Model of the Anisotropic Energy Gap in Superconducting Zinc*

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A simple model for the anisotropic energy gap in superconducting zinc is shown to be sufficient in describing microwave-absorption measurements. The value assigned to the energy gap near the c axis is uncertain because of the possibility of photon absorption occurring simultaneously with a diffuse scattering of quasiparticles at the surface.

I. INTRODUCTION

THE results of microwave-absorption measurements in single crystals of superconducting zinc suggest that the dominant energy gap is $2\Delta(t=T/T_c=0.5)=(3.0\pm0.1)kT_c$, whereas the energy gap near the c axis is much larger.[1] Noting the intersection of the free-electron Fermi surface with the second Brillouin zone of zinc, as in Fig. 1, one is led to assume that the larger energy gap is associated with the caps along the c axis. Farrell, Park, and Coles[2] have found it necessary to make the same assumption in explaining the effects of impurity doping on T_c, the superconducting transition temperature. In their calculation, a value of 37° was taken for θ_0, the polar angle which describes the intersection of the free-electron Fermi surface with the second Brillouin zone. In our calculation of the ratio of the surface resistance in the superconducting state to that in the normal state, $r\equiv R/R_n$, θ_0 is an adjustable parameter in the model for the anisotropic energy gap. A value for θ_0 can be determined which gives the best fit between the calculated and experimental surface-resistance ratios corresponding to different orientations of the microwave field to the zinc crystal.

II. CALCULATION

The minimum quasiparticle energy Δ_p for an electron of momentum $\mathbf{p}=\mathbf{p}(\theta,\phi)$ depends on the polar and azimuthal angles (θ,ϕ). In our model for the energy gap in zinc, we assume that Δ_p is constant and equal to Δ_c for $0\leq\theta\leq\theta_0$. For $\theta_0\leq\theta\leq\pi/2$, Δ_p is constant and equal to Δ_a. The magnitudes for Δ_c and Δ_a are fixed by the thresholds in the microwave-absorption experiments.[1]

The expression for the surface-resistance ratio will depend on whether or not photon absorption occurs simultaneously with a diffuse scattering of quasiparticles at the surface of the metal. For the latter case, A, in which momentum is conserved in the photon absorption, Clem[3] and Nam[4] have given expressions for R/R_n in the extreme anomalous limit. Since the photon momentum for microwaves is much less than the Fermi momentum, the final-state electron momentum for photon absorption is set equal to the initial-state momentum. For the former case, B, in which momentum is not conserved in the photon absorption (the direction of electron momentum is randomized by a diffuse scattering at the sample surface), Garfunkel[5] has discussed the calculation of R/R_n as it applies to considering the effect of a magnetic field. Here the final- and initial-state electron momenta are unrelated. We have calculated R/R_n for the two cases, based on the above model for the energy gap. The density of electron states in the normal state is assumed to be isotropic over the Fermi surface.

A. Initial- and Final-State Electron Momenta Equal

The extreme anomalous limit (Pippard limit) for superconductors occurs for $\lambda/\xi_0\ll1$ where λ is the superconducting penetration depth and ξ_0 is the coherence length. In this limit and assuming momentum is conserved in the photon absorption, the surface-resistance ratio is given by[3]

$$R/R_n=\mathrm{Re}\{(1+i\sqrt{3})[(\sigma_{s1}/\sigma_n)-i(\sigma_{s2}/\sigma_n)]^{-1/3}\},$$

where

$$\frac{\sigma_{s1,2}}{\sigma_n}=\pi^{-1}\int d\Omega\,(\hat{p}\cdot\hat{E}_\mu)^2\delta(\hat{p}\cdot\hat{q})\sigma_{1,2}(\Delta_p,\omega),$$

and

$$\sigma_1(\Delta_p,\omega)=\omega^{-1}\int_{-\infty}^{+\infty}d\omega'[f(\omega')-f(\omega'')]\times\left[\mathrm{Re}\left(\frac{\omega'}{(\omega'^2-\Delta_p^2)^{1/2}}\right)\mathrm{Re}\left(\frac{\omega''}{(\omega''^2-\Delta_p^2)^{1/2}}\right)+\mathrm{Re}\left(\frac{\Delta_p}{(\omega'^2-\Delta_p^2)^{1/2}}\right)\mathrm{Re}\left(\frac{\Delta_p}{(\omega''^2-\Delta_p^2)^{1/2}}\right)\right];\quad(1a)$$

$$\sigma_2(\Delta_p,\omega)=\omega^{-1}\int_{-\infty}^{+\infty}d\omega'\,[1-2f(\omega'')]\times\left[\mathrm{Im}\left(\frac{\omega'}{(\omega'^2-\Delta_p^2)^{1/2}}\right)\mathrm{Re}\left(\frac{\omega''}{(\omega''^2-\Delta_p^2)^{1/2}}\right)+\mathrm{Im}\left(\frac{\Delta_p}{(\omega'^2-\Delta_p^2)^{1/2}}\right)\mathrm{Re}\left(\frac{\Delta_p}{(\omega''^2-\Delta_p^2)^{1/2}}\right)\right].\quad(1b)$$

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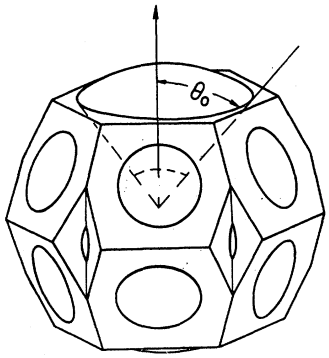

FIG. 1. Intersection of the second Brillouin zone of zinc with the free-electron Fermi surface of two electrons/atom [after Farrell *et al.* (Ref. 2)].

It is understood that $\omega''=\omega+\omega'$, $f(\omega')$ is the Fermi function, $[1+\exp(\omega'/kT)]^{-1}$, and $\hat{p}$, $\hat{q}$, and $\hat{E}_\mu$ are unit vectors in the direction of electron momentum, photon momentum, and microwave electric field, respectively. The δ function $\delta(\hat{p}\cdot\hat{q})$ indicates that effective electrons for photon absorption are those which move parallel to the surface of the metal.

Calculations of the complex conductivity have been made for three crystal orientations, relative to the microwave field, with the parameters of θ_0, $2\Delta_a(0.5)=3.0kT_c$ and $2\Delta_c(0.5)=3.9kT_c$.[1] Since the model has only two angular regions for which the energy gap differs, one can separate each of the integrals for σ_{s1}/σ_n and σ_{s2}/σ_n into, at the most, two parts.

For a sample orientation in which the c axis is parallel to $\mathbf{q}$ (perpendicular to sample plane), we find that

$$\sigma_{s1,2}/\sigma_n=\sigma_{1,2}(\Delta_a,\omega). \tag{2}$$

For the c axis perpendicular to $\mathbf{q}$ and parallel to $\mathbf{E}_\mu$, we find that

$$\frac{\sigma_{s1,2}}{\sigma_n}=\frac{4}{\pi}\int_0^{\theta_0}\cos^2\phi\,\sigma_{1,2}(\Delta_c,\omega)\,d\phi+\frac{4}{\pi}\int_{\theta_0}^{\pi/2}\cos^2\phi\,\sigma_{1,2}(\Delta_a,\omega)\,d\phi. \tag{3}$$

Similarly, for the c axis perpendicular to both $\mathbf{q}$ and $\mathbf{E}_\mu$

$$\frac{\sigma_{s1,2}}{\sigma_n}=\frac{4}{\pi}\int_{\pi/2-\theta_0}^{\pi/2}\cos^2\phi\,\sigma_{1,2}(\Delta_c,\omega)\,d\phi+\frac{4}{\pi}\int_0^{\pi/2-\theta_0}\cos^2\phi\,\sigma_{1,2}(\Delta_a,\omega)\,d\phi. \tag{4}$$

For $t=0$, we have calculated the surface-resistance ratios from the conductivity expressions of Eqs. (2)–(4) for θ_0 values of 25°, 30°, and 35°. As discussed below, we find that a reasonable fit of the calculated to the corresponding experimental curves can be made for $\theta_0=(30\pm5)°$. Figure 2 compares the experimental and calculated surface-resistance ratios where $t=0.5$ and $\theta_0=30°$. $\sigma_{1,2}(\Delta_p,\omega)$ for $t=0.5$ was obtained from a tabulation by Waldram.[6]

The calculated curves lie below the experimental curves because the calculation was made in the extreme anomalous limit. Miller[7] has calculated r for finite λ/ξ_0.

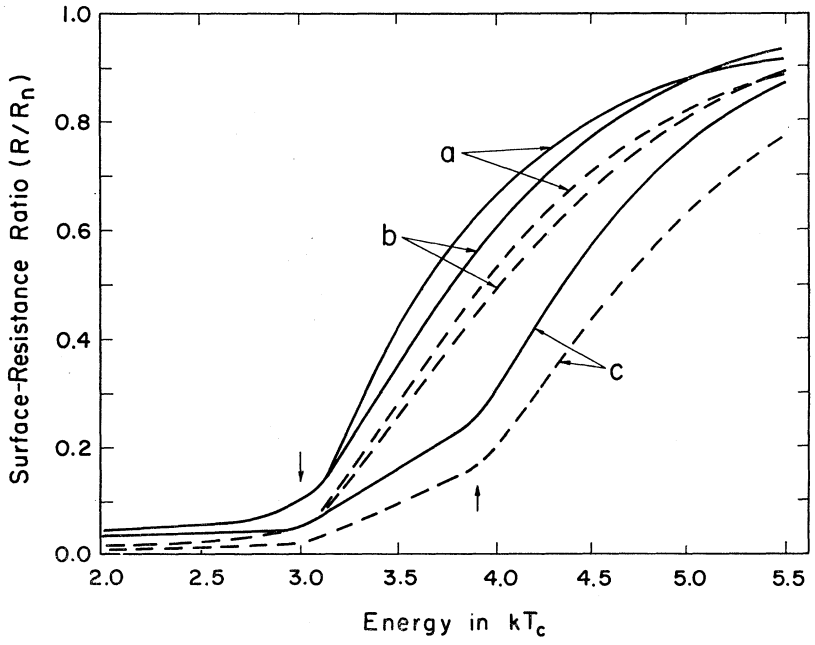

FIG. 2. Surface-resistance ratio for zinc at $t=0.5$ as a function of photon energy in units of kT_c, k being the Boltzmann constant. The experimental results (solid lines) are compared with the theory (dashed lines) for (a) the c axis parallel to $\mathbf{q}$ (perpendicular to the sample plane), (b) c axis perpendicular to both $\mathbf{q}$ and $\mathbf{E}_\mu$, and (c) c axis perpendicular to $\mathbf{q}$ but parallel to $\mathbf{E}_\mu$.

[6] J. R. Waldram, Royal Society Mond Laboratory, Cambridge University, Cambridge, England, 1963 (unpublished).
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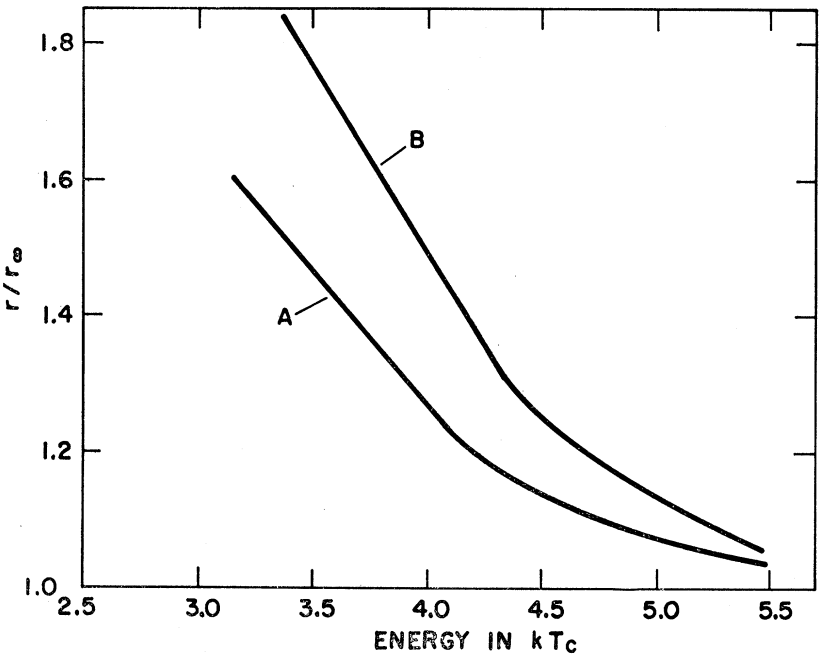

FIG. 3. Ratio r/r_∞ as a function of photon energy where r is the experimental surface-resistance ratio for $\mathbf{q}$ parallel to the c axis and r_∞ is the surface-resistance ratio calculated in the extreme anomalous limit. For the curves A(B), r_∞ was calculated for the initial- and final-state electron momenta equal (unrelated) in the photon absorption.

For aluminum, where λ/ξ_0 is 0.03, the ratio of r to r_∞ (r calculated in the extreme anomalous limit) is approximately 1.3 for photon energies near the energy gap. Since we estimate λ/ξ_0 for zinc to be near 0.03, we expect r/r_∞ for zinc and aluminum to be comparable.

Curve A of Fig. 3 displays the ratio r/r_∞ for zinc where r is the experimental surface-resistance ratio for $\hat{q}$ parallel to the c axis and r_∞ is the surface-resistance ratio calculated in the extreme anomalous limit for the same crystal orientation. The curve is somewhat higher than one expects from theory, unless our estimate for λ/ξ_0 is too low.[7]

In determining the value of θ_0 which gives the best fit of the calculated to the experimental surface-resistance ratios, we have formed differences in R/R_n for three crystal orientations. The upper experimental (solid) and calculated (dashed) curves of Fig. 4, (*a-c*), correspond to the difference between R/R_n for: (a)

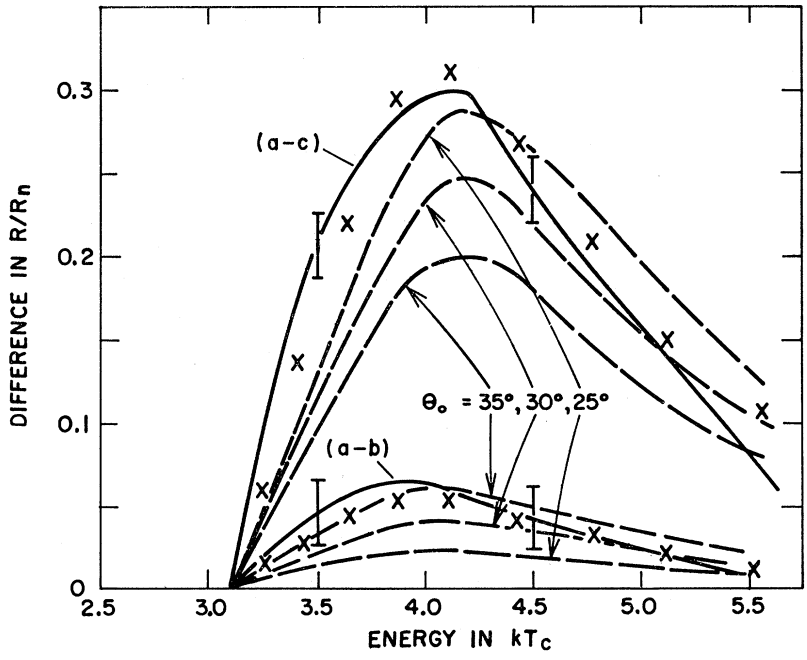

FIG. 4. Difference in the surface-resistance ratios, for $t=0$, as a function of photon energy. The upper experimental (solid) and calculated (dashed) curves, (*a-c*), represent the difference between R/R_n for: (a) the c axis parallel to $\mathbf{q}$ and (c) c axis perpendicular to $\mathbf{q}$ but parallel to $\mathbf{E}_\mu$. The lower curves, (*a-b*), represent the difference between R/R_n for: (a) c axis parallel to $\mathbf{q}$, and (b) c axis perpendicular to $\mathbf{q}$ and $\mathbf{E}_\mu$. The calculated curves are based on the model, A, in which the initial- and final-state electron momenta are equal in the photon absorption. The curves denoted by the crosses were obtained by multiplying the calculated curves of $\theta_0=30°$ by the factor r/r_∞ of Fig. 3, curve A.

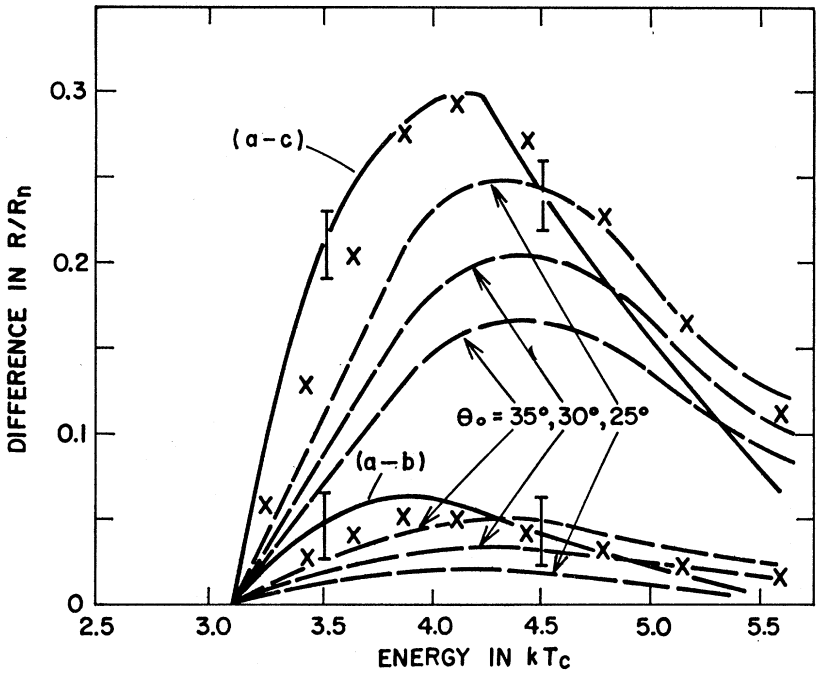

FIG. 5. Difference in the surface-resistance ratios for $t=0$. Same as Fig. 4 except the calculated curves are based on the model, B, in which the initial- and final-state electron momenta are unrelated. Curve B of Fig. 3 was used to obtain the curve denoted by crosses.

c axis parallel to $\mathbf{q}$, and (c) c axis perpendicular to $\mathbf{q}$ but parallel to $\mathbf{E}_\mu$. The lower curves, (a-b), correspond to the difference between R/R_n for: (a) c axis parallel to $\mathbf{q}$, and (b) c axis perpendicular to $\mathbf{q}$ and $\mathbf{E}_\mu$. We have assumed that the differences in the experimental R/R_n for $t=0.5$ are nearly the same for $t=0$. The calculated curves of Fig. 4 need to be corrected by the ratio r/r_∞ obtained from curve A of Fig. 3. Applying the correction to the curves calculated for $\theta_0=30°$, we obtain the curves denoted by the crosses. The fit to the experimental curves is reasonably good for $\theta_0=(30\pm5)°$.

B. Initial- and Final-State Electron Momenta Unrelated

It is of interest to consider the possibility of photon absorption occurring simultaneously with diffuse scattering of quasiparticles at the surface of the metal.[5] We consider two groups of quasiparticles that contribute to the absorption: (1) those which are initially moving nearly parallel to the surface and then scatter into any direction within the metal, and (2) those which are initially moving toward the surface in any direction and then scatter into a direction nearly parallel with the surface. One might expect Eqs. (1a) and (1b) to be modified such that for the first (second) group of quasiparticles, $\cos\theta_0$ (normalized solid angle) of the final- (initial-) state terms would be associated with Δ_a and $(1-\cos\theta_0)$ would be associated with Δ_c. The results of calculating R/R_n, for $t=0$, for different values of θ_0 are qualitatively the same as our previous calculation except now the upper threshold of Fig. 2 corresponds to $\omega=\Delta_a+\Delta_c$. This implies that $2\Delta_a(0)=3.1kT_c$ and $2\Delta_c(0)=4.9kT_c$.

In Fig. 5, we display curves of differences in R/R_n calculated from the above model. Applying the correction r/r_∞ of curve B in Fig. 3 to the curves calculated for $\theta_0=30°$, we obtain the curves denoted by the crosses. We note that the fit is reasonable, although it could be improved by choosing a somewhat smaller value for Δ_c.

III. DISCUSSION

From the anisotropic energy gap model one can calculate the results of other experiments on superconducting zinc. We compare other experimental results with the energy-gap model of case A, i.e., $2\Delta_a(0)=3.1kT_c$ and $2\Delta_c(0)=4.0kT_c$ and case B, i.e., $2\Delta_a(0)=3.1kT_c$ and $2\Delta_c(0)=4.9kT_c$.

Zemon and Boorse[8] have measured the microwave absorption of polycrystalline zinc and find an energy gap of $(3.01\pm0.09)kT_c$. From tunneling experiments with zinc films, Donaldson[9] finds an average gap of $(3.2\pm0.1)kT_c$. Averaging the experimental curves of Fig. 2, we expect an energy gap of $2\Delta_{av}(0)=(3.1\pm0.1)kT_c$ for a polycrystalline sample. Assuming that R_n is not highly anisotropic, we can compare the average of the three experimental curves of Fig. 2 with the polycrystalline measurements. The average of the three experimental curves of Fig. 2 is closely represented by R/R_n calculated in the extreme anomalous limit, just as Zemon and Boorse[8] found with their polycrystalline data.

Farrell *et al.*,[2] and Boato, Gallinaro, and Rizzuto[10]

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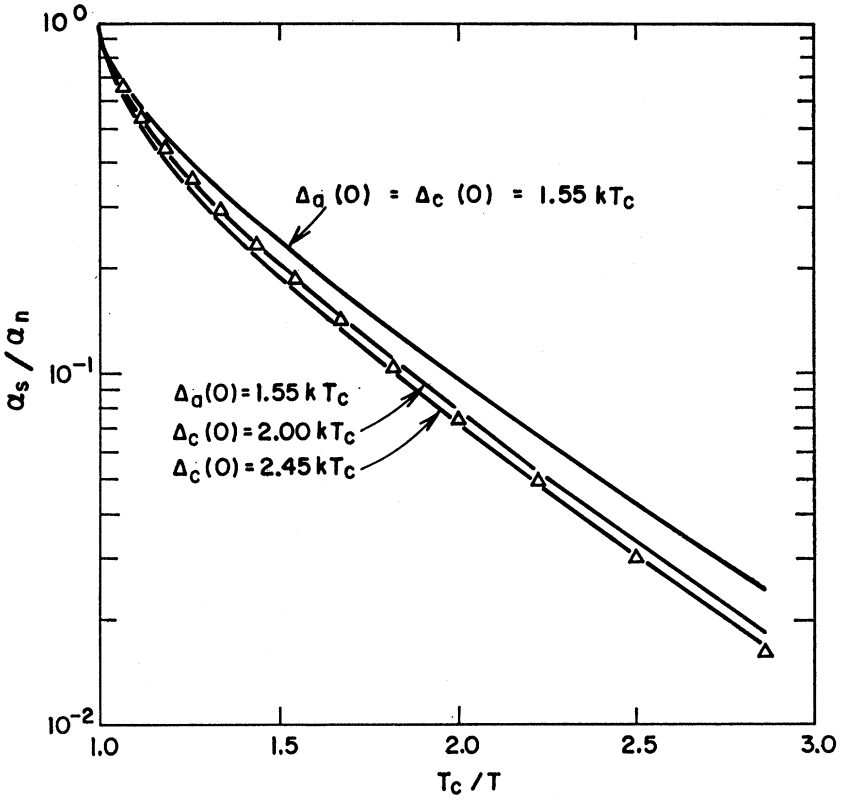

FIG. 6. $\ln(\alpha_s/\alpha_n)$ versus T_c/T where α_s/α_n is given by Eq. (6). Curves labeled $\Delta_c(0)=2.00kT_c$ and $2.45kT_c$ are based on the energy-gap models of cases A and B, respectively, for sound propagation in the basal plane. Both curves are reasonably approximated by the curve denoted by triangles which is based on an isotropic energy gap of $2\Delta(0)=3.4kT_c$. For sound propagation parallel to the c axis, the upper solid curve of $\Delta_a(0)=\Delta_c(0)=1.55kT_c$ is expected for both models.

have measured T_c of zinc as a function of nonmagnetic impurity doping. From the theory of Markowitz and Kadanoff,[11] one can determine a mean-squared anisotropy parameter which is defined as

$$\langle a^2\rangle \equiv \langle(\Delta_p - \langle\Delta_p\rangle_{av})^2\rangle_{av}/\langle\Delta_p\rangle_{av}^2, \quad (5)$$

where the averages are over the Fermi surface.

For zinc, $\langle a^2\rangle$ is experimentally determined to be 0.05 which is large compared with a typical superconductor, i.e., 0.01–0.02. From our models, we calculate $\langle a^2\rangle$ as 0.009 for case A and 0.033 for case B.

Farrell *et al.*,[2] have also determined the change in T_c due to a change in electron concentration while keeping the impurity level fixed. Since the change in T_c was found to be strongly dependent on electron concentration, a model for the energy gap was assumed which is similar to the model considered here. From their results, one can calculate the ratio of the energy gap $2\Delta_c$ to $2\Delta_a$ which provides the required dependence of T_c on electron concentration. This ratio is approximately 1.6 which is in reasonably good agreement with our ratio of case B.

From ultrasonic attenuation measurements, Bohm and Horwitz[12] have determined energy gaps of $(3.8\pm0.2)kT_c$ and $(3.4\pm0.2)kT_c$ for longitudinal propagation along $[\bar{1}210]$ and $[10\bar{1}0]$, respectively. Measurements by Lea and Dobbs[13] give $(3.64\pm0.1)kT_c$ for $[\bar{1}210]$, $(3.79\pm0.1)kT_c$ for $[10\bar{1}0]$, and $(3.41\pm0.1)kT_c$ for $[0001]$ or the c axis. Our model for the two cases would predict an energy gap near $3.1kT_c$ for propagation along $[0001]$ since only the thermal excitations in the plane perpendicular to the sound propagation are effective in the attenuation. For propagation in the basal plane, the attenuation will be determined by some weighted average of energy gaps in the plane perpendicular to the sound propagation. Claiborne and Einspruch[14] in ultrasonic studies of tin have introduced an expression for the ratio of attenuation in the superconducting state to that in the normal state, α_s/α_n, which describes the effect of multiple energy gaps on the attenuation. For our models of two energy gaps their expression becomes

$$\alpha_s/\alpha_n = A_a[1+e^{\Delta_a(t)/kT}]^{-1} + A_c[1+e^{\Delta_c(t)/kT}]^{-1}, \quad (6)$$

where $A_a+A_c=2$. We have calculated α_s/α_n for $A_a=\frac{4}{3}$, $A_c=\frac{2}{3}$ (based on $\theta_0=30°$), $\Delta_a(t)=1.55kT_c[\Delta(t)/\Delta(0)]$, $\Delta_c(t)=2.00kT_c[\Delta(t)/\Delta(0)]$ for case A, and $\Delta_c(t)=2.45kT_c[\Delta(t)/\Delta(0)]$ for case B. The analytic expression for $[\Delta(t)/\Delta(0)]$ was obtained from Clem.[3] Figure

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6 is a plot of $\ln(\alpha_s/\alpha_n)$ versus T_c/T for sound propagation in the basal plane. We have included the curves corresponding to the isotropic energy gaps of $2\Delta(0) = 3.1kT_c$ (upper solid) and $3.4kT_c$ (triangles) for comparison with the curves calculated from the two models. We find that the curves based on our models lie between the isotropic energy gap curves of 3.3 and $3.5kT_c$, the best fit being $3.4kT_c$. We note that the anisotropy observed by Lea and Dobbs[13] is approximately $0.3kT_c$, the approximate anisotropy expected from our models.

We have not compared the results of our two models with electronic specific heat and thermal conductivity measurements. However, such measurements on zinc indicate that the anisotropy in the energy gap is expected to be larger than in most superconductors.

IV. CONCLUSION

We find that microwave-absorption measurements in superconducting zinc can be described by a simple model for the anisotropic energy gap. The minimum quasiparticle energy, Δ_p, for an electron of momentum $\mathbf{p}=\mathbf{p}(\theta,\phi)$ is taken to be constant and equal to Δ_c for $0\leq\theta\lesssim\pi/6$. For $\pi/6\lesssim\theta\leq\pi/2$, Δ_p is constant and equal to $\Delta_a(0)=1.55kT_c$. The magnitude of Δ_c depends on whether or not one assumes that photon absorption occurs simultaneously with a diffuse scattering of quasiparticles at the surface of the metal. For the latter case, A, in which the initial- and final-state electron momenta are equal, $\Delta_c(0)=2.00kT_c$. For the former case, B, in which the initial- and final-state electron momenta are unrelated $\Delta_c(0)=2.45kT_c$.

We have compared our models for the anisotropic energy gap with the energy gaps obtained from measurements of various superconducting properties. Reasonable agreement is obtained but we are not able to decide, based on the present measurements, which of our models is correct. Tunneling experiments with single crystals should be decisive in determining the correct model and, therefore, the nature of photon absorption.

We would like to emphasize that our models are undoubtedly an oversimplification of the true anisotropic energy gap. The models are based on microwave-absorption measurements for which the angular averages involved can obscure any complicated variation of the energy gap. In view of this, our models are only descriptive of the gross features for the anisotropic energy gap.

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Superconducting Tunneling in Single-Crystal and Polycrystal Films of Aluminum*

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The energy gap (2Δ) and transition temperature (T_c) of aluminum films in Al-insulator-M tunnel junctions was measured. The orientation and crystallite size of the aluminum film was changed for different tunnel junctions by changing the substrate and/or substrate temperature at evaporation. The second metal (M) was either aluminum or indium. It was found that the strain on the aluminum film due to differential thermal expansion could account for most of the osberved variation in T_c. If M was indium, both 2Δ and T_c were changed. Empirically, it was found that T_c was increased by 3.2% and 2Δ was decreased by 3.3% owing to the indium film. This effect is not understood. The energy gaps of the aluminum films were $3.64kT_c$ for tunneling in the [100] direction, $3.52kT_c$ for tunneling in "isotropic" material, and $3.41kT_c$ for tunneling in the [111] direction. This anisotropy is in approximate agreement with theoretical predictions.

I. INTRODUCTION

ELECTRON tunneling between aluminum films and other metals has been extensively studied for the past several years, since aluminum films easily oxidize to form a tunneling barrier. However, with few exceptions, the characteristics of the aluminum films have not been studied in detail. Blackford and March[1] report the most extensive study of aluminum films and show that the gap ratio $2\Delta_0/kT_c$ for aluminum in Al-Al tunnel junctions on glass and quartz substrates is 3.53, the predicted weak-coupling value. In contrast to that experiment, most other measurements of the gap ratio in aluminum[2–4] have been made on Al-M tunnel junc-

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