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Specific Heat of the Superconducting State

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A semiempirical argument is presented which shows that for tin the lattice specific heat of the normal state is also present in the superconducting state. This result follows from the law of similarity for the threshold field curves. It is also shown that the so-called "electronic specific heat" of the superconducting state contains a large contribution from the motions of the ions in the lattice.

I. INTRODUCTION

In two recent publications,[1,2] new measurements on the specific heat of superconducting vanadium and tin have been reported. These measurements are particularly significant because they are more accurate and extend to lower temperatures than any previous measurements. In the analysis of these data it was assumed that the so-called "lattice specific heat" of the normal state was also present in the superconducting state. The notion of an independent lattice specific heat in the normal state arises because it is nearly always possible to write the total specific heat of this state, C_n, in the following form,

$$C_n = \gamma T + A(T/\theta)^3. \tag{1.1}$$

In this equation, γ and A are independent of the temperature. The linear term is naturally interpreted as the contribution of the electronic motions in a static lattice and the T^3 term is interpreted as the contribution of the low-frequency lattice vibrations. This simple interpretation receives considerable support from the following facts: (i) that γ is known,[3] in a few cases, to be independent of the ionic mass; and (ii) that, at sufficiently low temperature, θ is a constant,[4] independent of the temperature.

The assumption that is made in the analysis of the specific heat data is simply that the term $A(T/\theta)^3$, of the normal state, is also present in the specific heat of the superconducting state. This term is subtracted from the total specific heat and the remainder is rather loosely referred to as the "electronic contribution." The new measurements we have referred to show that, at low temperatures, this electronic contribution has the form $aT_c\gamma\exp(-bT_c/T)$, where a and b appear to be universal constants and T_c is the transition temperature. It has been suggested[5] that this exponential form can be interpreted in terms of a gap in a one-electron energy spectrum.

The purpose of this note is to show firstly, that for tin, the equality of the lattice specific heat in the normal and superconducting state follows from the fact that the threshold fields, for the different isotopic specimens of this substance, obey a similarity law; and secondly, that in general, the "electronic contribution" to the specific heat contains a large contribution from the motion of the ions in the lattice. This fact would appear to make it rather difficult to interpret this contribution directly in terms of a simple one-electron spectrum.

We shall discuss these two points in Secs. II and III, respectively.

II. THE INVARIANCE OF THE LATTICE SPECIFIC HEAT

The law of similarity for the threshold fields for the isotopes of tin was discovered by Lock, Shoenberg, and Pippard.[6] For our purpose it can be conveniently summarized by means of the following equation:

$$H_c = (\bar{M})^{-\alpha}\phi((\bar{M})^{\alpha}T). \tag{2.1}$$

Here H_c is the threshold field for a specimen whose average isotopic mass is $\bar{M}$, T is the absolute temperature, and the function ϕ is a universal function of its argument $(\bar{M})^{\alpha}T$. The exponent is equal to 0.50 to within a few percent. The threshold fields of the different specimens of tin are known to obey this law to within 1 part in 800. This law therefore expresses, in a very precise way, the functional dependence of H_c on $\bar{M}$ and T.

From this law we can deduce the functional dependence of $C_n - C_s$ on $\bar{M}$ and T, where C_n and C_s are the specific heats in the normal and superconducting states, respectively. To do this we merely have to use the well-known thermodynamic relation,

$$G_n - G_s = H_c^2 V/8\pi. \tag{2.2}$$

where G_n and G_s are the Gibbs free energies at zero magnetic field in the normal and superconducting states, respectively, and V is the volume of the specimen. Henceforth we shall use the symbol $\sim$ to indicate the functional dependence of any quantity on $\bar{M}$ and T.

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[4] M. Blackman, *Handbuch der Physik* (Springer-Verlag, Berlin, 1955), Vol. 7, part I, pp. 325.

[5] Corak, Goodman, Satterthwaite, and Wexler, *Conference de Physique des Basses Temperatures, 1955* (Centrenational de la Recherche Scientifique and UNESCO, Paris, 1956), pp. 503–506.

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If we substitute Eq. (2.1) in Eq. (2.2), we can write

$$G_n - G_s \sim (\bar{M})^{-2\alpha}\chi((\bar{M})^{\alpha}T). \tag{2.3}$$

Now $C = -T(\partial^2 G/\partial T^2)_P$, and therefore,

$$C_n - C_s \sim (\bar{M})^{-\alpha}\psi((\bar{M})^{\alpha}T). \tag{2.4}$$

It follows that any term in C_n which has a different functional dependence on the isotopic masses and the absolute temperature, from that indicated on the right-hand side of this equation, must be exactly cancelled by an identical term in C_s. Now C_n is the sum of two terms, γT and $A(T/\theta)^3$. Since γ is known to be independent of the isotopic masses,[4] $\gamma T \sim (\bar{M})^{-\alpha}((\bar{M})^{\alpha}T)$, and this term therefore has the correct functional dependence on $\bar{M}$ and T. However, if we identify $A(T/\theta)^3$ with the contribution from the low-frequency lattice vibrations, then we can easily show that this term does not have the required functional dependence.

The most general expression for the lattice specific heat, which we denote by $C_n{}^L$, is given by the following equation:

$$C_n{}^L = k\sum_j f(\omega_j/kT), \tag{2.5}$$

where

$$f(x) = x^2 e^x/(e^x - 1)^2 \tag{2.6}$$

and k is Boltzmann's constant. In Eq. (2.5) the summation is over all the lattice frequencies ω_j; these are the solutions of the secular equation,[7]

$$D(\omega) = \begin{vmatrix} a_{11}+M_1\omega^2 & a_{12} & a_{13} & \cdots \\ a_{21} & a_{22}+M_2\omega^2 & a_{23} & \cdots \\ \cdots & \cdots & \cdots & \cdots \end{vmatrix} \tag{2.7}$$

where the a_{ij} are related to the force constants and the M_i are the masses of the atoms in the lattice. It is now a simple matter to express the lattice specific heat in terms of the determinant $D(\omega)$. We have in fact that[8]

$$C_n{}^L = \frac{1}{2\pi i}\int_C f(z/kT)\frac{D'(z)}{D(z)}dz; \quad D'(z) = \frac{dD}{dz}. \tag{2.8}$$

The contour C is such that it includes all the zeros of D but none of the poles. From Eq. (2.8), we have that

$$C_n{}^L = \frac{1}{2\pi i}\int_C f(u)\frac{D'(kTu)}{D(kTu)}du; \quad D' = \frac{dD}{du}. \tag{2.9}$$

Consequently $C_n{}^L$ depends on the masses M_i and the temperature T only through the variables $u_i = M_i T^2$. For example, if all the masses are equal to M, then $C_n{}^L$ depends on the mass and temperature only through the variable MT^2. Clearly $C_n{}^L$ does not have the required functional dependence on $\bar{M}$ and T. We therefore see that if Eq. (2.4) is valid, $C_n{}^L$ must be exactly cancelled by an identical term in C_s. We have thus shown that if the similarity law is true, then the lattice specific heat of the normal state must also be present in the superconducting state. If the similarity law is general, then our conclusions are equally general. Unfortunately, however, tin is the only substance for which an accurate similarity law has been established and we therefore cannot at the moment generalize the argument.

III. THE ELECTRONIC CONTRIBUTION TO THE SPECIFIC HEAT

If the lattice specific heat of the normal state $C_n{}^L$ is subtracted from C_s, then it is found that the remainder, C_{es}, has the form

$$C_{es} = a\gamma T_c \exp(-bT_c/T). \tag{3.1}$$

This equation appears to be valid for tin,[2] vanadium,[1] and aluminum,[9] with the same values for the constants a and b.

We have shown elsewhere[10] that if G is the Gibbs free energy of any system and $\bar{K}_M$ is the mean kinetic energy of the particles of mass M in the system, then

$$\bar{K}_M = -M(\partial G/\partial M)_{T,P}. \tag{3.2}$$

Since the difference between C_p and C_v is very small for a solid superconductor we will assume the following form for C:

$$C = C_v = (\partial U/\partial T)_V. \tag{3.3}$$

The contribution of $\bar{K}_M$ to C is therefore $(\partial\bar{K}_M/\partial T)_V$. If we denote this contribution by $C^{(M)}$, we have, from Eq. (3.2), that

$$C^{(M)} = +M(\partial S/\partial M)_{T,V}. \tag{3.4}$$

Let us now apply this equation to the "electronic specific heat." We find that

$$C_{es}{}^{(M)} = M(\partial S_{es}/\partial M)_{T,V}, \tag{3.5}$$

where $C_{es}{}^{(M)}$ is the contribution of the kinetic energy of the ions to C_{es}. From Eq. (3.1) we can easily calculate S_{es},

$$S_{es} = a\gamma T_c \int_0^{T/T_c} \frac{\exp(-b/x)}{x}. \tag{3.6}$$

Now since a and b appear to be universal constants, we can reasonably assume that they are independent of the mass M. Combining Eqs. (3.5) and (3.6), we find that

$$C_{es}{}^{(M)} = \tfrac{1}{2}(C_{es} - S_{es}), \tag{3.7}$$

where we have used the empirical relation $T_c \propto M^{-\frac{1}{2}}$. The right-hand side of Eq. (3.7) is always positive and is clearly of the same order of magnitude as C_{es}. For

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[9] B. B. Goodman, *Conference de Physique des Basses Temperatures, 1955*, (Centrenational de la Recherche Scientifique and UNESCO, Paris, 1956), pp. 506–511.

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example at $T=T_c/2$, $\frac{1}{2}(C_{es}-S_{es})\simeq C_{es}/3$. We therefore see that the so-called electronic term contains a large positive contribution from the kinetic energy of the ions in the lattice. This fact implies that considerable caution should be exercised in any attempt to interpret C_{es} in terms of a one-electron energy spectrum. On the other hand, it does not imply that such an interpretation is completely impossible. However, an alternative interpretation of this term would be that it arises from the excitation of elementary (charged) excitations across an energy gap. The magnitude of the gap may, and indeed must, depend on M. These excitations could be supposed to arise from the cooperative nature of the interaction between the electrons and the lattice vibrations. This kind of interpretation does not suppose that any separation of the nuclear and electronic motions is possible and there is no reason to identify the elementary excitations with electrons.

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Observed Dependence of the Low-Temperature Thermal and Electrical Conductivity of Graphite on Temperature, Type, Neutron Irradiation, and Bromination*

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The thermal conductivity of various graphites in the temperature interval 10° to 300°K has been determined and the effect of neutron irradiation and bromination investigated. The thermal conductivity of large crystallite natural graphite and of nonpitch-bonded graphite is found to vary as T^2 at low temperatures, as does the specific heat, in accordance with the simple theory of lattice heat conduction. This is in contrast to the anomalous $T^{2.7}$ dependence exhibited by various pitch-bonded graphites. The anomaly is explained in a subsequent paper in terms of the effect of ungraphitized pitch on the total thermal resistivity of pitch-bonded graphites.

Neutron irradiation is observed to cause the thermal conductivity of graphite to decrease markedly at a rate which decreases with exposure time. Also, the exponent of the temperature dependence decreases with exposure. The effect of bromination on the thermal conductivity of graphite is determined and compared with the effect of neutron irradiation. The results indicate that the change in the concentration of conduction electrons is not the principal mechanism by which neutron irradiation decreases the thermal conductivity.

The electrical resistivity shows a negative temperature coefficient for all graphites, except the large crystallite natural graphite. Neutron irradiation increases the electrical resistivity to a saturation value and decreases the magnitude of the temperature coefficient.

I. INTRODUCTION

As a part of a general program[1] to study the effect of radiation damage on the properties of graphite, the thermal and electrical conductivity of various types of graphite have been determined as a function of neutron exposure and temperature in the interval 10° to 300°K. The thermal conductivity of unirradiated artificial polycrystalline graphite at low temperatures has been reported by Tyler and Wilson[2] and by Berman.[3] These authors reported an anomalous temperature dependence which has been confirmed by an independent experimental method[4] in the present study. Accordingly, graphite is the only nonmetallic substance known at present in which, at low temperatures, the thermal conductivity varies more rapidly with temperature (up to $T^{2.7}$) than the specific heat[2] (T^2). Klemens[5] has treated this anomaly as due to different vibrational modes being responsible for thermal conduction and specific heat in thin graphite plates. Smith[6,7] and Hove[8] have explained it as due to the presence of small regions of nongraphitic carbon, presumably in the pitch binder, in the artificial graphites. Since the latter explanation depends critically on the effect of the nongraphitic pitch binder, the behavior of graphites in which it is essentially absent has also

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