4\pi(2\pi)^{-3}j_0(kr)k^2dk$$
$$\cong[j_0(k_Fr)\cos(\epsilon_kr/\hbar v_F)-j_1(k_Fr)\sin(\epsilon_kr/\hbar v_F)]N(0)d\epsilon_k, \tag{11}$$

where j_0 and j_1 are the spherical Bessel functions, and $N(0)$ is the density of one-electron states per unit energy, for a given spin, per unit volume of superconductor. Since

$$[h_k(1-h_k)]^{1/2}(1-2f_k)$$
$$=[\epsilon_{0k}/2(\epsilon_k^2+\epsilon_{0k}^2)^{1/2}]\tanh[\tfrac{1}{2}\beta(\epsilon_k^2+\epsilon_{0k}^2)^{1/2}] \tag{12}$$

is an *even* function of ϵ_k, when we multiply (11) by (12) and integrate with respect to ϵ_k, only the j_0 term on the right-hand side of (11) will contribute. Thus

$$\chi(r)=\left(\frac{\sin k_Fr}{k_Fr}\right)N(0)\int_0^{\hbar\omega}d\epsilon_k\cos\left(\frac{\epsilon_kr}{\hbar v_F}\right)$$
$$\times[\epsilon_{0k}/(\epsilon_k^2+\epsilon_{0k}^2)^{1/2}]\tanh[\tfrac{1}{2}\beta(\epsilon_k^2+\epsilon_{0k}^2)^{1/2}]. \tag{13}$$

We see that $\chi(\nu a)$ contains the factor

$$\sin(k_F\nu a)=\sin(2\pi\nu a/\lambda_F),$$

which oscillates rapidly as a function of a, since $a\gg\lambda_F$. As with the other terms in the free energy, we now average (7) with respect to these rapid oscillations, with the result

$$\langle\sum_{kk'}V_{kk'}[h_k(1-h_k)h_{k'}(1-h_{k'})]^{1/2}(1-2f_k)(1-2f_{k'})\rangle_{\mathrm{Av}}$$
$$=a^3(2\pi)^{-6}\int\int_{|\epsilon k|,|\epsilon k'|<\hbar\omega}d^3kd^3k'V_{kk'}^{\mathrm{eff}}$$
$$\times[h_k(1-h_k)h_{k'}(1-h_{k'})]^{1/2}(1-2f_k)(1-2f_{k'}), \tag{14}$$

where we have defined the effective interaction

$$V_{kk'}^{\mathrm{eff}}\equiv V\left[1+\sum_{\nu}{}'\frac{1}{(k_F\nu a)^2}\cos\left(\frac{\epsilon_k\nu a}{\hbar v_F}\right)\cos\left(\frac{\epsilon_{k'}\nu a}{\hbar v_F}\right)\right]. \tag{15}$$

The prime on the ν sum indicates that the $\nu=0$ term is missing. The scalar ν in the summand is the magnitude of the vector ν over which we are summing. This sum represents the correction to the BCS result. We see that the size effect modifies the free energy density only in that it influences the effective interaction $V_{kk'}^{\mathrm{eff}}$.

We choose the variational parameter

$$h_k\equiv\tfrac{1}{2}[1-\epsilon_k(\epsilon_k^2+\epsilon_{0k}^2)^{-1/2}] \tag{16}$$

such that it minimizes F. This leads to the integral equation

$$\epsilon_{0k}=N(0)\int_0^{\hbar\omega}V_{kk'}^{\mathrm{eff}}\tanh[\tfrac{1}{2}\beta(\epsilon_{k'}^2+\epsilon_{0k'}^2)^{1/2}]$$
$$\times[\epsilon_{0k'}/(\epsilon_{k'}^2+\epsilon_{0k'}^2)^{1/2}]d\epsilon_{k'}. \tag{17}$$

We wish to solve (17) for ϵ_{0k} at $k=k_F(\epsilon_k=0)$. As an approximation, we shall treat $\epsilon_{0k'}$ as independent of k' in the integrand on the right-hand side of (17), approximating $\epsilon_{0k'}$ by its value at the Fermi surface. Thus we get

$$[N(0)V]^{-1}=\int_0^{\hbar\omega}\tanh[\tfrac{1}{2}\beta(\epsilon^2+\epsilon_0^2)^{1/2}]\frac{d\epsilon}{(\epsilon^2+\epsilon_0^2)^{1/2}}$$
$$+\sum_{\nu}{}'\frac{1}{(k_F\nu a)^2}\int_0^{\infty}\cos\left(\frac{\epsilon\nu a}{\hbar v_F}\right)$$
$$\times\tanh[\tfrac{1}{2}\beta(\epsilon^2+\epsilon_0^2)][d\epsilon/(\epsilon^2+\epsilon_0^2)^{1/2}]. \tag{18}$$

Because of the cosine factor, large values of ϵ do not contribute appreciably to the second integral, so that

[16] See, e.g., L. N. Cooper, R. L. Mills, and A M. Sessler, Phys. Rev. 114, 1377 (1959).

we have made no appreciable error in replacing $\hbar\omega$, the correct upper limit, by infinity.

It can be shown that when a is comparable with, or greater than, the Pippard coherence distance ξ_0, then the primed ν series of (18) converges very rapidly. Because of the common factor

$$(k_F a)^{-2}=(\lambda_F/2\pi a)^2,$$

however, the total sum is negligibly small, compared with $[N(0)V]^{-1}$ at such values of a. It is only when a is made much smaller than ξ_0 (but still much larger than λ_F) that the primed ν sum becomes comparable with the other terms of (18). Under such conditions, the series converges, but very slowly. We therefore replace $\sum_\nu'$ by the corresponding integral $\int 4\pi\nu^2 d\nu$. Strictly speaking, we should set the lower limit of this integral so that the integration volume does not include a sphere of unit volume centered on the origin. This corresponds to the $\nu=0$ term not being present in $\sum_\nu'$. However, it can be checked that negligible error is made by setting the lower limit of $\int 4\pi\nu^2 d\nu$ equal to zero. Thus

$$[N(0)V]^{-1}=\int_0^{\hbar\omega}\tanh[\tfrac{1}{2}\beta(\epsilon^2+\epsilon_0^2)^{1/2}]\frac{d\epsilon}{(\epsilon^2+\epsilon_0^2)^{1/2}}+\pi^{-1}\left(\frac{\lambda_F}{a}\right)^2\int_0^\infty d\nu\int_0^\infty\frac{d\epsilon}{(\epsilon^2+\epsilon_0^2)^{1/2}}\cos\left(\frac{\epsilon\nu a}{\hbar v_F}\right)\times\tanh[\tfrac{1}{2}\beta(\epsilon^2+\epsilon_0^2)^{1/2}]. \tag{19}$$

Equation (19) is the desired final form of integral equation that allows us to determine the dependence of energy gap $2\epsilon_0$ and transition temperature T_c upon grain size a. We are especially fortunate in being able to evaluate analytically the necessary integrals in the two limiting cases $T=0$ and $T=T_c$. At $T=0$, we have

$$\begin{aligned}[N(0)V]^{-1}&=\int_0^{\hbar\omega}\frac{d\epsilon}{(\epsilon^2+\epsilon_0^2)^{1/2}}+\pi^{-1}\left(\frac{\lambda_F}{a}\right)^2\times\int_0^\infty d\nu\int_0^\infty\frac{d\epsilon}{(\epsilon^2+\epsilon_0^2)^{1/2}}\cos\left(\frac{\epsilon\nu a}{\hbar v_F}\right)\\&\cong\ln\left(\frac{2\hbar\omega}{\epsilon_0}\right)+\pi^{-1}\left(\frac{\lambda_F}{a}\right)^2\int_0^\infty d\nu K_0\left(\frac{\epsilon_0 a\nu}{\hbar v_F}\right)\\&=\ln\left(\frac{2\hbar\omega}{\epsilon_0}\right)+\tfrac{1}{2}\left(\frac{\lambda_F}{a}\right)^2\left(\frac{\hbar v_F}{\epsilon_0 a}\right).\end{aligned} \tag{20}$$

Let us define a characteristic length

$$L\equiv(\lambda_F^2\xi_0)^{1/3}, \tag{21}$$

where

$$\xi_0=(\hbar v_F/\pi\epsilon_{0\infty}) \tag{22}$$

is the $T=0$ Pippard coherence distance for the bulk superconductor. Here we are using the terminology $\epsilon_{0\infty}$ to denote the BCS value of ϵ_0 at $T=0$,

$$\epsilon_{0\infty}=2\hbar\omega\exp[-1/N(0)V]. \tag{23}$$

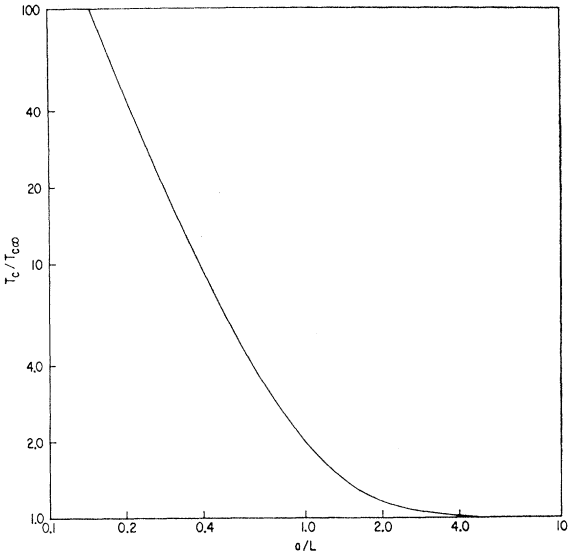

FIG. 1. $(T_c/T_{c\infty})$ versus (a/L) (see Ref. 17).

Now (20) can be rewritten as

$$\alpha\ln\alpha=\tfrac{1}{2}\pi(L/a)^3, \tag{24}$$

where

$$\alpha\equiv(\epsilon_0/\epsilon_{0\infty}) \tag{25}$$

represents the enhancement factor of the energy gap at $T=0$.

At $T=T_c$ where $\epsilon_0=0$, Eq. (19) becomes

$$\begin{aligned}[N(0)V]^{-1}&=\int_0^{\hbar\omega}\frac{d\epsilon}{\epsilon}\tanh(\tfrac{1}{2}\beta_c\epsilon)+\pi^{-1}(\lambda_F/a)^2\times\int_0^\infty d\nu\int_0^\infty\frac{d\epsilon}{\epsilon}\cos\left(\frac{\epsilon\nu a}{\hbar v_F}\right)\tanh(\tfrac{1}{2}\beta_c\epsilon)\\&=\ln(\tfrac{1}{2}\beta_c\hbar\omega)+\gamma+\ln(4/\pi)+\pi^{-1}(\lambda_F/a)^2\times\int_0^\infty d\nu\ln\coth\left(\tfrac{1}{4}\pi\frac{2a\nu}{\beta_c\hbar v_F}\right)\\&=\ln(\tfrac{1}{2}\beta_c\hbar\omega)+\gamma+\ln(4/\pi)+\pi^{-1}(\lambda_F/a)^2\times\left(\frac{\beta_c\hbar v_F}{\pi a}\right)\int_0^1\ln\left(\frac{1+y}{1-y}\right)\frac{dy}{y},\end{aligned} \tag{26}$$

where $\gamma=0.5772$ is Euler's constant. Let

$$\alpha'=(T_c/T_{c\infty}) \tag{27}$$

represent the enhancement factor of the transition temperature T_c over that of the bulk superconductor $T_{c\infty}$. Equation (26) can be rewritten as

$$\alpha'\ln\alpha'=\tfrac{1}{2}\pi(L/a)^3(C/4), \tag{28}$$

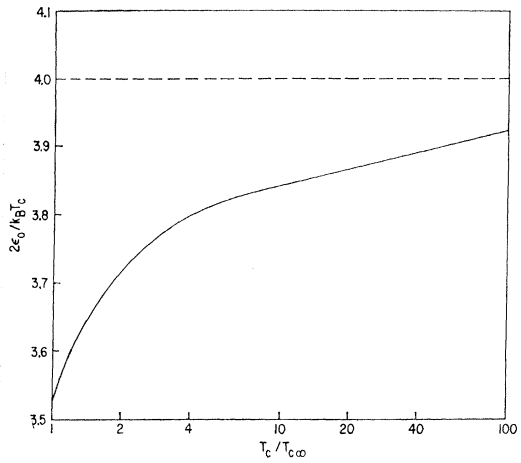

FIG. 2. $(2\epsilon_0/k_BT_c)$ versus $(T_c/T_{c\infty})$.

where

$$C\equiv(2\epsilon_{0\infty}/k_BT_{c\infty})=2\pi e^{-\gamma}=3.528 \tag{29}$$

is the BCS value of the ratio of energy gap at $T=0$ to Boltzmann's constant times transition temperature.

Note that (28) would be identical with (24) if it were not for the highly significant factor $C/4$. The energy gap at $T=0$ increases slightly more rapidly than does the transition temperature as the grain size is lowered. Whereas at very large a, the energy-gap–transition-temperature ratio is 3.528, at small a it increases toward 4. This is a direct consequence of Eqs. (24) and (28). But an energy-gap–transition-temperature ratio of 4 is characteristic of a strong-coupling superconductor.[13] The process of reducing the grain size in effect converts a weak-coupling superconductor into a strong-coupling superconductor.

When plotting in reduced coordinates the curves of energy gap versus temperature, one finds that the weak-coupling and strong-coupling cases lead to nearly identical curves.[13] This suggests that the same may hold true for the intermediate-coupling case being considered here. If so, one would not need to solve Eq. (19) at intermediate temperatures; one could infer the gap at a given temperature and grain size from (24) and (28) combined with the "universal" curve of reduced energy gap versus reduced temperature.

A plot of $\alpha'=(T_c/T_{c\infty})$ versus (a/L) is shown in Fig. 1. At $a=L$, T_c is approximately double $T_{c\infty}$. For $a<L$, T_c is roughly inversely proportional to the volume of the grain size. For $a>L$, T_c approaches $T_{c\infty}$ with approximately exponential dependence on the inverse of the grain volume.[17] A plot of $(2\epsilon_0/k_BT_c)$ versus α' is shown in Fig. 2. It can be seen that $(2\epsilon_0/k_BT_c)$ increases from the weak-coupling value of 3.528 toward the strong-coupling value of 4.

One of the most interesting results of the present calculation[18] is the prediction that the size effect on the transition temperature becomes important when the grain volume becomes comparable with

$$L^3=\lambda_F{}^2\xi_0. \tag{30}$$

As an example, in aluminum $L\cong 62$ Å. Such a critical size seems qualitatively consistent with the experimental results for aluminum.[4]

It is possible to modify the present theory in order to get a qualitative estimate of the quenching of size-effect enhancement as the coupling between grains is increased. This is especially easy in the case $a<L$, where the enhancement of free energy is inversely proportional to grain volume a^3. Consider the case of a barrier transmissivity t, appreciable in size but not too close to unity. This corresponds roughly to the situation where there is a *double* grain volume during a fraction t of the time. Thus we should use an effective grain size $\langle a\rangle$ given by

$$\langle a\rangle^{-3}=a^{-3}(1-t)+\tfrac{1}{2}a^{-3}t$$

or

$$\langle a\rangle^3=a^3(1-\tfrac{1}{2}t)^{-1}$$

When a and $\langle a\rangle$ are both less than L, T_c for finite t will be less than T_c for zero t by a factor $(1-\frac{1}{2}t)$.

In a very interesting recent letter,[19] Abeles *et al.* ruled out the mechanism of size-effect enhancement in their granular aluminum films because of the strength of the coupling between grains. For their films of maximum transmissivity, $L=62$ Å, $a=40$ Å, $t=0.4$, so that $\langle a\rangle=43$ Å. This shows that appreciable size-effect enhancement is still to be expected in these films.

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[17] L is just the grain size where the mean spacing (at the Fermi level) between one-electron energy levels becomes comparable with the bulk superconducting energy gap. Furthermore, for smaller grain sizes, the energy gap increases in step with the increasing spacing between one-electron levels.

[18] A calculation of size-effect enhancement of superconductivity has recently been carried out by E. A. Shapoval, Zh. Eksperim. i Teor. Fiz., Pis'ma v Redaktsiyu **5**, 57 (1967) [English transl.: Soviet Phys.—JETP Letters **5**, 45 (1967)]. Shapoval's enhancement, which sets in only at grain sizes much smaller than L, depends on an interaction enhancement due to one-electron wave-function renormalization. The normalization is affected by the fact that the one-electron orbitals damp out near the bounding surface of the grain (within distances comparable to λ_F).

[19] B. Abeles, R. W. Cohen, and W. R. Stowell, Phys. Rev. Letters **18**, 902 (1967).