effect of the free surface of the experimental specimen must be eliminated either geometrically or by an appropriate coating of normal metal.[19]

[19] L. J. Barnes and H. J. Fink, Phys. Letters **20**, 583 (1966); J. P. Hurault, *ibid.* **20**, 587 (1966). In the paper by Hurault it is shown that for a normal metal N deposited on a superconductor S with perfect electrical contact, $H_{11}>H_{c2}$ only if the conductivity σ_N of N is smaller than the normal-state conductivity σ_S of S.

So far as I know, Hurault's paper is the only calculation prior to mine of the nucleation field of an internal phase boundary. The physical situation considered by Hurault is, however, quite different from that considered here. One expects the sheath at an NS phase boundary with perfect transmissivity to be one dimensional (no fluxoids at the boundary), hence ψ may be assumed real without the vector potential becoming discontinuous at the phase boundary. Furthermore, the temperature T is necessarily distant from the critical temperature of at least one of the two metals, so that one may not argue that ψ in the bulk varies slowly over the range of the kernel in Gorkov's integral equation for the nucleation field. The field dependence of the logarithmic derivative of ψ at the boundary in Hurault's problem is due to the extremely rapid exponential variation of ψ in N near the barrier for large H. There is of course no question of this occurring in the tunneling-barrier problem near T_c, in which ψ varies slowly on both sides of the barrier.

The critical-field ratio H_{11}/H_{c2} calculated by Hurault is strongly temperature-dependent, but his curves are concave up in the Ginzburg-Landau region of the superconductor, in contrast to our Fig. 2.

Since H_{11}/H_{c2} is especially sensitive to temperature very close to T_c, it might seem that measurements in this temperature range will be the most crucial test of the validity of our theory. For this reason one should choose material with a narrow transition width. However, we must sound a warning: If the composition of the metal near the barrier differs from that of the bulk, it may have a slightly different critical temperature, in which case it is possible that our results may not be strictly applicable for temperatures extremely close to T_c. For any given alloy system, it would be wise to choose a composition at which T_c has an extremum, so that small variations in composition will not appreciably affect T_c.

We wish to point out that the effect we have predicted may be useful as a tool for the experimental investigation of the electronic properties of grain boundaries in polycrystalline metal.

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Impurity Dependence of the Critical Field in Anisotropic Superconductors*

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The effect of anisotropy of the superconducting energy-gap parameter upon the critical field H_c when nonmagnetic impurities are present is theoretically examined. Gap anisotropy is shown to produce corrections, of the order of the mean-squared anisotropy $\langle a^2\rangle$, to the isotropic-gap values of H_c. With an anisotropic BCS-like model introduced by Markowitz and Kadanoff, the reduction of these corrections as impurities are added is calculated. An upward shift in the value of $H_0^2/8\pi\gamma T_c^2$ and in the curve of $h=H_c/H_0$ vs $t=T/T_c$ results when impurities are added to an anisotropic, moderately weak-coupling superconductor. Expressions for these shifts are given.

I. INTRODUCTION

THE presence of anisotropy of the superconducting energy-gap parameter has many interesting effects upon the properties of superconductors. One way to observe these effects is to add nonmagnetic impurities to pure superconducting crystals and measure certain properties as a function of the impurity concentration. If these properties depend upon gap anisotropy, then they will change in a theoretically predictable way as the scattering produced by the impurities reduces the effect of the anisotropy. An example of this kind of experiment is the behavior of the critical temperature as a function of impurity concentration,[1–4] which has been treated theoretically by a number of authors,[5–11] in

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particular by Markowitz and Kadanoff.[12] Another example of this kind of experiment, and one which forms the topic for the present paper, is the behavior of the critical field as a function of impurity concentration.[13]

The effect of anisotropy upon critical-field curves, as was shown by the author[14] with the use of a simple BCS-like model for the anisotropy, is to introduce corrections of order $\langle a^2\rangle$ to each of the relevant quantities H_0, T_c, and $h=H_c/H_0$ versus $t=T/T_c$. The quantity $\langle a^2\rangle$, called the mean-squared anisotropy, may be defined in terms of the Fermi-surface average of the square of the deviation of the gap parameter Δ_p from its average value in the absence of impurities:

$$\langle a^2\rangle \equiv \langle(\Delta_p-\langle\Delta_p\rangle_{\rm av})^2\rangle_{\rm av}/\langle\Delta_p\rangle_{\rm av}^2\,, \tag{1}$$

and is a small quantity (typically, $\langle a^2\rangle\approx 0.02$) for most superconductors.[12] As impurities are added, the resulting scattering reduces the magnitude of the anisotropic part of the gap parameter,[15] which in turn causes the small $\langle a^2\rangle$ corrections to disappear. It is the purpose of this work to investigate and describe this reduction of the anisotropy effect upon the superconducting critical field as nonmagnetic impurities are added.

In Sec. II we shall perform a calculation of the impurity dependence of the anisotropy effect for a simple model of an anisotropic weak-coupling superconductor. We shall study first the behavior of the gap parameter and then that of the critical field to derive a function, $X_H(t,\lambda)$, of the reduced temperature and impurity concentration which describes the effectiveness of anisotropy corrections. In Sec. III we shall discuss in terms of $X_H(t,\lambda)$ the expected behavior of the experimentally measurable quantities.

II. CALCULATION OF THE CRITICAL FIELD

A. Impurity Dependence of the Gap Parameter

In order to perform a calculation of the critical field, we choose to study the model of a weak-coupling superconductor for which the BCS effective electron-electron matrix element[16] has the separable form,[12,14,15] $V_{pp'}=(1+a_p)V(1+a_{p'})$, where a_p is an anisotropy function chosen to have zero average over the Fermi surface. The anisotropic energy-gap parameter $\Delta(\mathbf{p},z)$ (as a function of the wave vector $\mathbf{p}$ and complex energy z in the upper half plane) can be obtained from the equation[12,15]

$$\Delta(\mathbf{p},z)=\epsilon_0(1+a_p)+\frac{i}{2\tau_a}\left\langle\frac{\Delta(\mathbf{p}',z)-\Delta(\mathbf{p},z)}{[z^2-\Delta^2(\mathbf{p}',z)]^{1/2}}\right\rangle_{\rm av}'\,. \tag{2}$$

Here, $\tau_a=(n_I v_F\sigma)^{-1}$ depends upon the density n_I of impurities, the Fermi velocity v_F, and the electron-impurity cross section σ (here assumed to be isotropic). The primed angular bracket refers to the averaging of $\mathbf{p}'$, rather than $\mathbf{p}$, over the Fermi surface. The quantity ϵ_0 must be determined self-consistently from Eq. (2) and[12,15]

$$\epsilon_0=\tfrac{1}{2}N_0V\,{\rm Re}\int_{-\omega_D}^{\omega_D}dz\left\langle(1+a_p)\frac{\Delta(\mathbf{p},z)}{[z^2-\Delta^2(\mathbf{p},z)]^{1/2}}\right\rangle_{\rm av}\times\tanh\tfrac{1}{2}\beta z\,. \tag{3}$$

Here, N_0 is the average density of states per unit energy of one spin at the Fermi level, $\beta=(kT)^{-1}$ where T is the temperature, and ω_D is a cutoff of the order of the Debye energy.

To obtain the effect of the impurity scattering upon ϵ_0, it is convenient to deform the integration contour such that it makes an arc from $-\omega_D$ to $i\omega_D$, runs down along the left side of the imaginary axis to the origin, runs back up along the right side of the imaginary axis to $i\omega_D$, then makes another arc to ω_D. With the neglect of the great-circle contribution this yields

$$1=2N_0V\sum_{\text{odd }\nu=1}^{\nu_D}\{(\nu^2+x)^{-1/2}+\langle a^2\rangle[\nu^4/(\nu^2+x)^2((\nu^2+x)^{1/2}+\lambda/t)-\nu^2x/2(\nu^2+x)^{3/2}((\nu^2+x)^{1/2}+\lambda/t)^2]\}\,, \tag{4}$$

where ν is an odd integer, $\nu_D\approx\beta\omega_D/\pi$, $x=[\beta\epsilon_0/\pi]^2$, $\lambda=(2\pi kT_c\tau_a)^{-1}$, and $t=T/T_c$. We have made use of

$$(i\pi/\beta\epsilon_0)\langle(1+a_p)\Delta(\mathbf{p},z_\nu)/[z_\nu^2-\Delta^2(\mathbf{p},z_\nu)]^{1/2}\rangle_{\rm av}=(\nu^2+x)^{-1/2}+\langle a^2\rangle[\nu^4/(\nu^2+x)^2((\nu^2+x)^{1/2}+\lambda/t)-\nu^2x/2(\nu^2+x)^{3/2}((\nu^2+x)^{1/2}+\lambda/t)^2]\,, \tag{5}$$

where $z_\nu=i\pi\nu/\beta$, which can be obtained from Eq. (2) as described in Ref. 14 by expanding in powers of the anisotropy function and keeping terms through order $\langle a^2\rangle\equiv\langle a_p^2\rangle_{\rm av}$.

At the critical temperature, Eq. (4) becomes

$$1=2N_0V\sum_{\text{odd }\nu=1}^{\nu_{Dc}}[\nu^{-1}+\langle a^2\rangle(\nu+\lambda)^{-1}]\,, \tag{6}$$

where $\nu_{Dc}\approx\beta_c\omega_D/\pi$. Since

$$2\sum_{\text{odd }\nu=1}^{\nu_{Dc}}\nu^{-1}=\ln 2\gamma_e\nu_{Dc}+O(\nu_{Dc}^{-1})\,, \tag{7}$$

where $\gamma_e=1.78107\cdots$, Eq. (6) yields in the weak-coupling limit

$$kT_c=(2\gamma_e\omega_D/\pi)\exp(-1/N_0V)(1+\langle a^2\rangle X_c)\,, \tag{8}$$

where

$$X_c(\lambda)=2\sum_{\text{odd }\nu=1}^{\nu_{Dc}}(\nu+\lambda)^{-1}\,. \tag{9}$$

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The function X_c describes the effectiveness of the anisotropy upon the critical temperature as a function of the impurity concentration. For small λ it obeys

$$X_c(\lambda)=1/N_0V-\tfrac{3}{2}\zeta(2)\lambda+(7/4)\zeta(3)\lambda^2+\cdots, \quad (10)$$

where ζ is the Riemann zeta function, and for $\lambda\gg\nu_{Dc}$ (or $2\omega_D\tau_a\ll1$) it obeys

$$X_c(\lambda)\approx\ln[1+(2\omega_D\tau_a)]. \quad (11)$$

It is related to the function I_c introduced by Markowitz and Kadanoff[12] via $X_c=1/N_0V-|I_c|$. We note that additional valence effects upon the critical temperature enter through the variation of ω_D, N_0, and V as a function of the impurity concentration.

By subtracting Eq. (6) from Eq. (4) we obtain

$$\begin{aligned}\ln t^{-1}=2\sum_{\text{odd }\nu=1}^{\nu_D}[\nu^{-1}-(\nu^2+x)^{-1/2}]+\langle a^2\rangle X_c\\ -2\langle a^2\rangle\sum_{\text{odd }\nu=1}^{\nu_D}\{\nu^4/[(\nu^2+x)^{1/2}+\lambda/t]\\ -\nu^2x/2(\nu^2+x)^{3/2}[(\nu^2+x)^{1/2}+\lambda/t]^2\}. \quad (12)\end{aligned}$$

This equation is to be regarded as determining $x=[\beta_c\epsilon_0(t)/\pi t]^2$ for a given reduced temperature t as a function of $\langle a^2\rangle$ and λ. We now wish to expand in powers of $\langle a^2\rangle$. Let us introduce the quantity $X_G(t,\lambda)$ via

$$\epsilon_0(t,\lambda)/kT_c=[1-\langle a^2\rangle X_G(t,\lambda)]\epsilon_0{}^0(t)/kT_c{}^0, \quad (13)$$

where the superscript "0" denotes the value of a given quantity if $\langle a^2\rangle$ were equal to zero. Then, inserting

$$x=x^0(1-2\langle a^2\rangle X_G) \quad (14)$$

into Eq. (12) we obtain

$$\ln t^{-1}=2\sum_{\text{odd }\nu=1}^{\nu_D{}^0}[\nu^{-1}-(\nu^2+x^0)^{-1/2}] \quad (15)$$

and

$$\begin{aligned}X_Gx^0\sum_{\text{odd }\nu=1}^{\nu_D{}^0}(\nu^2+x^0)^{-3/2}=\sum_{\text{odd }\nu=1}^{\nu_{Dc}{}^0}(\nu+\lambda^0)^{-1}\\ -\sum_{\text{odd }\nu=1}^{\nu_D{}^0}\{\nu^4/(\nu^2+x^0)^2[(\nu^2+x^0)^{1/2}+\lambda^0/t]\\ -\nu^2x^0/2(\nu^2+x^0)^{3/2}[(\nu^2+x^0)^{1/2}+\lambda^0/t]^2\}, \quad (16)\end{aligned}$$

where we have neglected terms of order $\epsilon_0{}^2/\omega_D{}^2$. Equation (15) yields for a given value of t the corresponding value of x^0 and, hence, of $\epsilon_0{}^0(t)/kT_c{}^0$. Mühlschlegel[17] first used this procedure (with $\nu_D{}^0=\infty$) to generate tables of thermodynamic functions for the BCS isotropic weak-coupling model. The known values of t and x^0 can then be inserted into Eq. (16) from which $X_G(t,\lambda)$ may be obtained.

We remark that the function $X_G(t,\lambda)$ provides the complete description of the anisotropy effect upon ϵ_0/kT_c as a function of temperature and impurity concentration. Some special values of X_G are

$$X_G(0,0)=\tfrac{3}{2},\quad X_G(1,0)=\tfrac{5}{2},\quad X_G(t,\infty)=0. \quad (17)$$

Although we could make use of Eq. (16) to display X_G for arbitrary t and λ, we shall now turn our attention to an examination of how the anisotropy effect which enters into ϵ_0/kT_c in turn influences the critical field.

B. Impurity Dependence of the Critical Field

An expression for the superconducting critical field in the presence of nonmagnetic impurities can be obtained by means of a procedure used by Skalski, Betbeder-Matibet, and Weiss,[18] suitably modified to account for anisotropy. The result is

$$\begin{aligned}H_c^2/8\pi=N_0\,\mathrm{Re}\int_{-\omega_D}^{\omega_D}dz\,[p(z)-1]\\ \times[z\tanh\tfrac{1}{2}\beta z-\omega_D]-\epsilon_0{}^2/V\\ +\frac{2N_0}{\beta}\mathrm{Re}\int_{-\omega_D}^{\omega_D}dz\,[p(z)-1]\\ \times\left[\ln(1+e^{-\beta z})+\frac{\beta z}{e^{\beta z}+1}\right], \quad (18)\end{aligned}$$

where

$$p(z)=\langle z/[z^2-\Delta^2(\mathbf{p},z)]^{1/2}\rangle_{\text{av}}. \quad (19)$$

With the introduction of

$$F(z)=\int dz\,[p(z)-1], \quad (20)$$

Eq. (18) can be converted via an integration by parts into the convenient form

$$\frac{H_c^2}{8\pi}=-\frac{\epsilon_0{}^2}{V}-N_0\,\mathrm{Re}\int_{-\omega_D}^{\omega_D}dz\,F(z)\tanh\tfrac{1}{2}\beta z. \quad (21)$$

We next make use of the analyticity of $F(z)$ in the upper half plane by deforming the contour as we did to obtain Eq. (4), which yields an expression for H_c in terms of the values of $F(z)$ at the poles $z_\nu=i\pi\nu/\beta$, where ν is an odd integer, of $\tanh\frac{1}{2}\beta z$. An expansion in powers of the anisotropy function similar to that used to obtain Eq. (5) yields

$$\begin{aligned}(i\pi/\beta)^{-1}F(z_\nu)=(\nu^2+x)^{1/2}-\nu\\ +\langle a^2\rangle\nu^2x/2(\nu^2+x)[(\nu^2+x)^{1/2}+\lambda/t]. \quad (22)\end{aligned}$$

Thus, we obtain with the use of Eq. (4) and $\gamma=\frac{2}{3}\pi^2N_0k^2$

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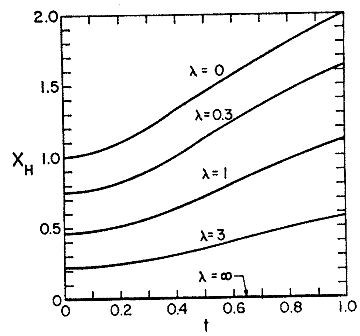

FIG. 1. $X_H(t,\lambda)$, which describes the effectiveness of anisotropy corrections to $H_c^2/8\pi\gamma T_c^2$ versus the reduced temperature t for various values of the impurity density parameter

$$\lambda\equiv(2\pi kT_c\tau_a)^{-1}.$$

the expression

$$\tilde{H}_c^2\equiv\frac{H_c^2}{8\pi\gamma T_c^2}=\tfrac{3}{2}t^2\sum_{\text{odd }\nu=1}^{\nu_D}\{4(\nu^2+x)^{1/2}-4\nu-2x/(\nu^2+x)^{1/2}$$
$$+\langle a^2\rangle[2\nu^2x^2/(\nu^2+x)^2((\nu^2+x)^{1/2}+\lambda/t)$$
$$+\nu^2x^2/(\nu^2+x)^{3/2}((\nu^2+x)^{1/2}+\lambda/t)^2]\}. \quad (23)$$

We next expand for a given value of t in powers of $\langle a^2\rangle$ as we did to obtain Eqs. (15) and (16). With the introduction of the function $X_H(t,\lambda)$ via

$$\tilde{H}_c^2(t,\lambda)=\tilde{H}_c^{02}(t)[1-2\langle a^2\rangle X_H(t,\lambda)], \quad (24)$$

we obtain with the help of Eq. (14)

$$\tilde{H}_c^{02}(t)$$
$$=\tfrac{3}{2}t^2\sum_{\text{odd }\nu=1}^{\nu_D^0}[4(\nu^2+x^0)^{1/2}-4\nu-2x^0/(\nu^2+x^0)^{1/2}] \quad (25)$$

and

$$X_H=\left[\frac{\epsilon_0^0(t)H_c^0(0)}{\epsilon_0^0(0)H_c^0(t)}\right]^2\tilde{X}_H, \quad (26)$$

where

$$\tilde{X}_H=2\sum_{\text{odd }\nu=1}^{\nu_{Dc}^0}(\nu+\lambda^0)^{-1}$$
$$-2\sum_{\text{odd }\nu=1}^{\nu_D^0}\nu^2/(\nu^2+x^0)[(\nu^2+x^0)^{1/2}+\lambda^0/t]. \quad (27)$$

Equation (25) yields $\tilde{H}_c^0(t)$ as a function of t. Equation (26) then determines X_H for a given t as a function of the impurity concentration. (In the following we shall suppress the superscript "0" wherever possible.) We observe from Eq. (24) that the function X_H, shown in Fig. 1, describes the effectiveness of anisotropy corrections to the critical field as a function of the impurity concentration. In the absence of impurities X_H is of order unity. For example,

$$X_H(0,0)=1, \quad X_H(1,0)=2, \quad (28)$$

and for intermediate temperatures

$$X_H(t,0)=\left[\frac{\epsilon_0(t)}{\epsilon_0(0)}\frac{H_0}{H_c(t)}\right]^2\frac{\Lambda(0)}{\Lambda(t)}, \quad (29)$$

where $\Lambda(t)$ is the penetration depth. As impurities are added, $X_H(t,\lambda)$ decreases in value, at first linearly with λ, then gradually tends to zero.

For numerical computation of X_H it is convenient to convert the upper limit ν_{Dc}^0 in Eq. (27) to ν_D^0, keeping track of the difference. Since $\tilde{X}_H(t,\lambda)$ is rather insensitive to the value of $\beta_c\omega_D$ for large $\beta_c\omega_D$, we then take the limit as $\beta_c\omega_D\rightarrow\infty$. With the help of Eq. (16) we then obtain

$$\tilde{X}_H(t,\lambda)=2\sum_{\text{odd }\nu=1}^{\infty}\{(\nu^2+x)^{-1/2}-\nu^2(\nu^2+x)^{-1}$$
$$\times[(\nu^2+x)^{1/2}+\lambda/t]^{-1}-[\nu^{-1}-(\nu+\lambda)^{-1}]\}. \quad (30)$$

As $t\rightarrow 0$, the summation involving x may be converted into an integral, yielding

$$\tilde{X}_H(0,\lambda)$$
$$=1+y\int_0^{\pi/2}d\theta\,\sin^2\theta(1+y\cos\theta)^{-1}-\chi(\lambda) \quad (31a)$$
$$=\pi/2y-(1-y^2)^{1/2}\cos^{-1}y/y-\chi(\lambda), \quad y\leq 1 \quad (31b)$$
$$=\pi/2y+(y^2-1)^{1/2}\cosh^{-1}y/y-\chi(\lambda), \quad y\geq 1, \quad (31c)$$

where $y=[2\epsilon_0(0)\tau_a]^{-1}=\gamma_e\lambda$ and $\chi(\lambda)$ is defined in terms of the digamma or psi function via

$$(\lambda)\equiv\psi\left(\frac{1+\lambda}{2}\right)-\psi(\tfrac{1}{2})=2\sum_{\text{odd }\nu=1}^{\infty}[\nu^{-1}-(\nu+\lambda)^{-1}]. \quad (32)$$

For a given λ an expansion of $\tilde{X}_H(t,\lambda)$ about the critical temperature in powers of $(1-t)$ can be obtained with the help of Eq. (15), with the result that

$$\tilde{X}_H(t,\lambda)=B_1(\lambda)(1-t)+B_2(\lambda)(1-t)^2+\cdots. \quad (33)$$

In terms of the derivatives $\chi^{(n)}(\lambda)=d^n\chi/d\lambda^n$ of $\chi(\lambda)$ and the derivatives $x^{(n)}(t)=d^nx/dt^n$ of $x(t)$ evaluated at $t=1$,

$$B_1(\lambda)=-x'(1)[\chi'(0)/\lambda-\chi(\lambda)/2\lambda^2-\chi'(\lambda)/2\lambda]$$
$$-[1-\lambda\chi'(\lambda)] \quad (34)$$

and

$$B_2(\lambda)=x''(1)[\chi'(0)/2\lambda-\chi(\lambda)/4\lambda^2-\chi'(\lambda)/4\lambda]$$
$$-[x'(1)]^2[\chi'''(0)/6\lambda+3\chi''(0)/16\lambda^2$$
$$+\chi(\lambda)/8\lambda^4-\chi'(\lambda)/8\lambda^3-\chi''(\lambda)/8\lambda^2]$$
$$+x'(1)[\chi'(0)/\lambda-\chi(\lambda)/\lambda^2+\chi''(\lambda)/2]$$
$$-[1/2-\lambda\chi'(\lambda)-\lambda^2\chi''(\lambda)/2], \quad (35)$$

where

$$x'(1)=-0.9508, \quad (36)$$

$$x''(1)=2.2457. \quad (37)$$

Some special values of B_1 and B_2 are

$$B_1(0)=2, \quad (38)$$

$$B_2(0)=1+\chi''''(0)/2[\chi''(0)]^2=-0.3620, \quad (39)$$

$$B_1(\infty)=B_2(\infty)=0. \quad (40)$$

The zero-temperature result (31) and the power-series expansion (33) together are sufficient to give a fairly good approximation to the behavior of $\tilde{X}_H(t,\lambda)$ vs t as a function of λ. These results are shown in Fig. 2 as dashed lines. The solid lines in Fig. 2 are sketches of the expected behavior of $\tilde{X}_H(t,\lambda)$ obtained by interpolating by eye between the dashed curves. The accuracy is estimated to be about 2%. Values of $\tilde{X}_H(t,\lambda)$ obtained in this way were combined via Eq. (26) with the tabulated values of $\epsilon_0(t)$ and $H_c(t)$ to obtain $X_H(t,\lambda)$ shown in Fig. 1. Note that $X_H(1,\lambda)=B_1(\lambda)$.

The zero-temperature critical field H_0 as a function of the impurity concentration may be written in terms of X_H and X_c as

$$H_0(\lambda)=4(\pi N_0)^{1/2}\omega_D \exp(-1/N_0V) \times\{1+\langle a^2\rangle[X_c(\lambda)-X_H(0,\lambda)]\}. \quad (41)$$

Because of the dependence of ω_D, N_0, and V upon the impurity concentration, H_0 exhibits valence effects similar to those of T_c.

The reduced critical field $h=H_c/H_0$ may be expressed as

$$h(t,\lambda)=h^0(t)\{1-\langle a^2\rangle[X_H(t,\lambda)-X_H(0,\lambda)]\}. \quad (42)$$

The fact that the anisotropy effect upon the critical field can be analyzed in terms of $\langle a^2\rangle$ is perhaps surprising, since the critical field is thermodynamically related to the superconducting electronic specific heat, which at low temperatures depends rather sensitively upon the anisotropy distribution.[14] Because expansions in powers of the anisotropy function a_p were performed, the above results should *not* be extended to cases where very small gap excitations play a significant role, as is the case for the low-temperature specific heat. However, this procedure may be applied successfully to H_c, since at no temperature is the magnitude of the critical field strongly affected by these excitations.

III. DISCUSSION

In the previous section we derived, using a simple, anisotropic weak-coupling model, the impurity dependence of the anisotropy effect upon the quantities T_c, H_0, and $h(t)$ which characterize the superconducting critical field $H_c(T)$. We next wish to cast these results into a form which will perhaps allow comparison with measurements of critical-field curves of moderately weak-coupling superconductors as nonmagnetic impurities are added. Since we are here solely interested in the effectiveness of the anisotropy as a function of the impurity concentration, there are two complications we wish to avoid: valence effects and strong-coupling, retardation effects.

In experiments upon samples of different impurity concentrations, one is faced with the possibility that changes in N_0, V, and ω_D influence the value of the experimental quantity in question. The critical temperature exhibits such effects, called valence effects.

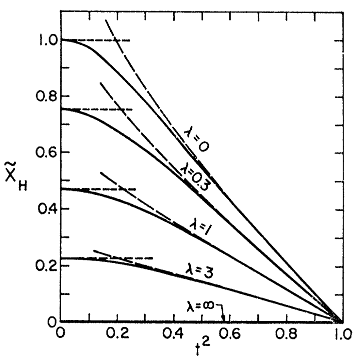

FIG. 2. $\tilde{X}_H(t,\lambda)$ versus t^2 as a function of $\lambda=(2\pi kT_c\tau_a)^{-1}$ as obtained by (1) Eq. (31) (short dash), (2) Eq. (33) (long dash), and (3) interpolation as described in the text (solid).

From Eq. (41) we see that H_0 should also exhibit similar valence effects, making H_0 itself somewhat undesirable for the study of the anisotropy effect. However, since in the weak-coupling calculation the valence effects upon H_0 enter by means of the proportionality of H_0^2 to $N_0T_c^2$, the quantity $\tilde{H}_0^2\equiv H_0^2/8\pi\gamma T_c^2$ should be very nearly free from valence effects. (Here γ is the coefficient of the temperature in the normal electronic contribution to the specific heat.) Furthermore, since $h\equiv H_c/H_0$ versus $t\equiv T/T_c$ is already relatively free from valence effects, it follows that an experimental study of $\tilde{H}_0$ and $h(t)$ as a function of impurity concentration is well suited for analysis in terms of the anisotropy effect.

Because of the high sensitivity of critical-field experiments, the behavior of $\tilde{H}_0$ and $h(t)$ often deviates noticeably from the results of the isotropic BCS model in the weak-coupling limit. However, since we are interested in the anisotropy-produced deviations of $\tilde{H}_0$ and $h(t)$ from their values appropriate to isotropy, only the changes in $\tilde{H}_0$ and $h(t)$ as impurities are added are of importance to us here. For the moderately weak-coupling superconductors with which we are concerned we shall assume that strong-coupling, retardation effects change much more slowly with increasing impurity concentration than does the anisotropy effect.

The experimental quantities which seem best suited for a study of the anisotropy effect as a function of impurity concentration are therefore

$$\delta\tilde{H}_0(\lambda)/\tilde{H}_0(0)=[\tilde{H}_0(\lambda)-\tilde{H}_0(0)]/\tilde{H}_0(0) \quad (43)$$

and

$$\delta h(t,\lambda)/h(t,0)=[h(t,\lambda)-h(t,0)]/h(t,0), \quad (44)$$

where

$$\tilde{H}_0^2(\lambda)=H_0^2(\lambda)/8\pi\gamma(\lambda)T_c^2(\lambda) \quad (45)$$

and

$$h(t,\lambda)=H_c(t,\lambda)/H_0(\lambda). \quad (46)$$

These quantities are directly comparable with the results of Sec. II by means of the relations

$$\delta\tilde{H}_0(\lambda)/\tilde{H}_0(0)=\langle a^2\rangle\delta_H(\lambda), \quad (47)$$

and

$$\delta h(t,\lambda)/h(t,0)=\langle a^2\rangle\delta_h(t,\lambda). \quad (48)$$

A procedure to obtain the connection between the experimentally measured resistivity ratio and

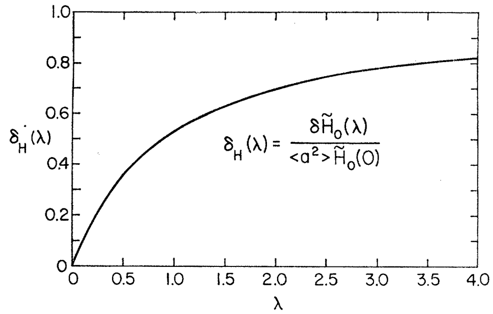

FIG. 3. $\delta_H(\lambda)$ versus λ, obtained from Eqs. (31) and (49), showing the expected increase in $\tilde{H}_0^2 = H_0^2/8\pi\gamma T_c^2$ as impurities are added.

$\lambda = (2\pi k T_c \tau_a)^{-1}$ has already been given by Markowitz and Kadanoff.[12] The quantities $\delta_H(\lambda)$ and $\delta_h(t,\lambda)$ are defined as

$$\delta_H \equiv X_H(0,0) - X_H(0,\lambda), \tag{49}$$

and

$$\delta_h(t,\lambda) \equiv [X_H(t,0) - X_H(0,0)] - [X_H(t,\lambda) - X_H(0,\lambda)]. \tag{50}$$

The quantity $\delta_H(\lambda)$, which describes the anticipated increase in $\tilde{H}_0$ as impurities are added, is shown in Fig. 3. The upward shift, $\delta h(t,\lambda)$, to be expected in curves of $h(t)$ versus t is shown in Fig. 4.

To obtain a feeling for the anisotropy effect upon $\tilde{H}_0$,[19] we first note that H_0 obeys

$$H_0^2/8\pi = \int_0^{T_c} dT\,[S_n(T) - S_s(T)]. \tag{51}$$

The normal-state entropy is given by $S_n(T) = \gamma T$, but the superconducting-state entropy $S_s(T)$ has a more complicated behavior, shown in Fig. 5, which depends

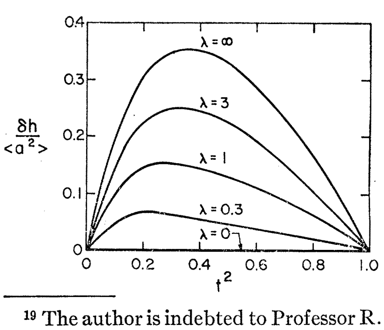

FIG. 4. $\delta h(t,\lambda)/\langle a^2\rangle = h(t,0)\delta_h(t,\lambda)$ versus t^2, obtained from Eq. (50) using for $h(t,0)$, for convenience, the BCS results tabulated in Ref. 16. These curves show the upward shift in curves of $h = H_c/H_0$ versus $t^2 = (T/T_c)^2$ as impurities are added.

[19] The author is indebted to Professor R. A. Ferrell for suggesting this point of view.

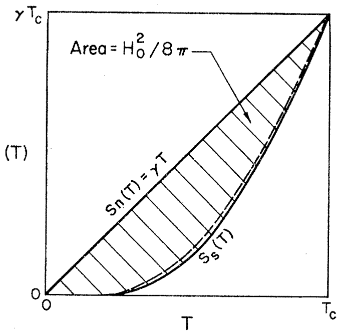

FIG. 5. Entropy versus temperature T for fixed T_c: normal-state entropy $S_n(T) = \gamma T$ (solid) and superconducting-state entropy $S_s(T)$ in the absence of gap anisotropy (solid) and in the presence of gap anisotropy (dashed).

upon the thermal probability for excitations above the energy gap. Both $S_n(T)$ and $S_s(T)$ for the isotropic gap case are shown in Fig. 5 as solid lines. We see that $H_0^2/8\pi$ is given by the cross-hatched area between the curves of $S_n(T)$ and $S_s(T)$. The effect of gap anisotropy is to enhance thermal excitation probability, thereby increasing the entropy $S_s(T)$ slightly, as shown by the dashed curve in Fig. 5. Thus, for fixed γ and T_c the area between the curves of $S_n(T)$ and $S_s(T)$ and hence the value of $\tilde{H}_0$ are reduced when anisotropy is present. However, as impurities are added, the magnitude of the anisotropic part of the gap parameter decreases,[15] the anisotropy effect diminishes, and the value of $\tilde{H}_0$ gradually increases, tending to that appropriate to the isotropic case.

The upward shift in curves of $h(t)$ as impurities are added for $t<0.3$ is a direct result of the behavior of $\tilde{H}_0$ discussed above. At higher temperatures this shift arises from a small upward shift in $\epsilon_0(t)/\epsilon_0(0)$ versus t with increasing impurity concentration.

In brief, the main conclusions of this paper are that: (1) The effect of anisotropy of the superconducting energy-gap parameter upon the critical field $H_c(T)$ is to produce corrections of order $\langle a^2\rangle$ to the corresponding isotropic gap values. (2) As nonmagnetic impurities are added, these anisotropy corrections decrease in magnitude, and their dependence upon impurity concentration can be calculated. (3) These effects should be observable in experimental studies of $\delta\tilde{H}_0/\tilde{H}_0$ and $\delta h/h$, which are relatively free from valence and strong-coupling, retardation effects.

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