Theory of the Specific Heat of Superconductors Based on an Energy-Gap Model*

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A two-fluid model of a superconductor is proposed, based on an approximation in which one-electron states within a range of the order of kT_c from the Fermi level are forbidden. It is assumed that the corresponding energy gap decreases with temperature and vanishes at the transition temperature; such an assumption is necessary in order to have a second-order transition. Assumptions are also made concerning the behavior of the electrons in a superconductor, and general formulas are developed involving two parameters which describe the approximate shape of the gap. Detailed calculations are presented for two different sets of values of these parameters, and our results for the electronic specific heat predict the general exponential dependence on temperature which agrees with recent experimental data for Sn and V.

1. INTRODUCTION

MANY of the features of superconductivity can be approximately described by a phenomenological two-fluid model. For instance, the Gorter and Casimir model‡ is in fair agreement with much of the specific heat and critical magnetic-field data and has been extensively used because of its simplicity. However, strong deviations from its predictions (*viz.*, T^3 specific heat and parabolic critical field) have been observed recently, and we propose here a two-fluid model based on an energy gap to account for these new data.

Recent specific heat[1–3] and thermal conductivity[4] measurements, as well as microwave and far infrared absorption experiments,[5] indicate that there is a finite energy difference between the ground state of a superconductor and its first excited state. On the other hand, a recent microscopic theory put forward by Bardeen and his group[6] predicts that the electron-phonon interaction, when strong enough to overcome the Coulomb repulsion, will provide a finite excitation energy of the right amount. Therefore we can say that there is both an experimental and a theoretical basis for such an energy difference.

2. ONE-ELECTRON APPROXIMATION

At the time the work to be described here was done, there was no satisfactory microscopic theory of superconductivity, i.e., no solution of the many-body problem had been found in which the excited states of the system as a whole had the characteristic features of a superconductor. Following a suggestion of Bardeen, we have worked out a phenomenological theory of the thermal properties of superconductors based on a one-electron approximation.

In this approximation the excited states of a superconductor as a whole are described in terms of individual-particle excitations. According to this picture the excited electrons in a superconductor behave similarly to excited electrons in normal metals. Further, for $T \ll T_c$ the bulk of the electrons is assumed to form a "condensed" superconducting component with a condensation energy $\phi(n)$, depending on the number of excited electrons per unit volume. The energy required to excite an electron-hole pair, $\Delta(T)$, then plays the role of a gap in the one-electron energy spectrum (E_G in Bardeen's Eq. 12):

$$\Delta(T) = (\partial\phi/\partial n)_{n=n(T)}.$$

Furthermore we assume that only the excited electrons (and their corresponding holes) contribute to the entropy. Experiments by Daunt and Mendelssohn[7] which show that the Thomson coefficient of superconductors vanishes seem to justify this assumption.

Under these assumptions we can write the free energy of a superconductor as a sum of two terms: (1) the temperature-dependent free energy of an electron ideal gas (the n excited electrons per unit volume), and (2) an additional term, $\phi(n)$, corresponding to the condensation energy of the superconducting electrons. The state of thermodynamic equilibrium will be found by minimizing the free energy with respect to n. From the minimum condition one can eliminate the number of excited electrons per unit volume from the expression for the free energy, which then becomes a function of the temperature alone, enabling the calculation of the specific heat by differentiation. Unfortunately the resulting equations cannot be solved analytically (as in

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[6] Bardeen, Cooper, and Schrieffer, Phys. Rev. **106**, 162 (1957). The author wishes to thank Dr. Bardeen for communicating their results prior to publication.
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the case of the Gorter and Casimir model), and we shall have to use numerical methods.

In Sec. 3 we work out the expressions for the free energy and specific heat for a model of this sort, and in Sec. 4 we apply the method to a specific case in which it is assumed that $\phi(n)=-\text{constant}\times(n_c-n)^2$. It is assumed further that the energy of the excited electrons and holes can be estimated from a temperature-dependent density of states, differing from that of the normal metal.

3. FREE ENERGY AND SPECIFIC HEAT

We base our discussion on a one-electron approximation in which, as a consequence of the interactions leading to superconductivity, the energy of a particular one-electron level depends strongly on the occupation numbers of all the other one-electron levels. Above a characteristic temperature this effect is small because there are a relatively large number of electrons outside the Fermi surface. However, as the temperature decreases, more and more electrons occupy states inside the Fermi surface, and as a result the energy shifts become appreciable. We assume that the nature of the interactions is such that the levels close to the Fermi surface are pushed apart and that the effect is small for levels far from the Fermi surface. This situation is represented schematically in Fig. 1. Above the characteristic temperature, Δ would be zero, and both a and b would vanish too. As the temperature decreases and the interactions become important, the gap width Δ would increase, with a tendency to saturate at very low temperatures. In the same way, just below the characteristic temperature, only the states near the edge of the gap would be affected; as the temperature decreases, the interaction extends its effect to levels farther away. The whole picture can be described by saying that both parameters a and b as well as Δ decrease with temperature and become negligible above the characteristic temperature.

The existence of an energy gap is equivalent to assuming a nonvanishing condensation energy, ϕ, for the superconducting electrons. We assume that the free energy of the superconducting state may be written as

$$F_s(n,T)=2kT\left\{n\ln\lambda-\int_0^\infty d\epsilon N_s(\epsilon)\ln(1+\lambda e^{-\epsilon/kT})\right\}+\phi(n), \quad (1)$$

where n=number of thermally excited electrons per unit volume, $\lambda=e^{\mu/kT}$ (μ being the chemical potential), T=absolute temperature, k=Boltzmann constant, ϵ=one-electron energy, $N_s(\epsilon)$=volume density of states, and $\phi(n)$=condensation energy.

In (1) the factor of 2 takes into account the free energy of the holes; also $N_s(\epsilon)$ may depend on a parameter and is not necessarily equal to the volume density of states in the normal metal, $N_n(\epsilon)$. The condensation energy cannot be simply proportional to n, because this would give a constant gap, and as a result we would not have a second-order transition at T_c without making rather artificial assumptions about $N_s(\epsilon)$.

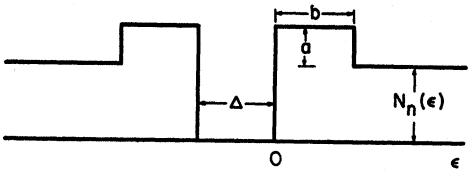

FIG. 1. Density of one-electron levels in a superconductor according to an individual-particle excitation approximation.

Imposing the minimal conditions on the free energy, i.e.,

$$\left[\frac{\partial}{\partial n}F_s(n,T)\right]_T=0, \quad (2)$$

we can solve for $n=n(T)$, which when substituted into $F_s(n,T)$ leads to

$$F_s(n(T),T)=\mathfrak{F}_s(T).$$

Carrying out the operation indicated in (2), we obtain

$$kT\ln\lambda(T)\equiv\mu=-\tfrac{1}{2}(\partial\phi/\partial n)_T. \quad (3)$$

In thermodynamic equilibrium the total number of excited electrons per unit volume is given by

$$n(T)=\int_0^\infty N_s(\epsilon)\frac{\lambda e^{-\epsilon/kT}}{1+\lambda e^{-\epsilon/kT}}d\epsilon.$$

If $N_s(\epsilon)$ has the form shown in Fig. 1, we have

$$n(T)=(1+a)N_n(0)kT\ln(1+\lambda)-aN_n(0)kT\ln[1+\lambda^{(2b+1)}], \quad (4)$$

where λ is given by Eq. (3).

At low temperatures, if $\partial\phi/\partial n\gg kT$, we can approximate (4) by

$$n(T)=(1+a)N_n(0)kT\exp\left(-\frac{\partial\phi}{\partial n}\Big/2kT\right)$$

which corresponds to the classical statistics approximation.

It will be possible to express the free energy as a function of the temperature alone, once we have solved Eq. (4) for n as a function of T. This cannot be done analytically because the right hand side of that equation also involves n, through λ. Nevertheless, the derivatives of $\mathfrak{F}_s(T)$ with respect to T can be formally expressed in terms of the derivatives of $F_s(n,T)$ and n with respect to T and n. We are particularly interested in the second derivative, since

$$C_s(T)=-T(d^2\mathfrak{F}_s/dT^2).$$

Thus

$$C_s(T)=-T\left(\frac{\partial^2 F_s}{\partial T^2}+\frac{\partial^2 F_s}{\partial n\partial T}\frac{dn}{dT}\right), \tag{5}$$

since $(\partial F_s/\partial n)_{\text{equilibrium}}=0$.

Combining Eqs. (1), (3), and (5) leads to

$$C_s(T)=2\left(\frac{\partial E}{\partial T}+\frac{\partial E}{\partial n}\frac{dn}{dT}\right)+\frac{\partial\phi}{\partial n}\frac{dn}{dT}, \tag{6}$$

where

$$E=\int_0^\infty N_s(\epsilon)\frac{\epsilon\lambda e^{-\epsilon/kT}}{1+\lambda e^{-\epsilon/kT}}d\epsilon$$

is the total energy of the excited electrons. We may write

$$C_s(T)=\frac{dE^{\text{electrons}}}{dT}+\frac{dE^{\text{holes}}}{dT}+\frac{d\phi}{dT},$$

which has an obvious interpretation.

Our program is to calculate $C_s(T)$. In order to do this we will calculate E. If $N_s(\epsilon)$ has the form shown in Fig. 1, we have

$$E=N_n(0)k^2T^2f(\lambda), \tag{7}$$

where $|\lambda|\leqslant 1$, and $f(\lambda)$ is given by

$$f(\lambda)=(1+a)\sum_{m=0}^{\infty}(-1)^m\frac{\lambda^{m+1}}{(m+1)^2}-a\sum_{m=0}^{\infty}(-1)^m\frac{\lambda^{(2b+1)(m+1)}}{(m+1)^2}$$
$$-2a\frac{\mu}{kT}\sum_{m=0}^{\infty}(-1)^m\frac{\lambda^{(2b+1)(m+1)}}{(m+1)},$$

a and b having the meaning given in Fig. 1.

All the variables will be expressed in terms of their values at T_c, i.e., $y\equiv n/n_c$, $t\equiv 1/x\equiv T/T_c$, $c_s(t)\equiv C_s(T)/C_n(T_c)$, and

$$g(n)\equiv\frac{\partial\phi}{\partial n}\Big/\delta kT_c.$$

Combining (6) and (7) then leads to

$$c_s(t)=\frac{6}{\pi^2}t\left[2f(\lambda)+t\frac{d\lambda}{dt}\frac{df}{d\lambda}\right]$$
$$+\frac{3}{\pi^2}\delta g(y)\frac{dy}{dt}\ln 2\equiv c_1(t)+c_2(t). \tag{8}$$

TABLE I. Calculated specific heat for Model (1): $a=0$, $b=0$ $\Delta=3.0$. Here $t\equiv 1/x\equiv T/T_c$, $y\equiv n/n_c$, and $c_s(t)\equiv C_s(T)/C_n(T_c)$.

x	y	λ	dy/dt	$c_1(t)$	$c_2(t)$	$c_s(t)$
1.10	0.438	0.397	1.48	0.852	0.524	1.40
1.50	0.126	0.14	0.74	0.270	0.405	0.68
2.00	0.040	0.057	0.34	0.091	0.205	0.30
3.00	0.0055	0.011	0.092	0.015	0.058	0.073
4.00	0.0009	0.0025	0.026	0.001	0.016	0.017

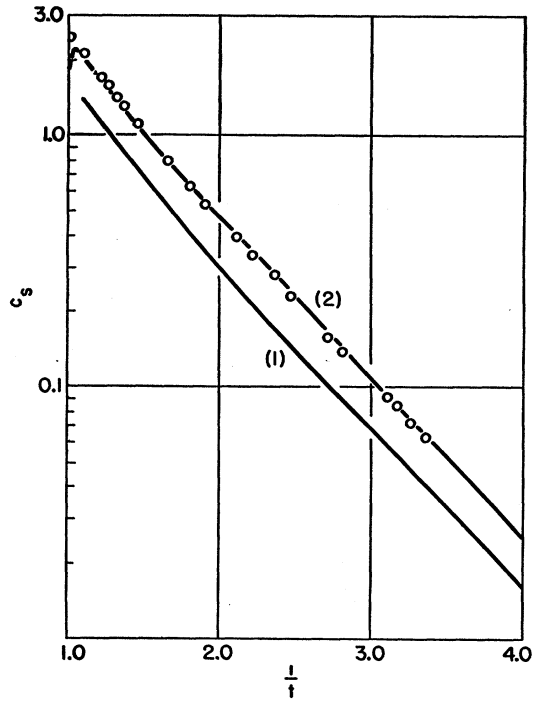

FIG. 2. Calculated values for the reduced specific heat, in the case of an energy gap $\Delta(0°\text{K})=3.0kT_c$ at 0°K. $C_s\equiv C_s(T)/C_n(T)$. $t\equiv T/T_c$. Curve (1) corresponds to the choice $a=0$ and $b=0$; curve (2) corresponds to $a=0.50$ and $b=1.0$. The experimental points are for Sn, and were taken from reference 2.

Detailed calculations are described in the following section.

4. RESULTS FOR THE SPECIFIC HEAT

In order to make use of the preceding results we must assume a functional relation, $g(n)$, between the condensation energy $\phi(n)$ and the number of excited electrons n per unit volume. Since there is no indication either from theory or experiment for the form of $g(n)$, we assume the simplest interpolation formula that satisfies the boundary conditions on the gap; *viz.*, $g(n)=(1-n/n_c)$. This choice corresponds to a condensation energy

$$\phi(n)=-(\delta/2n_c)kT_c(n_c-n)^2.$$

Based on this assumption, the equations become, in terms of the reduced variables,

$$y(t)=\frac{t}{\ln 2}\left\{(1+a)\ln\left[1+\exp\left(-\frac{\delta}{2t}(1-y)\right)\right]\right.$$
$$\left.-a\ln\left[1+\exp\left(-(2b+1)\frac{\delta}{2t}(1-y)\right)\right]\right\}, \tag{9}$$

$$\lambda=e^{-(\delta/2t)(1-y)}, \tag{10}$$

and

$$\frac{dy}{dt}=\frac{\frac{y}{t}+\frac{(1-y)}{t}\frac{\lambda\delta}{2\ln 2}\left[\frac{1+a}{1+\lambda}-\frac{a(2b+1)\lambda^{2b}}{1+\lambda^{2b+1}}\right]}{1-\frac{\lambda\delta}{2\ln 2}\left[\frac{1+a}{1+\lambda}-\frac{a(2b+1)\lambda^{2b}}{1+\lambda^{2b+1}}\right]}. \quad (11)$$

We are interested in solutions of (9), $y\leqslant 1$; we see that when $t=1$, $y=1$ is a solution, while at low temperatures $y(t)=(1+a)\exp(-\delta/2t)/\ln 2$. In other words, at the transition temperature $n=n_c$, so that the condensation energy vanishes while at low temperatures the number of excited electrons per unit volume decreases exponentially.

We have calculated the specific heat under two different assumptions, *viz.*, (1) $a=0$, $b=0$, $\Delta=3.00kT_c(1-y)$, and (2) $a=0.5$, $b=1$, $\Delta=3.00kT_c(1-y)$; the total number of states is conserved in the second model, but not in the first one. Tables I and II show the results of our calculations, and in Fig. 2 the specific heat is compared with the latest measurements on tin.[2]

Model (1): $a=0$, $b=0$, and $\Delta=3.00$.—The calculated specific heat is much too large for $1/t<1.10$ (not shown in Fig. 3), and this is essentially due to (a) nonconservation of the total number of states, and (b) the assumption $g(y)=(1-y)$ which may not be valid for y close to unity. Nevertheless for $1/t>1.10$ our results, if multiplied by 1.50, are in very good agreement with the experimental values for Sn and V. However we cannot justify this factor of 1.50 without assuming $N_s(\epsilon)\neq N_n(\epsilon)$. Hence we assumed $b=\infty$, and a suitable $a(t)$ was found empirically (Fig. 3) in such a way that the over-all effect was to multiply our curve (1) by 1.50. This model is not too realistic since the low-lying levels are hardly affected even at low temperatures. Furthermore the total number of states is not conserved.

Model (2): $a=0.5$, $b=1.0$, and $\Delta=3.00$.—For this model, which conserves the total number of states, the calculations are in very good agreement with experiments, except again for $1/t<1.10$, where the calculated values are too small. However, the calculated discontinuity in the specific heat at the transition temperature, $c_s(1)-c_n(1)$, is 0.65 whereas the experimental values are close to 1.7. In fact, any values $a=$constant and $b=\frac{1}{2}a$, predicts the same jump, 0.65, in the specific heat,

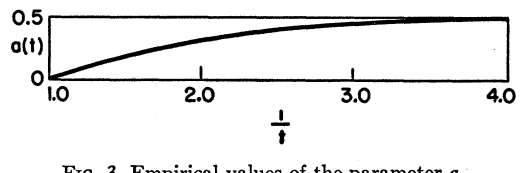

FIG. 3. Empirical values of the parameter a, as a function of temperature.

TABLE II. Calculated specific heat for Model (2): $a=0.50$, $b=1.0$, $\Delta=3.0$. In this table $t\equiv 1/x\equiv T/T_c$, $y\equiv n/n_c$, and $c_s(t)\equiv C_s(T)/C_n(T_c)$.

x	y	λ	dy/dt	$c_1(t)$	$c_2(t)$	$c_s(t)$
1.00	1.00	1.00	1.00	1.65	0.00	1.65
1.10	0.895	0.841	1.41	1.86	0.94	1.95
1.50	0.230	0.177	1.15	0.55	0.56	1.11
2.00	0.065	0.061	0.525	0.15	0.31	0.46
3.00	0.0082	0.011	0.137	0.022	0.086	0.11
4.00	0.0009	0.0025	0.036	0.0014	0.023	0.024

and the assumption $g(y)=(1-y)$ must be the source of this error.

5. CONCLUSIONS

From our calculations we can conclude that an energy-gap model of a superconductor can provide a specific heat in agreement with experiment. The gap at 0°K should be of the order of $3kT_c$,[8] decreasing with temperature, and vanishing at T_c, where the transition to the normal state occurs. Furthermore, the density of one-electron levels near the Fermi level in the superconducting state should increase as compared with the density of one-electron levels in the normal state. This increase may be of the order of 50% at $T=0.25T_c$. Below this temperature there need be no further increase in the density of one-electron levels in the superconductor, since most of the electrons (about 99.8%) have already condensed at $T=0.25T_c$. Preliminary measurements of the spin-lattice relaxation time in superconductors being carried out at the University of Illinois[9] indicate an increase in the density of one-electron levels near the edge of the gap. We may hope that further developments of the microscopic theory of superconductivity will provide a quantum-mechanical basis for such an energy-gap model.[10]

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[8] Bardeen *et al.*[6] found $3.7kT_c$ for Sn.

[9] C. P. Slichter and L. C. Hebel (private communication).

[10] The theory of Bardeen *et al.* gives an effective single-particle energy in the superconducting state, $E_s=[(E_n-E_F)^2+\frac{1}{4}E_G^2]^{\frac{1}{2}}$, where E_n is the energy of the corresponding state in the normal phase and E_G is the energy gap, equal to about $3.5kT_c$ at $T=0$°K and decreasing to zero at T_c. This gives an infinite (but integrable) density of states just above the gap.