THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. 91, NO. 5 SEPTEMBER 1, 1953

Two-Fluid Models of Superconductivity with Application to Isotope Effects*†

PAUL M. MARCUS, *Department of Physics, Carnegie Institute of Technology, Pittsburgh, Pennsylvania*

AND

E. MAXWELL, *Cryogenics Section, National Bureau of Standards, Washington, D. C.*

(Received April 30, 1953)

A general form of the two-fluid model of a superconductor, which includes all previous forms, is set up and the underlying assumptions examined in the light of the lattice vibration theory of superconductivity. Thermodynamic relations are derived and their consistency with the observed isotope effects indicated. Specialization to the α model of Casimir and Gorter permits fitting recent precise critical field data and evaluation of the parameter α characterizing different superconductors. Comparison is made with Koppe's form of the two-fluid model, which is shown not to fit all the data, and simplified and limiting forms of his equations are given.

1. INTRODUCTION

THE two-fluid model of a superconductor was proposed originally to describe the second-order phase transition and the temperature dependence of both the thermodynamic functions and the critical field curve. This it succeeded in doing in a remarkably simple way.[1] The model has acquired fresh support in recent years by its success in interpreting other properties of superconductors. In particular the temperature dependence of the penetration depth is correctly predicted,[2] and the model may be extended to describe behavior in a magnetic field, leading to a theory of the surface energy between normal and superconducting phases and to the field dependence of the penetration depth.[3]

Additional support for the model, in that it is consistent with the observed effects of the change of isotopic mass on the electronic entropy, has been pointed out by one of us[4] and will be developed further here.

Other recent papers which make use of the model will be referred to at appropriate points. (See references 5, 23, and 24.)

One of the purposes of this paper is to refine the the comparison of the two-fluid model with measured values by taking advantage of recent precise critical field data. In particular, the observed deviations from the parabolic law may be brought within the framework of the model by using a more general form of the model containing an adjustable parameter, different for each superconductor.

We also take the occasion to develop the two-fluid model in full generality and to examine the underlying phenomenological assumptions and show these are plausible in the light of the usual band description of electrons in metals and the lattice vibration interaction theory of superconductivity. The resulting general representation of the equilibrium properties of superconductors affords an illuminating example of a second-order phase transition which has a particularly simple, explicit, and apparently quite accurate representation. Thus the dependence of the various thermodynamic functions on an inner parameter which measures the gradually increasing degree of condensation below the transition may be examined in detail.

---

* Work begun at the University of Illinois, Urbana, Illinois, and supported there by the U. S. Office of Naval Research.

† Supported in part by Office of Scientific Research, Air Research and Development Command.

[1] C. J. Gorter and H. B. G. Casimir, Physik. Z. **35**, 963 (1934). An electrodynamic two-fluid model had been suggested by H. London, Nature **133**, 497 (1934).

[2] Daunt, Miller, Pippard, and Shoenberg, Phys. Rev. **74**, 842 (1948).

[3] L. Landau and V. Ginsburg, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 1064 (1950); A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 210 (1950); J. Bardeen (to be published); also Phys. Rev. **81**, 1070 (1951).

[4] E. Maxwell, Phys. Rev. **87**, 1126 (1952); Physics Today **5**, 14 (1952).

Section 2 contains the general formulation of the model, presented with reference to the lattice vibration theory and the underlying statistical basis for the model afforded by that theory. Particular attention is paid to the assumption that the condensation process takes place essentially for electrons close to the Fermi level and to the effect of condensation on the lattice contribution to the free energy. The interrelations of the various thermodynamic quantities are given in detail, since they contain all previous relations for special forms of the model.

Section 3 shows how the general form of the model leads plausibly to the invariance of various reduced quantities to change of isotopic mass and discusses the necessary assumption that the temperature dependent part of the lattice contribution to the free energy must be independent of the degree of condensation.

Section 4 first analyzes the requirements on the general form of the model which follow from the condition that the transition be second order, with no discontinuous changes in degree of condensation. Arguments are given for the conclusion that the effective number of normal electrons approaches 0 at 0°K. The α model of Casimir and Gorter is shown to be a plausible assumption satisfying the requirements obtained previously, and with sufficient flexibility to represent present data adequately; α is then evaluated from experimental data for tin, mercury, thallium, and indium. The need for precise measurements in fixing α is emphasized, since all values are quite close to the simple parabolic case. The Koppe-Heisenberg form of the model with its unique prediction for the reduced quantities of all superconductors is compared both with the α model and with the experimental values. It is shown not to fit all of the experimental data and also markedly deviates from the α model at very low temperatures. The equations for this model are given in detail in Appendix II in substantially simplified form which reduces them to tabulated functions. It is noted that fundamental justification for any of these forms of the model has not yet been established.

2. GENERAL FORMULATION OF THE TWO-FLUID MODEL

The phenomenological formulation of the model postulates a mixture of two electronic phases in the superconductor when in the superconducting state. One is a degenerate Fermi gas, the "normal" phase, and the other a condensed phase with no temperature excitation (hence no entropy), the "superconducting" phase, and they are assumed to be in equilibrium with each other (and the lattice). The degree of condensation is measured by a parameter ω, which by definition takes only values from 0 to 1 as the temperature falls below the transition temperature T_c (in zero magnetic field). The free energy and internal energy of the system decreases by the condensation energy $-\beta\omega$ where β is a constant, as the condensation proceeds. We may think of ω as measuring the "degree of superconductivity," or the "fraction of superconducting electrons" (relative to the number at 0°K), or as a long-range order parameter in the electron distribution, but it is essentially introduced as a measure of the condensation energy.[5]

The normal phase electrons are assumed to show the temperature excitation of the degenerate Fermi gas, specific heat γT per mole, but the effective number of normal electrons will be assumed proportional to a function of the degree of condensation, $K(\omega)$, where $K(0)=1$ and $K(1)=0$.[6] This dependence on ω is not surprising if we anticipate the statistical explanation of the model,[7] and note that in the ordinary band picture of a metal the effective number of electrons is determined by the density of states at the Fermi surface. This density may be expected to alter strongly in the development of the superconducting state as is specifically indicated by calculations based on the theory introducing interactions of electrons with lattice vibrations.

On the basis of these assumptions, a reasonable form for the Helmholtz free energy per mole of the metal in the superconducting state is

$$F_s(T,\omega)=U_0-\beta\omega-\tfrac{1}{2}\gamma T^2K(\omega)+F_L(T), \qquad (2.1)$$

where two further assumptions have been introduced. First, the zero-point energy of the electron distribution and of the lattice vibrations or internal energy of the metal per mole at 0°K, U_0, is assumed unaltered as electrons transfer from the normal to the superconducting phase, except for the part specifically taken into account by the condensation energy, $-\beta\omega$. Thus the model does not imply that each electronic phase separately builds up its own degenerate Fermi distribution with rapidly changing total numbers of electrons below T_c. Rather the condensation is concerned with processes taking place at the surface of the single Fermi distribution of all the electrons which alter electron energies very slightly near that surface, but no change occurs in the vast bulk of the electrons in the interior of the Fermi sphere whose energies make up the large zero-point energy.

Second, the temperature dependent lattice contribution to the free energy, $F_L(T)$, is assumed independent of ω, i.e., unchanged by the transition to the superconducting state. Although the lattice vibration theory of superconductivity specifically assumes that a strong interaction between electrons and lattice vibrations sets

---

[5] In view of the direct physical interpretation of ω in the statistical picture, it seems advisable to retain it as the fundamental parameter rather than use the parameter $x=1-\omega$ advocated by P. L. Bender and C. J. Gorter, Physica **18**, 597 (1952), p. 600, on the basis of the analogy with the two-fluid model of liquid helium. In fact the effective number of normal electrons is not proportional to $1-\omega$, as shown by Eq. (2.1).

[6] A discussion is given later (Sec. 4), of the significance of and evidence for the assumption $K(1)=0$.

[7] A plausible statistical basis for the two-fluid model will be developed in detail elsewhere by one of us (P. M. M.).

in at the transition, this is consistent with the assumption about $F_L(T)$ if we assume that the important interactions are only with the short wavelength vibrations at the top of the frequency distribution. At the low temperature of the transition (compared to the Debye temperature), these short wavelengths are not excited being present only in the zero-point oscillation, hence change of ω will affect only the zero-point energies, not $F_L(T)$, and will be absorbed in the condensation energy, $-\beta\omega$.[8]

In fact, the success of the model in accounting for the observed thermodynamic properties will be support for the assumption that the important interactions are with short wavelength zero-point oscillations. In particular, the correct prediction of the behavior under change of isotopic mass will be significant because $F_L(T)$ depends strongly on lattice mass, as will be brought out later (Sec. 3).

In the normal state (unstable in the absence of a magnetic field for $T<T_c$), the free energy corresponding to (1) is

$$F_n(T)=U_0-\tfrac{1}{2}\gamma T^2+F_L(T). \qquad (2.2)$$

The equilibrium value of ω, ω_e at any temperature is determined by minimizing F_s, yielding the implicit equation for ω_e as a function of T,

$$K'(\omega_e)=-2\beta/\gamma T^2=K'(0)(T_c/T)^2. \qquad (2.3)$$

In the right hand form of Eq. (2.3), ω_e has been set equal to zero at the transition temperature, T_c, thereby assuming that the transition is second order and no abrupt change of ω occurs at T_c.

The critical field H_c at any T is related to the free energy difference by

$$\left.\begin{aligned} H_c^2V_m/8\pi&=F_n(T)-F_s(T,\omega_e) &&\text{(a)}\\ &=\beta\omega_e-\tfrac{1}{2}\gamma T^2[1-K(\omega_e)], &&\text{(b)}\end{aligned}\right\} \qquad (2.4)$$

on neglecting penetration effects, so that the Gibbs free energy of the superconducting phase in the field is obtained from F_s simply by adding the term $H^2V_m/8\pi$ per mole,[9] where V_m is the molar volume.

Since by definition $\omega_e=1$ at $T=0$, Eq. (2.4) gives

$$\beta=H_0^2V_m/8\pi, \qquad (2.5)$$

where H_0 is the critical field at 0°K. Putting Eq. (2.5) in Eq. (2.3) gives

$$\gamma=-H_0^2V_m/T_c^24\pi K'(0), \qquad (2.6)$$

a generalization of Kok's relation, derived originally for the case of a parabolic critical field,[10] for which case, as will be shown later, $K'(0)=-\tfrac{1}{2}$.

Substitution of Eq. (2.6) and Eq. (2.5) in Eq. (2.4) gives the critical field curve, which is, in reduced form,

$$h^2=\omega_e+t^2[1-K(\omega_e)]/K'(0), \qquad (2.7)$$

where

$$h=H_c/H_0;\quad t=T/T_c. \qquad (2.8)$$

Differentiating Eq. (2.7), and using Eq. (2.3), gives the simple formula for the slope of the reduced field curve:[11]

$$dh/dt=h/t-\omega_e/ht, \qquad (2.9)$$

which reduces at the transition temperature where $t=1$, $h=\omega_e=0$, to

$$(dh/dt)_{t=1}=-[-(d\omega_e/dt)_{t=1}]^{\frac{1}{2}}. \qquad (2.10)$$

Substitution of Eq. (2.10) in Eq. (2.6) gives

$$\gamma=\left(\frac{dH}{dT}\right)^2_{T=T_c}\frac{V_m}{4\pi K'(0)(d\omega_e/d^{t})_{t=1}}, \qquad (2.11)$$

a formula permitting γ to be determined from the initial slope of the critical field curve once the model is fixed, i.e., once $K(\omega)$ is known.

Finally, using Eq. (2.4), the entropy differences are

---

[8] In the Debye approximation the lattice zero-point energy included in U_0 is $(9/8)h\nu_mN$, where $\nu_m=kT/\theta$ is the maximum lattice frequency and N the atom density (per mole). The temperature dependent part of the lattice free energy is $F_L(T)=-\frac{1}{5}\pi^4NkT(T/\theta)^3$. Condensation energies in the electron distribution and decreases in the zero-point energies of lattice vibrations cannot really be distinguished, since we are dealing with an interaction in which the energy is not uniquely assigned to either. A further argument that the significant interactions are with short wavelength vibrations has been given by J. Bardeen, Phys. Rev. **81**, 1070 (1951), namely that the transition temperature of films or colloids, 5×10^{-6} cm in dimension, is essentially the same as for bulk material. Hence the long wavelength part of the vibrational spectrum, comparable with 5×10^{-6} cm or greater, which is affected by the small size, is not important for the interaction producing the condensation.

[9] See, for example, P. M. Marcus, Phys. Rev. **88**, 373 (1952), Eq. (3.5) with $\Phi=0$.

[10] J. A. Kok, Physica **1**, 1103 (1934). Bender and Gorter (reference 5) also give an equation equivalent to Eq. (2.6) [their Eq. (12)], in which the function $r(x, T)$, $x=1-\omega$, replaces our $K(\omega)$. The additional generality implied in introducing T explicitly in r does not lead in a simple way to a critical field curve expressed in pure reduced form, as required to explain the isotope effects (Sec. 3), and is not in accord with a statistical picture based on a mean potential which varies with ω (see reference 25). A relation like Eq. (2.6) may, in fact, be established without a model, simply in terms of the form of $h(t)$ near $t=0$ see Eq. (2.7)), by assuming that the entropy difference S_n-S_s (given by Eq. (2.12)) is dominated by a linear term in t, as $t\to0$, which comes from the normal state electronic entropy. This assumption leads to the form $h(t)=1-t^2q(t)$ where $q(0)$ is finite (and $q(1)=1$), and gives $\gamma=H_0^2V_mq(0)/2\pi T_c^2$. It is not necessary to assume the derivatives of $q(t)$ exist at $t=0$, as is done by A. Sommerfeld, Z. Physik **118**, 467 (1941), which in fact is not generally possible for the two fluid model. Compare also Lock, Pippard, and Shoenberg, Proc. Cambridge Phil. Soc. **47**, 811 (1951), p. 818.

[11] Equation (2.9) also follows as a direct consequence of the identity:

$$F_n-F_s=\beta\omega_e+\tfrac{1}{2}T\partial/(\partial T)_V(F_n-F_s),$$

a form not unlike the Gibbs-Helmholtz equation which is obtained by using Eq. (2.12a) in Eq. (2.4). Equation (2.9) could then be used to obtain $\omega_e(t)$ directly from $h(t)$. Equation (2.7) would then give the corresponding value of $K(\omega_e)$, provided that $K'(0)$ is known. Alternatively, differentiating h^2 leads to the simple relation $K(\omega_e)=1-K'(0)[d(h^2)/d(t^2)]$ which also permits evaluating $K(\omega_e)$ from experimental data. If $K(1)=0$, then $K'(0)=1/[d(h^2)/d(t^2)]_{t=0}$. Arguments for $K(1)=0$ are given in Sec. 4, and this is shown to be equivalent to lack of a linear term in S_s, the assumption used in (see reference 10).

given by

$$\left.\begin{aligned} S_n-S_s&=-[\partial(F_n(T)-F_s(T,\omega))/\partial T]_{V,\omega=\omega_e} && \text{(a)}\\ &=-[\partial(F_n(T)-F_s(T,\omega_e))/\partial T]_V && \text{(b)}\\ &=\gamma T[1-K(\omega_e)], && \text{(c)}\end{aligned}\right\}(2.12)$$

which evidently satisfies the requirements of the third law of thermodynamics. Note that ω does not have to be held constant in the differentiation if it has its equilibrium value, ω_e, since $[\partial F_s(T,\omega)/\partial\omega]_{\omega=\omega_e}=0$. Equation (2.12) may also be written in terms of the electronic entropies in the two states as

$$S_n^{\text{elect}}=\gamma T;\quad S_s^{\text{elect}}=\gamma TK(\omega_e). \qquad (2.13)$$

Correspondingly the specific heats (all at constant volume) are given by

$$\begin{aligned} C_n^{\text{elect}}/\gamma T&=1, && \text{(a)}\\ C_s^{\text{elect}}/\gamma T&=K(\omega_e)+(K'(0)/t)(d\omega_e/dt) && \text{(b)} \quad (2.14)\\ &=K(\omega_e)-2[K'(0)]^2/t^4K''(\omega_e), && \text{(c)}\end{aligned}$$

and the discontinuity in specific heat at T_c is then

$$[(C_s-C_n)/\gamma T_c]_{t=1}=-K'(0)(dh/dt)^2_{t=1}. \qquad (2.15)$$

Another useful result which follows from Eq. (2.9) may be mentioned here. On making use of the limiting form

$$h\underset{t\to 0}{\longrightarrow}1+t^2/2K'(0),$$

it can be shown that

$$\omega_e\underset{t\to 0}{\longrightarrow}1-t^4/4[K'(0)]^2. \qquad (2.16)$$

3. RELATION TO ISOTOPE EFFECTS

The implications of the generalized two-fluid model with respect to isotopic change of lattice mass, M, are obtained from the assumption that $K(\omega)$ is a function characteristic of the electron distribution and independent of M. In addition, γ, the electronic specific heat coefficient in the normal state, a function of the electron distribution and interatomic potential, is plausibly assumed independent of M. The assumption about $K(\omega)$ is not entirely obvious since the lattice vibrations, which depend on M, interact with the electron distribution. However, change of M affects the amplitudes of zero-point oscillations (and the frequencies, although not the wave numbers), hence, may reasonably be thought to affect the strength of the interaction but not the manner of alteration of the electron distribution when the condensation starts, i.e., not the particular way the mean potential alters as the electrons condense. In other words the distortion of the mean potential, or mean energy function for individual electrons, and the consequent effective number of normal electrons, is conceived to depend only on the extent to which the electronic wave functions have altered as a result of condensation, and this extent is measured by the single parameter ω. The distortion is the same even though the same value of ω may be obtained at different T, depending on the strength of the interaction with the lattice vibrations, e.g., as is brought about by change of M.[12] Thus, β or H_0 and T_c are dependent on M, but we assume $K(\omega)$, and γ are not. Hence, ω_e, determined by Eq. (2.3), and $K'(0)$, are functions only of reduced temperature and not of M.

The immediate result of this assumption is that the reduced critical field curve, given by Eq. (2.7), is invariant to change of M, as are the ratio H_0/T_c by Eq. (2.6),[13] and the initial slope of the critical field curve, $(dH/dT)_{T_c}$ by Eq. (2.11) or Eq. (2.10). These conclusions are in agreement with experiment.[14,15] In addition, the reduced electronic entropy and specific heat are invariant functions of reduced temperature, as shown by (2.13), (2.14), (2.15), and as indicated previously for the α model,[4] and termed the similarity property.

Now if the temperature-dependent lattice contribution to the free energy, $F_L(T)$, were a function of ω as well as of T, these conclusions about invariance with respect to M would not follow, since the derivation of Eq. (2.7), depending on Eq. (2.4), would turn up terms involving $F_L(T,\omega)$ which could not be written in reduced form.[16] This means the critical field curve could not be given in purely reduced form, in contradiction to its observed invariance with respect to M. Thus the initial assumption that $F_L(T)$ is independent of ω is supported.

4. SPECIAL FORMS OF K(ω) AND EXPERIMENTAL COMPARISONS

Although $K(\omega)$, the effective number of normal electrons (relative to the normal state), cannot be determined without a detailed theory of the interaction producing the electron condensation, some information about $K(\omega)$ follows from the condition that the phase transition be a second-order transition (an assumption already used in the general analysis of Sec. 2). Thus ω must shown no sudden jumps at T_c or at lower T (note all considerations are for zero magnetic field). It will follow that the α model of Casimir and Gorter is a permissible and plausible choice to represent $K(\omega)$ which then permits systematic and satisfactory repre-

---

[12] For example, Bardeen's interaction term in the Hamiltonian is assumed proportional to the lattice vibration amplitudes [Phys. Rev. **80**, 567 (1950), Eq. (2.6)], and this makes the interaction energy, or H_0^2 [Eq. (4.26)], proportional to M^{-1}, as observed in the isotope shift.

[13] Note that the relation between γ and $q(0)$ in reference 10 established without any model shows that the invariance of H_0/T_c to change of M follows directly from the invariance of $h(t)$ and γ, and is thus not an independent test of the model.

[14] E. Maxwell, Phys. Rev. **86**, 235 (1952).

[15] Lock, Pippard, and Shoenberg, Proc. Cambridge Phil. Soc. **47**, 811 (1951).

[16] The critical field curve becomes

$$h^2=\omega_e+t^2\frac{[1-K(\omega_e)]}{K'(0)}-t^2\frac{[1-K(\omega_e)]}{\beta K(0)}\frac{\partial F_L(T,\omega_e)}{\partial\omega_e}+\frac{1}{\beta}[F_L(T,0)-F_L(T,\omega_e)].$$

sentation of the measured values of thermodynamic properties.

By definition ω takes values only in the restricted, positive range from 0 to 1, and β, the condensation energy, is an intrinsically positive quantity, as shown by Eq. (2.5). Then $K(\omega)$ must decrease as ω increases from 0, for if $K(\omega)$ increased with ω, finite values of ω would be favorable at all T since $F_s(T, \omega)$, as given by Eq. (2.1), would then decrease. Also $K(0)=1$, since by definition $\omega=0$ in the normal state, corresponding to F_n given by Eq. (2.2).

Evidently values of $\omega>0$ will not be favorable as long as $(\partial F_s(T,\omega)/\partial\omega)_{\omega=0}>0$. The transition point, given by

$$(\partial F_s(T_c,\omega)/\partial\omega)_{\omega=0}=-\beta-\tfrac{1}{2}\gamma T_c^2K'(0)=0, \quad (4.1)$$

marks the beginning of the temperature range in which finite values of ω are favorable. However, if a finite jump increase in ω at T_c is not to be favorable, we must have

$$(\partial^2F_s(T_c,\omega)/\partial\omega^2)_{\omega=0}=-\tfrac{1}{2}\gamma T_c^2K''(0)>0, \quad (4.2)$$

since the second derivative will dominate the change of F_s with ω at T_c. From Eq. (4.1) or Eq. (2.3), $K'(0)<0$, and from Eq. (4.2), $K''(0)<0$.

The same arguments apply at any $T<T_c$ if no finite jumps in ω are to occur and lead to the general conditions:[17]

$$K'(\omega)<0;\quad K''(\omega)<0;\quad 0\leq\omega\leq 1. \quad (4.3)$$

A further interesting general result is that ω_e must be a monotonically increasing function of t as t decreases, since by Eq. (4.3) $K'(\omega)$ is negative and decreasing as ω increases, and by Eq. (2.3) which gives ω_e as a function of t, $K'(\omega_e)$ monotonically decreases (algebraically) as t decreases.

In addition to the conditions Eq. (4.3) on $K(\omega)$, $K(0)=1$ as noted above and it is reasonable to take $K(1)=0$. The latter implies that the effective number of normal electrons vanishes at 0°K, a conclusion for which there is some evidence from the specific heat and from the behavior of the high-frequency losses. Thus if $K(1)$ is finite, there will be a linear term in the specific heat of the superconducting phase.[18] Since no linear term has been observed, this is also evidence that $K(1)=0$. Pippard[19] has shown that the losses in tin at 3-cm wavelength approach zero at 0°K, hence $K(\omega)$ should approach zero at 0°K, since it is plausible that the same $K(\omega)$ enters into the effective number of normal electrons determining both the specific heat and the Ohmic conductivity (at sufficiently low frequencies —at higher frequencies excited electrons produced by internal photoeffect might be expected to produce additional Ohmic currents).

Now a general function that satisfies the boundary conditions $K(0)=1$, $K(1)=0$ can be given in the form

$$K(\omega)=(1-\omega)^{\alpha(\omega)}. \quad (4.4)$$

$\alpha(\omega)$ might be reasonably expected to be a slowly varying function of ω, since the boundary conditions at $\omega=0$, 1 are automatically satisfied for any finite α (which is positive at $\omega=1$). The conditions Eq. (4.3) will now give restrictions on the slowness of variation of $\alpha(\omega)$, namely on its derivatives, but it will be sufficient here to show that constant α provides enough flexibility to reproduce the measured values. This is the original model of Casimir and Gorter,[1] conveniently termed the α model. The conditions, Eq. (4.3) then require[20]

$$0<\alpha<1. \quad (4.5)$$

The general relations of Sec. 2 reduce to special forms for the α model. These are tabulated briefly for

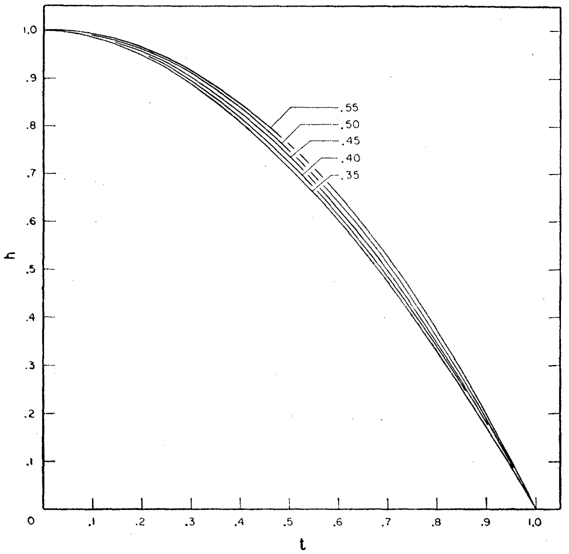

FIG. 1. Reduced critical field curves according to the α model for various values of α.

---

[17] The argument is really repeated at $\omega=\omega_e$ for each $t<1$, at which $(\partial F_s(T,\omega_e)/\partial\omega)=0$, but this covers $0\leq\omega\leq 1$. Conditions similar to (4.3) are obtained by Landau and Lifshitz at the Curie point of a general order-disorder transformation, also by consideration of expansions in powers of the order parameter. See L. Landau and E. Lifshitz, *Statistical Physics* (Oxford University Press, London, 1938), e.g., p. 207, Eq. (69.5).

[18] If $K(1)$ were finite it would follow from Eq. (2.13) that S_s^{elect} would contain a linear term (plus higher order terms). Consequently C_s^{elect} would also contain a linear term. Otherwise stated a linear term in Eq. (2.14b) would arise only from $K(1)\neq 0$, since, as a consequence of Eq. (2.16), the term $[K'(0)/t](d\omega_e/dt)\rightarrow 0$ as $t\rightarrow 0$.

[19] A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 98 (1950).

[20] In a certain sense a superconductor with larger α may be regarded as more strongly superconducting since $\alpha\rightarrow 1$ tends to convert the second-order transition into the stronger first-order type. Smaller α makes the transition less abrupt (possibly nonsuperconductors can be interpreted as having $\alpha<0$). α measures how strongly the electron condensation affects the mean potential acting on all electrons, but does not measure the size of the condensation energy which is what determines T_c. It will be readily seen that α is given by $-K'(0)$, the rate at which the effective number of normal electrons decreases as the condensation process starts.

reference in Appendix I together with the special simple case $\alpha=\frac{1}{2}$ which leads to the well-known parabolic critical field law and has a special place in the theory.

The significance of the case $\alpha=\frac{1}{2}$ with its particularly simple formulas is shown by the reduced critical field curves in Fig. 1. The curves cross at $t=0$ and 1, and all have zero slope at $t=0$. In fact the curves for the general case with arbitrary $K(\omega)$ are all parabolic for small t, although with different curvatures, since the temperature-dependent part of (2.4) is then dominated by the term $-\frac{1}{2}\gamma T^2$ which arises from the Fermi-Dirac statistics.[21] In addition the curves are rather insensitive to change of α around $\frac{1}{2}$; thus a 20 percent change from 0.5 to 0.4 produces a maximum deviation in h values of only 5 percent. The curves therefore all tend to look parabolic, and rather good precision (of the order of a few tenths of a percent), only recently attained, is required to fix α more exactly from experimental data.

Curves showing the deviations from the parabolic case, $h_{\frac{1}{2}}-h_\alpha$, plotted in Fig. 2 against t^2, are convenient for analyzing the experimental results.[22] Some of the experimental data for tin, thallium, indium, and mercury are shown in Fig. 2, for purposes of comparison. The general trend of these data is consistent with the form suggested by the α model in the measured range of temperature. The fact that tin, thallium, and indium appear to be characterized by the same value of α (0.38) is probably without significance. The internal consistency of the data is good, as indicated by the relatively small scatter. Nevertheless the degree of convexity of the experimental curves, and consequently the appropriate α, is sensitive to small changes in the value of H_0 used for normalization. H_0 is obtained by an extrapolation procedure which involves fitting the data to some smooth function, in the case of Fig. 2, a cubic equation. However with another and equally reasonable choice of smoothing function it was observed that the indium and thallium points shifted down to the neighborhood of the $\alpha=0.45$ curve while the tin points continued to cluster around $\alpha=0.40$. Nevertheless the curves are definitely convex in spite of the fact that α cannot be precisely specified. For mercury, however, the data are very closely parabolic. A fuller discussion of these and other experimental matters will appear in another paper.[22]

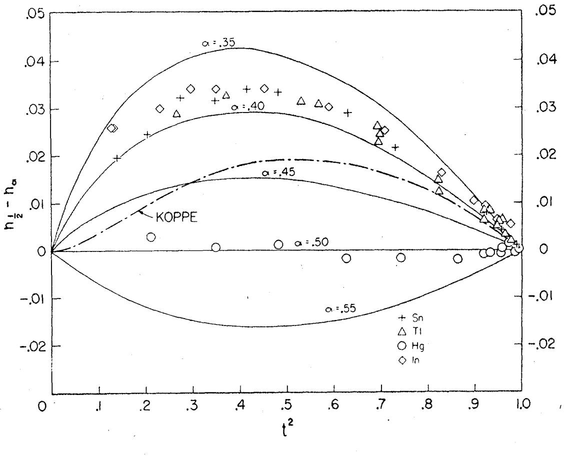

FIG. 2. Plots of the deviation of the critical fields from parabolic form for the α model, the K model, and the experimental data.

Also plotted in Fig. 2 are the predicted values given by an interesting special form of the two-fluid model due to Koppe[23] which has been used in two recent papers to compare with experimental results.[24] Koppe obtains a unique form for $K(\omega)$ and the various thermodynamic functions by means of a statistical assumption derived from Heisenberg's theory of superconductivity. Koppe's curve is not inconsistent with the indium and thallium data, if we take into account the uncertainties in H_0 discussed above. There would appear to be a small, but not very serious disagreement with the tin data. For these three metals both the Koppe model and the α model are plausible descriptions at temperatures above 1°K. The mercury data are, however, accurately parabolic and hence conflict with Koppe's model which predicts a universal (nonparabolic) critical field curve for all superconductors. The parabolic behavior was first observed both in a mercury sample contained in a glass capillary and later confirmed for a single-crystal free rod, thus minimizing the possibility of secondary effects due to strain.

No single value of α will fit Koppe's curve, as shown by Fig. 3 where the equivalent α values, i.e., the values of constant α giving the same h at that t, are plotted against t. [These are not quite the values of $\alpha(\omega)$ that would occur in a representation of Koppe's curve in the form Eq. (4.4).] The difference from the α model is particularly marked at low t, where Koppe's values for the effective number of normal electrons, n_e, proportional to $K(\omega)$, decrease more rapidly than any α model and the decrease is, in fact, exponential as shown by (II.18). Analysis of electronic specific heat and thermal conductivity measurements should be useful here, since they depend directly on n_e, whereas h is rather insensitive to n_e at low t (all curves becoming parabolic with zero slope at $t=0$; Koppe's curve has also the same curvature as the simple parabola of the case $\alpha=\frac{1}{2}$). (See remarks under footnote 26.)

Koppe's equations follow from the assumption that the density of electron states (in energy) has a discontinuity at the Fermi level (for 0°K), ϵ_0, remaining the same below ϵ_0, but being reduced by the factor $(1-\omega)$ above ϵ_0. This is qualitatively deduced from Heisenberg's picture of a condensation of a portion ω of the electrons at the Fermi surface resulting from Coulomb

---

[21] $K(1)=0$ and $(1-\omega_e)/t^2\rightarrow 0$ as $t\rightarrow 0$ as in reference 19.

[22] E. Maxwell and O. S. Lutes (to be published).

[23] H. Koppe, Ann. Physik (6), **1**, 405 (1947).

[24] Reference 5 and Worley, Zemansky, and Boorse, Phys. Rev. **87**, 1142(L) (1952).

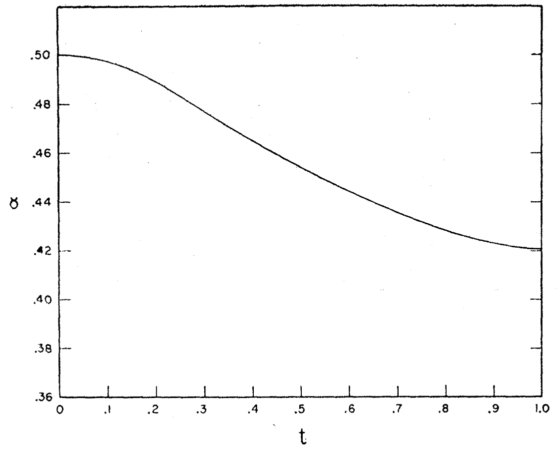

FIG. 3. The equivalent values of α for the Koppe model expressed as a function of t.

interactions between electrons.[25] The density of states is thus not defined at the Fermi level because of the discontinuity, but it is not surprising that the statistical calculation gives for $K(\omega)$ a value close to the geometric mean of the two values above and below the discontinuity, namely $(1-\omega)^{\frac{1}{2}}$. Koppe's formulas may be obtained in simplified form by evaluating the Fermi-Dirac integrals differently (without the usual integration by parts), and in fact reduced to tabulated functions, so that it seems worth while to repeat some of them here, and they are listed in Appendix II.[26] Goodman has independently obtained simplifications of Koppe's equation similar to those given here (Cambridge thesis, unpublished).

In view, on the one hand, of the recent successes of the lattice vibration interaction theory and, on the other hand, of various severe criticisms of the Heisenberg theory, it would seem that the original basis for Koppe's assumptions is very doubtful. His resulting value for $K(\omega)$ is, however, quite reasonable, although it is quantitatively in disagreement with experimental results for mercury. The greater flexibility of the α model permits fairly accurate characterization of all the measurements, although it too has as yet no fundamental justification.

It is noteworthy that Koppe has made a definite and quite simple statistical assumption in deriving his results, thus going one stage further back than the discussion of the α model given above. However a similar, although not as simple, statistical assumption could easily be introduced to obtain the α model[27] and eventually the lattice vibration theory may derive some statistical basis of this kind. Meanwhile the adequacy of the α model should be tested by additional measurements, both on more superconductors, and at lower temperatures where the predictions of the two models above differ substantially with regard to the effective number of normal electrons.

The authors are indebted to Dr. J. Bardeen for helpful comment and discussion.

APPENDIX I

Tabulated Relations for the α Model

		General α	Case $\alpha=\frac{1}{2}$	
$K(\omega)$	=	$(1-\omega)^{\alpha}$	$(1-\omega)^{\frac{1}{2}}$	(I.1)
$K'(0)$	=	$-\alpha$	$-\frac{1}{2}$	(I.2)
ω_e	=	$1-t^{2/(1-\alpha)}$	$1-t^4$	(I.3)
$K(\omega_e)$	=	$t^{2\alpha/(1-\alpha)}$	t^2	(I.4)
h^2	=	$1-t^2/\alpha+(1/\alpha-1)t^{2/(1-\alpha)}$	$(1-t^2)^2$	(I.5)
$(dh/dt)_{t=1}$	=	$[2/(1-\alpha)]^{\frac{1}{2}}$	2	(I.6)
γ	=	$H_0^2V_m/T_c^2 4\pi\alpha$	$H_0^2V_m/T_c^2 2\pi$	(I.7)
γ	=	$(dH/dT)^2{}_{T=T_c}V_m(1-\alpha)/8\pi\alpha$	$(dH/dT)^2{}_{T=T_c}V_m/8\pi$	(I.8)
$S_s{}^{\text{elect}}/\gamma T$	=	$t^{2\alpha/(1-\alpha)}$	t^2	(I.9)
$C_s{}^{\text{elect}}/\gamma T$	=	$t^{2\alpha/(1-\alpha)}(1+\alpha)/(1-\alpha)$	$3t^2$	(I.10)
$(C_s-C_n)/\gamma T_c$	=	$2\alpha/(1-\alpha)$	2	(I.11)

---

[25] The relation of Koppe's theory to a more general statistical treatment of the superconducting condensation will be given in more detail separately (see reference 7). This treatment relates the condensation to the usual band theory of metals by introducing a mean potential for any of the electrons, which depends on and which determines the quantum levels over which all the electrons are distributed according to the Fermi-Dirac statistics. The treatment is qualitatively linked to the lattice vibration interaction theory.

[26] Preliminary reports of thermal conductivity measurements at very low t do indicate an exponential form for the effective number of normal electrons; B. B. Goodman, Cambridge thesis (unpublished) also Report on Oxford Conference for Very Low Temperature Physics (1951); Proc. Phys. Soc. (London) **A66**, 217 (1953); J. G. Daunt *et al.*, Proceedings of Schenectady Cryogenics Conference (1952). Thus while the α model may be adequate for $t>0.3$, a form of $K(\omega)$ like that of Koppe's may be better at lower t, although it should be noted that Koppe predicts the same exponential for all superconductors, as shown by (II.18).

[27] Assume the density of states for energies greater than ϵ_0 is reduced by a factor $g(\omega)$ rather than $(1-\omega)$. Then for each α, $g(\omega)$ can be determined to give $K(\omega)=(1-\omega)^{\alpha}$. (II.1), (II.2) are simply modified by replacing by $1-g(\omega)$ wherever ω appears explicitly. (II.4), (II.5) have similar, although slightly different, replacements.

APPENDIX II

Simplified and Limiting Forms of Koppe's Model

$$K(\omega)=(1-\omega)(1+3a^2/\pi^2\omega)+(6\omega/\pi^2)f(1/(1+e^a)), \qquad \text{(II.1)}$$

$$\omega=a/\ln(1+e^a), \qquad \text{(II.2)}$$

$$f(x)=-\int_0^x dx\ln(1-x)/x=\sum_{n=1}^{\infty}x^n/n^2, \qquad \text{(II.3)}$$

$$K'(\omega)=-1+3a^2(1-2\omega)/\pi^2\omega^2+(6/\pi^2)f[1/(1+e^a)], \qquad \text{(II.4)}$$

$$K''(\omega)=-(6a/\pi^2\omega)(da/d\omega). \qquad \text{(II.5)}$$

Together with Eqs. (2.3)–(2.15), (II.1)–(II.5) permit simple numerical calculation of the various thermodynamic functions and the critical field curve. The function $f(x)$ has been discussed and tabulated by Mitchell.[28] In the present application the complete range of interest is $0\leqslant x\leqslant 0.5$ for which the series converges rapidly; in the worst case, $x=0.5$, only 8 terms are required for four place accuracy.

Of particular interest are the limiting forms of the functions in (II.1)–(II.5) and various other functions, as t approaches 1 and 0, since these permit direct comparison with the α model. Thus, when

$$t\rightarrow 1, \quad \omega_e\rightarrow 0, \quad a_e\rightarrow 0, \qquad \text{(II.6)}$$

$$a\cong\omega(1+\omega/2)\ln 2+O(\omega^3), \qquad \text{(II.7)}$$

$$K(\omega)\cong K(0)+\omega K'(0)+(\omega^2/2)K''(0)+O(\omega^3) \qquad \text{(II.8)}$$

$$=1-(\omega/2)-(3/\pi^2)(\ln^2 2)\omega^2+O(\omega^3),$$

$$\omega_e\cong(\pi^2/6\ln^2 2)(1-t)+O[(1-t)^2], \qquad \text{(II.9)}$$

$$[(C_s-C_n)/\gamma T_c]_{t=1}=(\pi^2/12\ln^2 2)=1.7118; \qquad \text{(II.10)}$$

and similarly when

$$t\rightarrow 0, \quad \omega_e\rightarrow 1, \quad a_e\rightarrow\infty, \qquad \text{(II.11)}$$

$$(1-\omega)\cong(e^{-a}/a)+O(e^{-2a}/a), \qquad \text{(II.12)}$$

$$K(\omega)\cong e^{-a}(3a/\pi^2+6/\pi^2+1/a)+O(ae^{-2a}), \qquad \text{(II.13)}$$

$$K'(\omega)=-1-3a^2/\pi^2+6e^{-a}/\pi^2+O(ae^{-2a}), \qquad \text{(II.14)}$$

$$a_e\cong(c/t)(1-t^2+O(t^4)+O(e^{-a_e}/a_e), \qquad \text{(II.15)}$$

where

$$c=(\pi^2/6)^{\frac{1}{2}}=1.2826, \qquad \text{(II.16)}$$

$$\omega_e=1-(t/c)e^{-c/t}[1+tc+(1+c^2/2)t^2+O(t^3)]+O(e^{-2a_e}/a_e), \qquad \text{(II.17)}$$

$$K(\omega_e)=(e^{-c/t}/2ct)[1+(c+2/c)t+(3+c^2/2)t^2+O(t^3)]+O(a_e e^{-2a_e}). \qquad \text{(II.18)}$$

---

[28] K. Mitchell, Phil. Mag. **40**, 351 (1949). $f(x)$ is tabulated over $x=-1.00(0.01)1.00:9D$ and over $x=0.000(0.001)0.500:9D$.