Specific Heat of the Mixed State in Superconducting Alloys*

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Based on the previous theory of superconducting alloys in magnetic fields, we made a detailed study of the specific heat of the mixed state in superconducting alloys. The jump of the specific heat at the transition from the mixed state to the normal state is explicitly calculated for various values of κ, the Ginzburg-Landau parameter. In fields just above the lower critical field H_{c1}, we find the specific heat at lower temperature is expressed in terms of H_{c1} as

$$C_m=-(1/4\pi)T(d^2H_{c1}/dT^2)B+(dH_{c1}/dT)(\partial B/\partial T),$$

where $B=(\pi/e)n$ (n being the number of flux lines per unit area), and the first term, coming from the free energy associated with a flux line, is proportional to T.

I. INTRODUCTION

In previous papers[1] (which we shall refer to as I and II, respectively), we have discussed the magnetic properties of superconducting alloys and shown that Abrikosov's theory[2] holds independently of temperature with a slight modification.

The purpose of this note is, as a continuation of the previous investigation, to study in more detail the temperature dependence of the specific heat of the mixed state in superconducting alloys.

In the next section we calculate the specific heat of the mixed state in the immediate subcritical region ($H_{c2}-H_0\ll H_{c2}$, where H_{c2} is the upper critical field and H_0 is the external field). It is shown that in this region the specific heat is expanded in powers of T, the temperature, thanks to the fact that the gap in the excitation spectrum vanishes in this region. The jump in the specific heat at the transition from the mixed state to the normal state is calculated for various values of κ, the Ginzburg-Landau parameter. We see that the jump in the specific heat decreases as the temperature decreases and vanishes as T^3 at $T=0°\mathrm{K}$ for superconductors having a sufficiently large κ, while it diverges at a certain temperature for superconductors with κ satisfying $1.01>\kappa>0.707$ as pointed out in I.

In Sec. III we consider the situation where the external magnetic field is slightly above H_{c1}, the lower critical field. In this field region we obtain the following expression for the specific heat of the mixed state in a constant external field H_0

$$C_m-C_s=-\frac{1}{4\pi}T\left\{B\frac{d^2H_{c1}}{dT^2}+\frac{dH_{c1}}{dT}\frac{\partial B}{\partial T}\right\}, \qquad (1)$$

where C_s is the specific heat of the superconducting state, B is the magnetic induction in a given external field and H_{c1} is the temperature-dependent critical field. As is well known, C_s vanishes like $e^{-\mathrm{const}(T_{c0}/T)}$ at low temperatures. The first term in the right-hand side of Eq. (1) comes from the free energy associated with each vortex line and gives rise to a term proportional to T, which dominates at lower temperatures. The second term is almost equivalent to one obtained by Goodman[3] based on Abrikosov's theory. This term, coming from the interaction energy between flux lines, diverges at the first transition point. The existence of the term proportional to T has been anticipated by Caroli, de Gennes, and Matricon[4] through the explicit calculation of the excitation spectrum of the quasiparticles in the core region of a flux line.

In the limit $\kappa\rightarrow\infty$, using the explicit expression for $H_{c1}(T)$ and B, we calculate the temperature dependence of C_m, which is in qualitative agreement with recent experiments on the specific heat of the mixed states.[5]

II. THE SPECIFIC HEAT OF THE MIXED STATE IN THE IMMEDIATE SUBCRITICAL REGION ($H_{c2}-H_0\ll H_{c2}$)

In the immediate subcritical region where the external field H_0 is slightly smaller than H_{c2}, Gibb's free energy is given as[1]

$$G_m-G_n=-\frac{1}{8\pi}\left\{H_0^2+\frac{(H_{c2}-H_0)^2}{(2\kappa_2^2(T)-1)\beta}\right\}, \qquad (2)$$

where the subscripts m and n refer to the mixed state and the normal state, respectively, $\beta=1.159$,[6] H_{c2} is the upper critical field, and κ_2 is a temperature-dependent parameter.[1]

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[1] K. Maki, Physics **1**, 21 (1964); **1**, 127 (1964). Errata **1**, 201 (1964).

[2] A. A. Abrikosov, Zh. Eksperim. i Teor. Fiz. **5**, 1174 (1957) [English transl.: Soviet Phys.—JETP **32**, 1442 (1957)].

[3] B. B. Goodman, Phys. Letters **12**, 6 (1964).

[4] C. Caroli, P. G. de Gennes, and J. Matricon, Phys. Letters **9**, 307 (1964).

[5] G. A. Alers, Phys. Rev. **119**, 1532 (1960); J. Ferreira da Silva, J. Sheffer, N. W. J. van Duykeren, and Z. Dokoupil, Phys. Letters **12**, 166 (1964); and P. H. Keesom and Ray Radebaugh, Phys. Rev. Letters **13**, 685 (1964).

[6] W. H. Kleiner, L. M. Roth, and S. H. Autler, Phys. Rev. **133**, A1226 (1964).

The specific heat is obtained from

$$C_m-C_n=-T\frac{\partial^2}{\partial T^2}[G_m-G_n],$$
$$\simeq\frac{1}{4\pi}\frac{T}{[2\kappa_2^2(T)-1]\beta}\times\left\{\left(\frac{dH_{c2}}{dT}\right)^2+\frac{d^2H_{c2}}{dT^2}(H_{c2}-H_0)\right\}. \quad (3)$$

We note here that the jump in the specific heat at the transition from the mixed state to the normal state is given by

$$\Delta C_{mn}=\frac{1}{4\pi}\frac{T}{[2\kappa_2^2(T)-1]\beta}\left(\frac{dH_{c2}}{dT}\right)^2. \quad (4)$$

In superconducting alloys, where the electronic mean free path is much shorter than the coherence length, we have

$$C_m-C_n=\tfrac{1}{3}mp_0T\frac{4\kappa_1^2(0)}{[2\kappa_2^2(T)-1]\beta}\left\{\frac{1}{3}\left(\frac{2\pi T}{\Delta_{00}}\right)^2-\frac{3}{5}\left(\frac{2\pi T}{\Delta_{00}}\right)^4-\left[1-\frac{27}{10}\left(\frac{2\pi T}{\Delta_{00}}\right)^2\right]\frac{H_{c2}(T)-H_0}{H_{c2}(0)}\right\},$$
$$\text{for}\quad T\ll T_{c0}, \quad (5)$$

$$=\frac{8}{7\zeta(3)}mp_0T\frac{\kappa^2}{[2\kappa_2^2(T)-1]\beta}\times\left\{\left[1-4\left(\frac{1}{2}-\frac{28}{\pi^4}\zeta(3)\right)\theta\right]-2\left(\frac{1}{2}-\frac{28}{\pi^4}\zeta(3)\right)\times\frac{H_{c2}(T)-H_0}{H_{c2}(T)}\right\},\quad \text{for}\quad T_{c0}-T\ll T_{c0}, \quad (6)$$

and

$$\Delta C_{mn}=\tfrac{1}{3}mp_0T\frac{4\kappa_1^2(0)}{[2\kappa_2^2(T)-1]\beta}\left\{\frac{1}{3}\left(\frac{2\pi T}{\Delta_{00}}\right)^2-\frac{3}{5}\left(\frac{2\pi T}{\Delta_{00}}\right)^4\right\},$$
$$\text{for}\quad T\ll T_{c0}, \quad (7)$$

$$=\frac{8}{7\zeta(3)}mp_0T\frac{\kappa^2}{[2\kappa_2^2(T)-1]\beta}\left\{1-4\left(\frac{1}{2}-\frac{28}{\pi^4}\zeta(3)\right)\theta\right\},$$
$$\text{for}\quad T_{c0}-T\ll T_{c0}, \quad (8)$$

where

$$\kappa_1(0)=1.20\kappa,\quad \kappa=\frac{3m}{2\pi^2\tau_{tr}e}\left(\frac{2\pi m}{p_0^5}7\zeta(3)\right)^{1/2},$$

the Ginzburg-Landau parameter, and $\theta=1-(T/T_{c0})$.

In deriving the above expressions we have made use of asymptotic expressions of the upper critical field given in I,

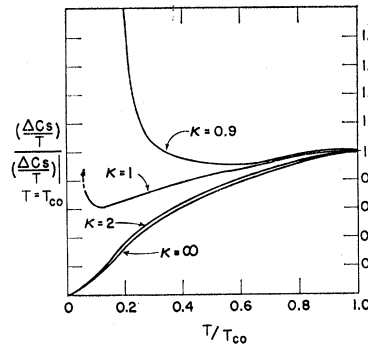

FIG. 1. The jump in the specific heat at the transition from the mixed state to the normal state is depicted for various values of κ, the Ginzburg-Landau parameter.

$$H_{c2}(T)=\frac{3\Delta_{00}}{2\tau_{tr}v^2e}\left[1-\frac{2}{3}\left(\frac{\pi T}{\Delta_{00}}\right)^2+\frac{6}{5}\left(\frac{\pi T}{\Delta_{00}}\right)^4\right],$$
$$\text{for}\quad T\ll T_{c0}, \quad (9)$$

$$=\frac{12T_{c0}}{\pi\tau_{tr}v^2e}\theta\left[1-\left(\frac{1}{2}-\frac{28}{\pi^4}\zeta(3)\right)\theta\right],$$
$$\text{for}\quad T_{c0}-T\ll T_{c0}, \quad (10)$$

where τ_{tr} is the transport collision time, v is the Fermi velocity, and Δ_{00} is the ordering parameter at $T=0$°K.

In this field region the superconductivity becomes gapless and there appears no exponential term in T in the expression of the specific heat.

From both Eqs. (7) and (8) we see that when κ is sufficiently large, the jump in the specific heat decreases as the temperature decreases and vanishes as T^3 at $T=0$°K, while it diverges at the temperature determined by $\kappa_2(T)=1/\sqrt{2}$ for superconductors with κ satisfying $1.01>\kappa>1/\sqrt{2}$ as pointed out in I. The numerical results of ΔC_{mn} for various values of κ are depicted in Fig. 1.

III. IN FIELDS JUST ABOVE THE LOWER CRITICAL FIELD ($H_0 \gtrsim H_{c1}$)

Now let us turn to the other limiting situation where the external field is slightly above H_{c1}, the lower critical field. In this region flux lines are well separated spatially and the free energy of the mixed state is given by[1]

$$G_m=G_s+\frac{1}{4\pi}B\left\{H_{c1}(T)-H_0+\frac{\alpha^2}{2e}\times\sum_{l^2+m^2+lm\geq 1}K_0\left[\alpha\left(\frac{2\pi(l^2+m^2+lm)}{\sqrt{3}eB}\right)^{1/2}\right]\right\}, \quad (11)$$

where B is the magnetic induction $[=(\pi/e)n$, where n is the number of flux lines per unit area and determined by $\partial F/\partial B=0]$, $H_{c1}(T)$ is the lower critical field, α^{-1} is the penetration depth given by[7]

$$\alpha^{-1}(T)=[(4\pi^2 eN/m)\tau_{\rm tr}\Delta\tanh(\Delta/2T)]^{-1/2}, \quad (12)$$

and K_0 is a Hankel function.

In deriving the above expression we assume that flux lines form an equilateral triangle lattice which is the most stable.[8]

The specific heat in a constant external field is obtained by

$$C_m-C_s=-T\frac{\partial^2}{\partial T^2}(G_m-G_s),$$

$$=-\frac{1}{4\pi}T\left\{\frac{d^2H_{c1}}{dT^2}B+\frac{dH_{c1}}{dT}\frac{\partial B}{\partial T}\right\}, \quad (13)$$

where we made use of the relation,

$$H_0-H_{c1}=(\alpha^2/4e)\sum(2K_0(x_{lm})+x_{lm}K_1(x_{lm})), \quad (14)$$

with

$$x_{lm}=\alpha(2\pi(l^2+m^2+lm)/\sqrt{3}eB)^{1/2}.$$

From Eq. (14) we have

$$\frac{\partial B}{\partial T}=2B\left[-\frac{4e}{\alpha^2}\frac{dH_{c1}}{dT}+\frac{1}{\alpha}\frac{d\alpha}{dT}\sum(x_{lm}^2-1)K_0(x_{lm})\right]$$
$$\times[\sum(x_{lm}^2K_0(x_{lm})+2x_{lm}K_1(x_{lm}))]^{-1}. \quad (15)$$

Substituting this expression in Eq. (13) we finally obtain

$$C_m-C_s=-\frac{1}{4\pi}TB\left\{\frac{d^2H_{c1}}{dT^2}+\frac{dH_{c1}}{dT}\right.$$
$$\times\left[-\frac{8e}{\alpha^2}\frac{dH_{c1}}{dT}+\frac{2}{\alpha}\frac{d\alpha}{dT}\sum(x_{lm}^2-1)K_0(x_{lm})\right]$$
$$\left.\times[\sum(x_{lm}^2K_0(x_{lm})+2x_{lm}K_1(x_{lm}))]^{-1}\right\}. \quad (16)$$

As we will see below the first term, coming from a free energy associated with each flux line, gives rise to a term proportional to T at lower temperature. The second term comes from the interaction energy between flux lines which diverges at the transition from the superconducting state to the normal state. The existence of the term proportional to T in the expression of specific heat has been suggested by Rosenblum and Cardona[9] based on the experiment on the microwave surface resistance of type-II superconductivity. Caroli, de Gennes, and Matricon[4] have shown the existence of the large low-lying-state density in the core region of a flux line. The present result is in qualitative agreement with their theoretical prediction.

In a field just above the lower critical field, Eq. (16) is much simplified:

$$C_m-C_s=-\frac{1}{4\pi}TB\left(\frac{d^2H_{c1}}{dT^2}+\frac{2}{\alpha}\frac{d\alpha}{dT}\frac{dH_{c1}}{dT}\right)$$
$$+\frac{1}{2\pi}T\frac{B}{H_0-H_{c1}}\left(\frac{\sqrt{3}eB}{2\pi\alpha^2}\right)^{1/2}\left(\frac{dH_{c1}}{dT}\right)^2, \quad (17)$$

where B is determined by

$$H_0-H_{c1}=(3\alpha^2/2e)(\pi\alpha/2)^{1/2}(2\pi/\sqrt{3}eB)^{1/4}$$
$$\times\exp[-\alpha(2\pi/\sqrt{3}eB)^{1/2}]. \quad (18)$$

Both C_s and $d\alpha/dT$ vanish like $e^{-\Delta/T}$ at lower temperature, and the temperature dependence of the specific heat is determined by that of H_{c1}.

Unfortunately no general expression for $H_{c1}(T)$ is available at present, which can be calculated, in principle, from the free energy associated with a single flux line.

In the following we restrict our consideration to the case of superconducting alloys with large κ, where we have[1]

$$H_{c1}(T)=\tfrac{1}{3}mp_0e\tau_{\rm tr}v^2\Delta\tanh(\Delta/2T)\ln\kappa_3(T), \quad (19)$$

with

$$\kappa_3(T)=\kappa_3(0)[1-\tfrac{2}{3}(\pi T/\Delta_{00})^2]^{1/2}, \quad \text{for} \quad T\ll T_{c0}. \quad (20)$$

We assume here that the temperature dependence of H_{c1} comes only from $\kappa_3(T)$ for simplicity. Strictly speaking $H_{c1}(T)$ might be affected by an additional constant term [independent of $\kappa_3(T)$] as well.

Substituting Eq. (19) in Eq. (17) we obtain

$$C_m=\frac{mp_0}{3}T\left\{\frac{\pi}{4}\frac{B}{H_{c2}(0)}\left[1+2\left(\frac{\pi T}{\Delta_{00}}\right)^2\right]\right.$$
$$\left.+\left(\frac{\sqrt{3}eB}{2\pi\alpha^2}\right)^{1/2}\frac{B}{H_0-H_{c1}}\frac{4}{3\kappa_3^2(0)}\left(\frac{\pi T}{\Delta_{00}}\right)^2\right\}$$
$$+O(T^5), \quad \text{for} \quad T\ll T_{c0}, \quad (21)$$

where $\kappa_3(0)=1.53\kappa$.

Contrary to the assertion made in II, there appears a term linear in T in the above expression.

When the external field H_0 is not so large, we expect that the above expression gives a correct coefficient of the linear term.

IV. CONCLUDING REMARKS

We have thus far discussed the temperature dependence of the specific heat of the mixed state based on the

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[7] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 9, 220 (1959) [English transl.: Soviet Phys.—JETP 36, 319 (1959)].

[8] Contrary to the statement made in Ref. 2, we find that an equilateral-triangle lattice is always stable rather than an equilateral-square one. We have compared the corresponding free energies in a given external field, not in a given magnetic induction B.

[9] B. Rosenblum and M. Cardona, Phys. Rev. Letters 12, 657 (1964).

previous theory of superconducting alloys.[1] We have seen that the jump in the specific heat at the transition from the mixed state to the normal state decreases as temperature decreases and vanishes as T^3 at lower temperature, if the transition is always of the second order. In the weak-field region we have found that there appears a term proportional to T in the expression of specific heat coming from the free energy associated with each flux line. Since this free energy is related to the lower critical field by

$$\epsilon(T)=(1/4e)H_{c1}(T),^{1,2} \qquad (22)$$

we have an interesting formula:

$$C_m\cong-\frac{1}{4\pi}TB\frac{d^2H_{c1}}{dT^2}+\frac{1}{2\pi}T\frac{B}{H_0-H_{c1}}\left(\frac{\sqrt{3}eB}{2\pi\alpha^2}\right)^{1/2}\left(\frac{dH_{c1}}{dT}\right)^2+O(e^{-\mathrm{const}(T_{c0}/T)}),\quad \text{for}\quad T\ll T_{c0}, \qquad (23)$$

which may be checked experimentally.

Although most of the detailed calculations are carried out by using expressions valid only for superconducting alloys, we believe that, as far as the qualitative features are concerned, the above results hold quite generally, independently of the assumption made on the electronic mean free path.

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Impurity Problem in the Tight-Binding Approximation: Application to Transition-Metal Alloys

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The characteristics of a metal with one impurity atom are deduced with a view towards application to dilute transition-metal alloys. We assume that the band structure of the pure metal is described by a tight-binding approximation. The scattering problem is expressed in a new representation whose basis functions have the symmetry of the point group of the metal. For example, it is shown that the Friedel sum rule can be expressed with a finite number of phase shifts, each of them being related to one irreducible representation of the point group. Two simple examples are studied, and detailed studies of the effects of the degeneracy and of the potential extension are made.

INTRODUCTION

THE dilute alloys of transition metals are studied assuming that the d band structure is well described in a tight-binding approximation. It is possible to describe such an alloy with a self-consistent formalism if the potential $V_p(\mathbf{r})$ associated with the impurity atom is assumed to be a perturbation.[1] When this approximation is impossible, the potential $V_p(\mathbf{r})$ is considered phenomenologically and is determined by auxiliary conditions (localization, Friedel sum rule, etc.). Such a formalism has been presented by Koster and Slater[2] in the Wannier representation. However, the applications are very difficult, not only because the band structure of pure metals is not well known, but also because a considerable mathematical complexity is involved in solving the Slater-Koster equations. The only case which has been completely solved is obtained by assuming that a matrix s band is perturbed by a localized potential extending only over the impurity atomic cell. This model is not directly valid in the case of transition-metal alloys.

We note that it is possible to solve much more general cases using a new representation which takes into account the symmetry properties: This is because the potential $V_p(\mathbf{r})$ induces transitions only between the basis functions of the same irreducible representations of the point group.

The first section of this paper is devoted to general considerations; in the second section the new representation is shown with some simple applications. This general formalism is first applied to the effect of a potential localized on one atomic cell; the effect of the degeneracy on the wave functions and on the displaced charge is studied (Sec. IC). In the following section the effect of a potential extending over the impurity atom and its nearest neighbors is discussed.

[1] F. Gautier, Ann. Phys. (Paris) 9, (1964).
[2] G. F. Koster and J. C. Slater, Phys. Rev. 95, 1167 (1954).