Two-Fluid Model of an "Energy-Gap" Superconductor

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It is pointed out that an exponential specific heat law in a superconductor leads to a uniquely specified form of two-fluid model. The properties of this model are derived, and compared with the corresponding properties of the usual Gorter-Casimir model.

I. INTRODUCTION

RECENTLY evidence[1] has begun to appear that, in some superconductors, the specific heat law does not conform at sufficiently low temperatures to that predicted by the two-fluid model of Gorter and Casimir.[2] Specifically, it appears that one can represent the specific heat law, to remarkable accuracy, by an expression of the form

$$C(T)/\gamma T_c = A \exp[-\alpha T_c/T], \qquad (1)$$

where C is the specific heat, T_c the critical temperature, and γT_c the specific heat of the normal metal at a temperature T equal to T_c. α is a constant of order unity, that seems to vary from metal to metal. It is the purpose of this work to point out that the most general two-fluid model that will yield (1), and which preserves the zero entropy characteristic of the superfluid electron, is completely determined by (1). In the remainder of this paper we will exhibit its form explicitly, and develop its consequences. A specific example of a two-fluid model that is different from the Gorter-Casimir model has been developed by Koppe[3] and discussed by Bender and Gorter.[4] The specific heat to which it leads is, at sufficiently low temperatures, intermediate between (1) and that given by the Gorter-Casimir model.

II. TWO-FLUID MODEL IN GENERAL

One can describe a two-fluid model completely by prescribing an order parameter ω, the so-called fraction of superfluid, and by expressing the Helmholtz free energy F per unit volume as a function of ω and T, the absolute temperature. Thus, for our case,

$$F = -A\omega - \tfrac{1}{2}K(\omega)\gamma T^2, \qquad (2)$$

where A is a constant, $K(\omega)$ is an arbitrary function, and γ is the electronic specific heat parameter. If $K(0)=1$, the free-energy expression reduces to the correct form for a normal electron gas. The linear form of the first term in (2) is determined by the requirement that no entropy be carried by the superfluid component. At absolute zero, where $\omega=1$, the free energy of the superconductor is known to be equal to $-H_0^2/8\pi$, where H_0 is the critical field at absolute zero. This determines A, which is equal to $H_0^2/8\pi$. Thus

$$F = -\omega H_0^2/8\pi - K(\omega)\gamma T^2/2 \qquad (3)$$

and the condition for equilibrium at a temperature T is given by

$$\left(\frac{\partial F}{\partial \omega}\right)_{\omega=\omega_e} = 0 = -H_0^2/8\pi - K'(\omega_e)\gamma T^2/2, \qquad (4)$$

whence we obtain

$$-K'(\omega_e) = H_0^2/4\pi\gamma T^2, \qquad (5)$$

which determines ω_e as a function of temperature. Since we want this to describe a second-order phase transition at the critical temperature T_c, we have

$$-K'(0) = H_0^2/4\pi\gamma T_c^2. \qquad (6)$$

For the Gorter-Casimir model, $K(\omega)=(1-\omega)^{\frac{1}{2}}$, so that $-K'(0)=\frac{1}{2}$. Equation (6) is then a well-known relation. In the more general case $-K'(0)$ will not be equal to $\frac{1}{2}$.

In view of (6), we can write (3) as follows:

$$8\pi F/H_0^2 = -\omega + t^2 K(\omega)/K'(0), \qquad (7)$$

where $t \equiv T/T_c$ is the reduced temperature. We can also write (5) in the form

$$K'(0) = t^2 K'(\omega_e), \qquad (8)$$

which determines the function $\omega_e(t)$.

The entropy of our system (again, per unit volume) is given by $S=-\partial F/\partial T$, so that

$$S = \gamma T K(\omega_e). \qquad (9)$$

The specific heat is $C(T)=TdS/dT$, so that

$$C(T)/\gamma T_c = tK(\omega_e) + t^2 K'(\omega_e)(d\omega_e/dt) \qquad (10)$$

or, using (8)

$$C(T)/\gamma T_c = tK(\omega_e) + K'(0)(d\omega_e/dt). \qquad (11)$$

It follows from (10) or (11) that $K(\omega_e)$ is determined, as a function of t, by the specific heat. By combining this with (8), therefore, $K(\omega)$ is itself determined parametrically, using t as a parameter. Then all the other details of the model are determined.

[1] B. B. Goodman and W. S. Corak, and Goodman, Satterthwaite, and Wexler, Proceedings of the Paris Low Temperature Conference, 1955, papers 64 and 75. Older references are listed in these papers.
[2] C. J. Gorter and H. B. G. Casimir, Physik. Z. 35, 963 (1934); Z. Physik 15, 539 (1934).
[3] H. Koppe, Ann. Physik 1, 405 (1947).
[4] P. L. Bender and C. J. Gorter, Physica 18, 597 (1952).

The quantity $\omega_e(t)$ is, of course, given by (8). If we suppose, as usual, that the penetration depth λ varies with temperature, as $[\omega_e(t)]^{-\frac{1}{2}}$, then

$$\lambda(T)/\lambda(0)=[\omega_e(t)]^{-\frac{1}{2}}. \quad (12)$$

If necessary, this relationship, which is based upon an interpretation of the London electrodynamics of a superconductor, can be changed. It is not very firmly based in the theory.

The critical field H_c at a temperature T is given by the difference in free energy between the normal and superconducting phases.

$$H_c^2/8\pi=F_n-F_s, \quad (13)$$

so that the reduced critical field $h\equiv H_c/H_0$ is given by

$$h^2(t)=\omega_e+t^2[1-K(\omega_e)]/K'(0). \quad (14)$$

The surface energy can be calculated, in the framework of the new phenomenological theories,[5] by using the free-energy form (3) instead of that given by the Gorter-Casimir model. The explicit consequences of the change will be postponed to a separate paper on the surface energy problem.

It is of some interest to note explicitly that the ratio of electronic specific heats just above and just below the transition is

$$\frac{C(T_c^{(-)})}{C(T_c^{(+)})}=1-2\frac{[K'(0)]^2}{K''(0)}. \quad (15)$$

For the Gorter-Casimir model, this ratio is 3.

We should also note the relation between H_0/T_c and $(dH_0/dT)_{T=T_c}$. We obtain, from (14) and (8)

$$-\left(\frac{dH_c}{dT}\right)_{T=T_c}=\frac{H_0}{T_c}\left[\frac{2K'(0)}{K''(0)}\right]^{\frac{1}{2}}. \quad (16)$$

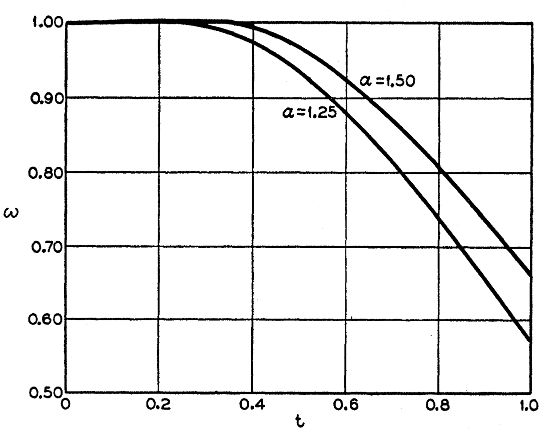

FIG. 1. Ratio of the "fraction of superfluid" $\omega(t)$ in the "energy-gap" model, to that in the Gorter-Casimir model. For the latter, $\omega(t)=1-t^4$.

[5] V. L. Ginzberg and L. D. Landau, J. Exptl. Theoret. Phys. (Japan) **20**, 1064 (1950); J. Bardeen, Phys. Rev. **94**, 554 (1954).

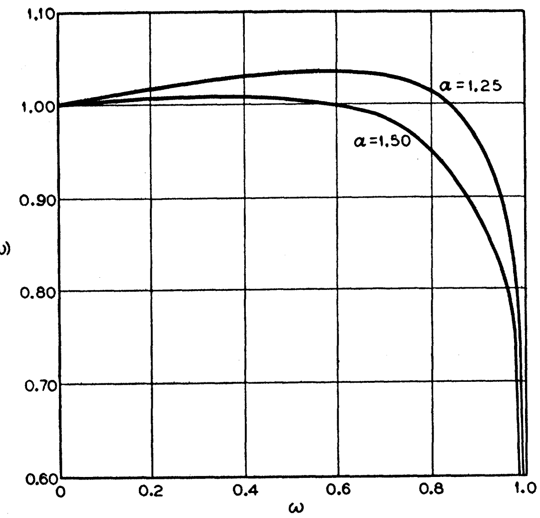

FIG. 2. Ratio of the function $K(\omega)$ for the "energy-gap" model to that in the Gorter-Casimir model. For the latter, $K(\omega)=(1-\omega)^{\frac{1}{2}}$.

For the Gorter-Casimir model, the expression in square brackets on the right side of (16) is equal to 4.

This summarizes the most important properties of the model. In the next section we will derive the specific results for the model determined by (1).

III. "ENERGY-GAP" MODEL, AND ITS CONSEQUENCES

For the particular form of the specific heat law given by (1), namely

$$c(t)\equiv C(T)/\gamma T_c=A\exp[-\alpha/t], \quad (17)$$

we want to find $K(\omega)$. To this end we first calculate the entropy

$$\sigma(t)\equiv S(T)/\gamma T_c=\int_0^t c(\tau)d\tau/\tau, \quad (18)$$

where we have taken into account the third law of thermodynamics in choosing the lower limit for the integral. Thus

$$\sigma(t)=A\int_0^t\frac{d\tau}{\tau}\exp[-\alpha/\tau]=AE(\alpha/t), \quad (19)$$

where we have used the terminology $E(x)$ for the standard exponential integral $\int_x^\infty e^{-\tau}d\tau/\tau$. This is the integral many mathematics books call $-\mathrm{Ei}(-x)$. We prefer to dispense with the two minus signs.

Since we want a second-order phase transition at $t=1$, A is determined by

$$AE(\alpha)=1, \quad (20)$$

so that only one of the parameters in (1) is really independent. It is gratifying to note that the parameters obtained by curve-fitting to the observed specific heats[1]

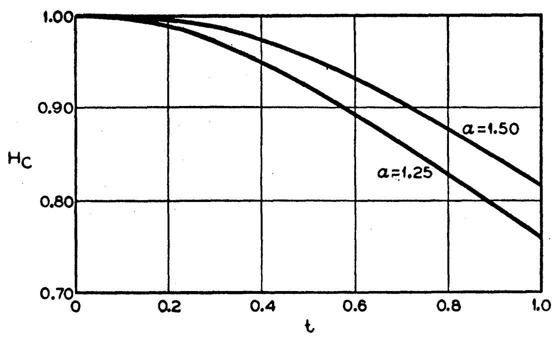

FIG. 3. Ratio of the critical field in the "energy-gap" model to that in the Gorter-Casimir model, normalized to the same value of H_0. For the latter, $h(t)=H_c(T)/H_0=1-t^2$.

do indeed closely satisfy (20). This is as it must be. It follows, therefore, that the ratio of specific heats just above and just below the transition is

$$C(T_c^-)/C(T_c^+)=\exp[-\alpha]/E(\alpha). \tag{21}$$

For the cases observed in practice, this is normally less than the value of 3 given by the Gorter-Casimir model.

We have then

$$E(\alpha)\sigma(t)=E(\alpha/t). \tag{22}$$

Combining this with (9), we find

$$\sigma(t)=tK(\omega_e)=\frac{E(\alpha/t)}{E(\alpha)}, \tag{23}$$

which determines $K(\omega_e)$ as a function of t. Using (8), we obtain

$$K'(0)\frac{d\omega_e}{dt}=t^2K'(\omega_e)\frac{d\omega_e}{dt}=t^2\frac{d}{dt}[K(\omega_e)], \tag{24}$$

so that

$$K'(0)E(\alpha)\frac{d\omega_e}{dt}=t\frac{dE(\alpha/t)}{dt}-E(\alpha/t) =\exp[-\alpha/t]-E(\alpha/t). \tag{25}$$

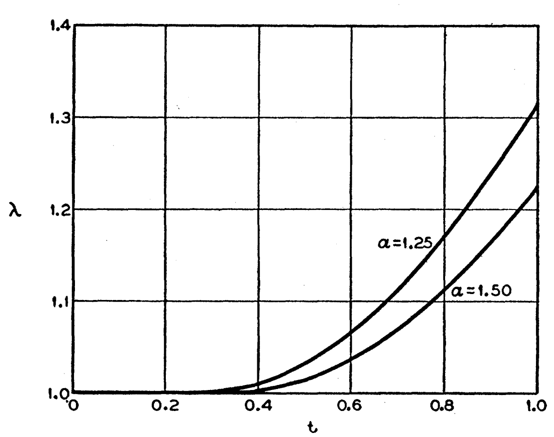

FIG. 4. Ratio of the penetration depth in the "energy-gap" model to that in the Gorter-Casimir model, both referred to the penetration depth at absolute zero. For the Gorter-Casimir model, this is $\lambda(T)/\lambda(0)=(1-t^4)^{-\frac{1}{2}}$.

Integrating this differential equation for ω_e, we find

$$K'(0)E(\alpha)[1-\omega_e(t)]=(2\alpha+t)E(\alpha/t) -2t\exp[-\alpha/t], \tag{26}$$

where we have had to specify $K'(0)$ in order to have the change in $\omega_e(t)$ from $t=0$ to $t=1$ come out equal to unity. The necessary value for $K'(0)$ is

$$K'(0)=1+2\alpha-2e^{-\alpha}/E(\alpha). \tag{27}$$

Equations (23), (26), and (27) now determine $K(\omega)$ parametrically, with t as a parameter. Then the rest of the properties of the model follow from the appropriate equations in Sec. II, and it is unnecessary to do more than to list them, leaving out the simple and straightforward derivations.

The properties of the most general model of the form (3) that will lead to a specific heat of the form (1)

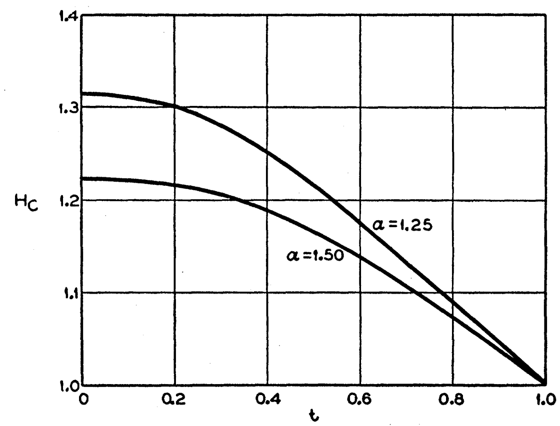

FIG. 5. Ratio of the critical field in the "energy-gap" model to that in the Gorter-Casimir model, normalized to the same slope at $T=T_c$.

or (17), are, then, as follows:

$$K'(0)=1+2\alpha-2e^{-\alpha}/E(\alpha), \tag{28}$$

$$K[\omega_e(t)]=E(\alpha/t)/tE(\alpha), \tag{29}$$

$$1-\omega_e(t)=\frac{(2\alpha+t)E(\alpha/t)-2t\exp(-\alpha/t)}{K'(0)E(\alpha)}. \tag{30}$$

The last two equations determine $K(\omega)$.

$$h^2=\omega_e(t)+\frac{t^2}{K'(0)}[1-K[\omega_e(t)]], \tag{31}$$

$$(H_0/T_c)^2=-4\pi\gamma K'(0), \tag{32}$$

$$-\left(\frac{dH_c}{dT}\right)_{T=T_c}=\left(\frac{H_0}{T_c}\right) \times\left[\frac{\exp(-\alpha)-E(\alpha)}{2\exp(-\alpha)-(1+2\alpha)E(\alpha)}\right]^{\frac{1}{2}}, \tag{33}$$

$$C(T_c^-)/C(T_c^+)=e^{-\alpha}/E(\alpha). \tag{34}$$

The corresponding expressions in the Gorter-Casimir two-fluid model are as follows:

$$K'(0)=-\tfrac{1}{2}, \tag{28GC}$$

$$K[\omega_e(t)]=t^2, \tag{29GC}$$

$$1-\omega_e(t)=t^4, \tag{30GC}$$

$$h^2=(1-t^2)^2, \tag{31GC}$$

$$(H_0/T_c)^2=2\pi\gamma, \tag{32GC}$$

$$-\left(\frac{dH_c}{dT}\right)_{T=T_c}=2\frac{H_0}{T_c}, \tag{33GC}$$

$$C(T_c^-)/C(T_c^+)=3. \tag{34GC}$$

As mentioned before, the variation of the surface energy with temperature is also changed from that given by the Gorter-Casimir model, but this will be discussed separately.

We exhibit in Figs. 1–4 for the "energy-gap" model with $\alpha=1.25$ and $\alpha=1.5$, $\omega_e(t)$, $K(\omega)$, $h(t)$ and $\lambda(t)/\lambda(0)=[\omega_e(t)]^{-\frac{1}{2}}$, respectively. In each case we have plotted the ratio to the corresponding expression for the Gorter-Casimir model, so that that model is represented by the horizontal line at unity. We show in Fig. 5 the ratio of the critical field in this model to that in the Gorter-Casimir model, when they are normalized to the same slope at $T=T_c$.

IV. DISCUSSION OF THE RESULTS

As one might expect, the main difference between the "energy-gap" model and the Gorter-Casimir model is that, in the former, all the physical quantities tend to their values at absolute zero more rapidly than in the latter. Thus, $C(T)$ goes to zero more rapidly, $\omega_e(t)$ goes to unity more rapidly, and H_c goes to H_0 more rapidly.

The jump in specific heat is changed, and for the chosen values of α, is reduced. This is given by (24).

The relation between H_0/T_c and the slope of the critical field curve at the transition temperature is changed to (33), so that parabolic extrapolation to find H_0 is no longer valid.

All these changes are quantitative rather than qualitative, and are subject to experimental check.

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Investigation of the Superconductivity of Hafnium

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The magnetic susceptibility of two polycrystalline rods of hafnium (Hf I and Hf II) was observed from 4.22°K down to 0.08°K. The electrical resistance of these specimens was also observed from room temperatures down to 0.08°K. While the magnetic measurements indicated unambiguously that no superconducting transition occurred, the electrical resistance did, however, exhibit a decrease at approximately 0.19°K for Hf I and 0.28°K for Hf II. The resistance did not fall to zero but remained finite down to the lowest temperatures obtained. The temperature at which this decrease occurred was found to be sensitive to an externally applied magnetic field. Critical field data were obtained for Hf I which indicated a $(dH/dt)_{T=T_c}$ of 450 gauss/degree. Magnetic and electrical measurements obtained for one of the specimens, subsequent to an anneal, indicated no marked change in these measured quantities. Both these specimens had a stated purity of 98.92%.

The magnetic susceptibility of a third specimen of hafnium was observed and a superconducting transition was noted at 0.173°K. This specimen was in the form of lathe turnings and was approximately 96% pure. A few critical field points were obtained which yield a value for $(dH/dT)_{T=T_c}$ of 130 gauss/degree.

From a consideration of all the available data concerning the superconductivity of hafnium, it is felt that pure hafnium is probably not a superconductor down to a temperature of 0.08°K.

I. INTRODUCTION

KURTI and Simon[1] observed the magnetic behavior of hafnium below 1.0°K and reported it to be a superconductor with a transition temperature (T_c) of 0.35±0.05°K. Roberts and Dabbs[2] investigated the magnetic susceptibility of several specimens of hafnium and detected no superconducting transitions down to 0.03°K. The specimens were then annealed after which one of the specimens exhibited a transition at 0.29°K. The specimen which showed superconductivity was in the form of lathe turnings and possessed a purity of 96%, the major impurity being zirconium (~4%). Smith and Daunt[3] failed to observe, magnetically, any superconductivity in a relatively pure hafnium sample (98.92%) down to a temperature of 0.15°K. The specimen was then annealed and a superconducting transi-

[1] N. Kurti and F. Simon, Proc. Roy. Soc. (London) **A151**, 610 (1935).

[2] L. D. Roberts and J. W. T. Dabbs, Phys. Rev. **86**, 622 (1952); and private communications.

[3] T. S. Smith and J. G. Daunt, Phys. Rev. **88**, 1172 (1952).