Difference between Normal and Superconducting States of a Metal

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Three general theorems of statistical mechanics are used to calculate the differences, between the normal and superconducting states of a metal in (i) the mean kinetic energy of the electrons, (ii) the mean kinetic energy of the lattice, and (iii) the mean potential energy of the entire system. The word "mean" implies thermal average at a given temperature and pressure. The formal properties of these differences are established and a numerical calculation is carried out in the case of tin. The most important results of this investigation are that (a) all three differences are of the same order of magnitude ($\sim 10^{-3}$ cal/mole for a typical superconductor) at all temperatures, (b) they all vanish at the transition temperature, (c) the mean kinetic energy of the electrons is greater in the superconducting state than in the normal state and depends strongly on the isotopic mass, (d) the mean kinetic energy of the lattice is less in the superconducting state than in the normal state and depends equally strongly on the electron mass, and (e) the mean potential energy of the entire system is also less in the superconducting state than in the normal state. In the final section these results are discussed from a physical point of view.

1. INTRODUCTION

IN this paper we shall use some general theorems of statistical mechanics to study the difference between the normal and superconducting states of a metal. We believe that the results we shall obtain are quite rigorous and general. However, in order to apply them to any given superconductor, we must know the dependence of the critical field H_c on the isotopic mass M. At present this dependence is known with any certainty only for a small number of superconductors.

Let us consider the well-known thermodynamic relationship,[1]

$$G_n - G_s = V H_c^2/8\pi; \qquad (1.1)$$

here G_n and G_s are the Gibbs free energies in the normal and superconducting states, respectively, V is the volume of the specimen, and H_c is the magnetic field required to destroy the superconducting state. We shall always calculate all extensive quantities for one mole, so in Eq. (1.1) G_n, G_s, and V refer to one mole. It will be convenient to denote by ΔX the difference in X between the normal and superconducting states. We shall refer to ΔX simply as the difference in X. Equation (1.1) can be used to calculate the difference in quantities such as G, S, and V (S is the entropy per mole and V the molar volume) from a knowledge of H_c as a function of temperature and pressure. The results of these calculations have always agreed with the direct experimental determinations of the quantities involved,[2] thereby confirming the validity of the thermodynamic arguments which led to Eq. (1.1).

Recently, however, a very important new item of experimental data has become available. This new piece of information is the dependence of H_c on the

isotopic mass of the superconductor. It is available for the four superconductors tin,[3] mercury,[4] thallium[5] and lead.[6] Now if we know the dependence of H_c on M, we can immediately calculate, with the help of Eq. (1.1), the dependence of ΔG on M. We shall show that this additional information enables us to calculate the differences, between the normal and superconducting states, in the mean kinetic energy of the electrons, the mean kinetic energy of the ions in the lattice, and the mean potential energy of the entire system. The word "mean" in the last sentence is to be interpreted as "thermal average at a given temperature and pressure." We shall denote these differences by $\Delta \bar{K}_m$, $\Delta \bar{K}_M$, and $\Delta \bar{\Phi}$, respectively. It will become clear that the accuracy with which we can calculate any of these quantities is limited only by the accuracy of the experiments that determine the dependence of H_c on T, P, and M.

In the next section we shall use three theorems in statistical mechanics to calculate these three differences. Section 3 is devoted to a discussion of the formal properties of the results of Sec. 2. At the end of this section we calculate, for tin, the temperature dependence of $\Delta \bar{K}_m$, $\Delta \bar{K}_M$ and $\Delta \bar{\Phi}$. The results of these calculations are shown in Fig. 1. In Sec. 4 we shall use the formal properties we derived in Sec. 3 to gain some insight into the probable nature of the superconducting transition.

Finally we should like to emphasize two features of the calculations presented in this paper. Firstly, the results we obtain are completely independent of any theoretical picture or "model" of the superconducting state. They are based entirely on the general principles of statistical mechanics, although to apply them to any given superconductor we require a knowl-

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[1] D. Shoenberg, *Superconductivity* (Cambridge University Press, Cambridge, 1938), Chap. 3, p. 57.
[2] Reference 1, page 62.
[3] Lock, Pippard, and Shoenberg, Proc. Cambridge Phil. Soc. 47, 811 (1951).
[4] Reynolds, Serin, and Nesbitt, Phys. Rev. 84, 691 (1951).
[5] E. A. Maxwell, National Bureau of Standards, Circular 519, 1952 (unpublished), p. 29.
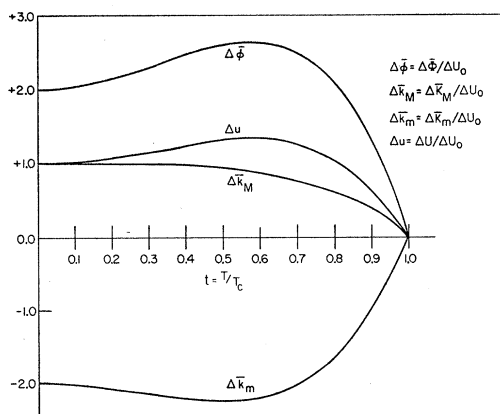[6] M. Olsen-Bär, Nature 168, 245 (1951).

FIG. 1. The dependence of $\Delta\bar{k}_m$, $\Delta\bar{k}_M$, and $\Delta\bar{\phi}$ on the reduced temperature $t=T/T_c$.

edge of the dependence of H_c on T, P, and M. This information is to be found from experiment. Secondly, we wish to point out that in this type of approach, which is by no means unknown in dealing with other physical phenomena, we reverse the usual order of procedure. Here we start from the experimental data, apply the general principles of statistical mechanics, and deduce some general results about the microscopic nature of the phenomenon. This is the reverse of the more usual procedure in which we start with some specific assumptions about the microscopic state, usually chosen so as to make the problem tractable, and then deduce with the aid of statistical mechanics some statements about the macroscopic behavior of the system.

2. CALCULATION OF THE DIFFERENCES $\Delta\bar{K}_m$, $\Delta\bar{K}_M$ AND $\Delta\bar{\Phi}$

Consider the Hamiltonian, H, for one mole of a pure isotope of any superconducting element. This can be written as

$$H = K_M + K_m + \Phi, \qquad (2.1)$$

where

$$K_m = \sum_{i=1}^{ZN} \frac{\mathbf{p}_i^2}{2m}, \qquad (2.2)$$

$$K_M = \sum_{i=1}^{N} \frac{P_i^2}{2M}, \qquad (2.3)$$

and

$$\Phi = \sum_{i<j}^{N} \frac{Z^2 e^2}{|\mathbf{R}_i - \mathbf{R}_j|} - \sum_{i=1}^{N} \sum_{j=1}^{ZN} \frac{Z e^2}{|\mathbf{R}_i - \mathbf{r}_j|}$$
$$+ \sum_{i<j}^{ZN} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}. \qquad (2.4)$$

In these equations, M and Z are the mass and atomic number of the isotope of the element concerned; m and e are the mass and charge of the electron. The

momentum and coordinate of the ith nucleus are denoted by $\mathbf{P}_i$ and $\mathbf{R}_i$, while those of the ith electron are denoted by $\mathbf{p}_i$ and $\mathbf{r}_i$. The operators K_M, K_m, and Φ are the kinetic energy of electrons, kinetic energy of the nuclei and potential energy of the entire system. In writing down this Hamiltonian, we have assumed that the metal can be thought of as being composed of N nuclei of charge Ze and ZN electrons of charge e. This assumption seems to us to be perfectly sound.

Next we state the three general theorems of statistical mechanics that we require. First the internal energy, U, of the system is given by,

$$U = \bar{H} = \bar{K}_M + \bar{K}_m + \bar{\Phi}, \qquad (2.5)$$

where $\bar{H}$ is the thermal average of the Hamiltonian H. The second theorem we shall need is the virial theorem.[7,8] This states that the product of the pressure, p, and volume, V, is given by

$$pV = \tfrac{2}{3}(\bar{K}_M + \bar{K}_m) + \tfrac{1}{3}\bar{\Xi}, \qquad (2.6)$$

where $\bar{\Xi}$ is the average of the virial of the interparticle forces and is given by

$$\bar{\Xi} = -\sum_{i<j}^{N}\langle \mathbf{R}_{ij}\cdot\nabla_{\mathbf{R}_{ij}} Z^2 e^2 / |\mathbf{R}_i - \mathbf{R}_j| \rangle_{\text{Av}}$$
$$+ \sum_{i=1}^{N} \sum_{j=1}^{ZN}\langle (\mathbf{R}_i - \mathbf{r}_j)\cdot\nabla_{(\mathbf{R}_i-\mathbf{r}_j)} Z e^2 / |\mathbf{R}_i - \mathbf{r}_j| \rangle_{\text{Av}}$$
$$- \sum_{i<j}^{ZN}\langle r_{ij}\cdot\nabla_{\mathbf{r}_{ij}} e^2 / |\mathbf{r}_i - \mathbf{r}_j| \rangle_{\text{Av}}. \qquad (2.7)$$

Now since the only interparticle forces present are Coulomb forces, it is easily seen that $\bar{\Xi} = \bar{\Phi}$. When this result is substituted into Eq. (2.6), we find that

$$\tfrac{3}{2}pV = \bar{K}_M + \bar{K}_m + \tfrac{1}{2}\bar{\Phi}. \qquad (2.8)$$

Equations (2.5) and (2.8) are well-known results in statistical mechanics. Finally we shall use the following equation,

$$-M(\partial G/\partial M)_{P,T} = \bar{K}_M. \qquad (2.9)$$

This equation, which is quite general, appears to be new and is derived in the appendix. A similar equation holds for the mean kinetic energy of the electrons, but we shall not require it. If we now express U and V in terms of the derivatives of G, we find that Eqs. (2.5), (2.8), and (2.9) can be written in the form

$$-P\left[\frac{\partial G}{\partial P}\right]_{T,M} - T^2\left[\frac{\partial (G/T)}{\partial T}\right]_{P,M} = \bar{K}_M + \bar{K}_m + \bar{\Phi}, \qquad (2.10)$$

$$\tfrac{3}{2}P\left[\frac{\partial G}{\partial P}\right]_{T,M} = \bar{K}_M + \bar{K}_m + \tfrac{1}{2}\bar{\Phi}, \qquad (2.11)$$

and

$$-M\left[\frac{\partial G}{\partial M}\right]_{T,P} = \bar{K}_M. \qquad (2.12)$$

[7] E. A. Milne, Phil. Mag. **50**, 409 (1925).

[8] J. de Boer, Repts. Progr. Phys. **12**, 305 (1948–1949).

Now we do not know the dependence of either G_s or G_n on P and M, so the above equations are of no use as they stand. However, we do know the dependence of ΔG on P and M. We therefore apply the operator Δ, where $\Delta X = X_n - X_s$, to both sides of the above equations and, noting that Δ can be interchanged with the operator of differentiation, we find that

$$-P\left[\frac{\partial \Delta G}{\partial P}\right]_{T,M} - T^2\left[\frac{\partial \Delta G/T}{\partial T}\right]_{P,M}$$
$$= \Delta \bar{K}_M + \Delta \bar{K}_m + \Delta \bar{\Phi}, \quad (2.13)$$

$$\tfrac{3}{2}P\left[\frac{\partial \Delta G}{\partial P}\right]_{T,M} = \Delta \bar{K}_M + \Delta \bar{K}_m + \tfrac{1}{2}\Delta \bar{\Phi}, \quad (2.14)$$

and

$$-M\left[\frac{\partial \Delta G}{\partial M}\right]_{T,P} = \Delta \bar{K}_M. \quad (2.15)$$

The left-hand sides of these equations can be expressed in terms of the derivatives of H_c with respect to T, P, and M, and we regard these derivatives as known quantities. We therefore have three linear equations for three unknown quantities $\Delta \bar{K}_m$, $\Delta \bar{K}_M$, and $\Delta \bar{\Phi}$. Solving for these quantities, we find

$$\Delta \bar{K}_m = M\left[\frac{\partial \Delta G}{\partial M}\right]_{T,P} + T^2\left[\frac{\partial \Delta G/T}{\partial T}\right]_{P,M}$$
$$+ 4P\left[\frac{\partial \Delta G}{\partial P}\right]_{T,M}, \quad (2.16)$$

$$\Delta \bar{K}_M = -M\left[\frac{\partial \Delta G}{\partial M}\right]_{T,P}, \quad (2.17)$$

and

$$\Delta \bar{\Phi} = -2T^2\left[\frac{\partial \Delta G/T}{\partial T}\right]_{P,M} - 5P\left[\frac{\partial \Delta G}{\partial P}\right]_{T,M}. \quad (2.18)$$

To calculate $\Delta \bar{K}_m$, $\Delta \bar{K}_M$, and $\Delta \bar{\Phi}$ in terms of the derivatives of H_c, we merely have to substitute $\Delta G = VH_c^2/8\pi$. It is convenient at this stage to make some simplifications. First, all the terms that arise from the derivatives of V with respect to T, P, and M are extremely small ($\sim 10^{-6}$ cal/mole at most) compared with the other terms ($\sim 10^{-3}$ cal/mole). Consequently we can neglect these terms. For similar reasons we can also neglect the terms that arise from the derivatives $\partial H_c/\partial P$. When we make these simplifications, we find that

$$\Delta \bar{K}_m = \frac{VH_c}{4\pi}\left[M\left(\frac{\partial H_c}{\partial M}\right)_{T,P} + T\left(\frac{\partial H_c}{\partial T}\right)_{P,M} - \frac{H_c}{2}\right], \quad (2.19)$$

$$\Delta \bar{K}_M = -\frac{VH_c}{4\pi}\left[M\frac{\partial H_c}{\partial M}\right]_{T,P}, \quad (2.20)$$

and

$$\Delta \bar{\Phi} = -\frac{VH_c}{4\pi}\left[2T\left(\frac{\partial H_c}{\partial T}\right)_{P,M} - H_c\right]. \quad (2.21)$$

Finally we express $\Delta \bar{K}_m$, $\Delta \bar{K}_M$, and $\Delta \bar{\Phi}$ in terms of the distribution functions[8] in momentum and configuration space. We have that

$$\bar{K}_m = \int \frac{\mathbf{p}^2}{2m}\sigma_e(\mathbf{p})d\mathbf{p}, \quad (2.22)$$

$$\bar{K}_M = \int \frac{\mathbf{P}^2}{2M}\sigma_N(\mathbf{P})d\mathbf{P}, \quad (2.23)$$

and

$$\bar{\Phi} = \int\int V_{ee}(\mathbf{r}_1,\mathbf{r}_2)\rho_e(\mathbf{r}_1,\mathbf{r}_2)d\mathbf{r}_1 d\mathbf{r}_2$$
$$+ \int\int V_{NN}(\mathbf{R}_1,\mathbf{R}_2)\rho_N(\mathbf{R}_1,\mathbf{R}_2)d\mathbf{R}_1 d\mathbf{R}_2$$
$$+ \int\int V_{Ne}(\mathbf{R}_1,\mathbf{r}_2)\rho_{Ne}(\mathbf{R}_1,\mathbf{r}_2)d\mathbf{R}_1 d\mathbf{r}_2. \quad (2.24)$$

Here $\sigma_e(\mathbf{p})$ and $\sigma_N(\mathbf{P})$ are the momentum distribution functions for the electrons and nuclei, respectively. The functions ρ_e, ρ_N, and ρ_{Ne} are the pair correlation functions for two electrons, two nuclei, and one electron and one nucleus, respectively. From these equations, we have at once that

$$\Delta \bar{K}_m = \int \frac{p^2}{2m}\Delta\sigma_e(\mathbf{p})d\mathbf{p}, \quad (2.25)$$

$$\Delta \bar{K}_M = \int \frac{\mathbf{P}^2}{2M}\Delta\sigma_N(\mathbf{P})d\mathbf{P}, \quad (2.26)$$

and

$$\Delta \bar{\Phi} = \int\int V_{ee}\Delta\rho_e d\mathbf{r}_1 d\mathbf{r}_2 + \int\int V_{NN}\Delta\rho_N d\mathbf{R}_1 d\mathbf{R}_2$$
$$+ \int\int V_{Ne}\Delta\rho_{Ne} d\mathbf{R}_1 d\mathbf{r}_2, \quad (2.27)$$

where, for example, $\Delta\sigma_e = (\sigma_e)_N - (\sigma_e)_s$, and is the difference between the momentum distributions for the electrons in the normal and superconducting states. Similar definitions hold for the other functions appearing in the above equations. We shall make use of these formal equations in Sec. 4.

3. PROPERTIES OF $\Delta \bar{K}_m$, $\Delta \bar{K}_M$, AND $\Delta \bar{\Phi}$

To make use of Eqs. (2.19)–(2.21), we must calculate $M(\partial H_c/\partial M)_{P,T}$ from the experimental data. The most convenient way to do this is as follows. The dependence

of H_c on T and M has been found experimentally[3] to be given by the equation

$$H_c = H_0 h(t), \tag{3.1}$$

where H_0 is the critical field at absolute zero, $t = T/T_c$, T_c is the transition temperature, $h(t)$ is a function that depends only on t and $h(0) = 1$. The function $h(t)$ is moreover identical for all the isotopes of any one superconductor.[9-11] The exact form of this function does not concern us at the moment. (In fact it can be rather accurately represented by the simple expression $1 - t^2$.) Equation (3.1) expresses the well-known law of similarity for the isotopes of any one superconductor. The different isotopes have, of course, different values of H_0 and T_c and the equation states that H_c/H_0 is a universal function of T/T_c. This law was first discovered by Lock, Pippard, and Shoenberg[3] who worked with the isotopes of tin. It is also likely that it is obeyed by the isotopes of mercury[4] and thallium.[5] In addition it is well established that for these three substance, T_c and H_0 both vary as $M^{-\alpha}$, where $\alpha = \frac{1}{2}$, within a few percent. In the case of lead, M. Olsen-Bär[6] found that H_0 and T_c varied as $M^{-\frac{1}{4}}$, approximately. This result has, however, never been confirmed. It is worth remarking at this point that it would be of great theoretical interest to have considerably more data on the dependence of H_0 and T_c on M, particularly for the lighter superconductors. In our theoretical calculations we shall assume that the critical fields of the isotopes of a given superconductor can be expressed in the form given by Eq. (3.1); but we shall assume, for the sake of generality, that $H_0 \propto M^{-\alpha}$ and $T_c \propto M^{-\beta}$.

With this assumption we can easily calculate $\Delta \bar{K}_m$, $\Delta \bar{K}_M$ and $\Delta \bar{\Phi}$ in terms of the function $h(t)$. We have that

$$\Delta \bar{K}_m = -\Delta U_0 h[(1+2\alpha)h - 2(1+\beta)th'], \tag{3.2}$$

$$\Delta \bar{K}_M = 2\Delta U_0 h[\alpha h - \beta th'], \tag{3.3}$$

and

$$\Delta \bar{\Phi} = 2\Delta U_0 h[h - 2th']. \tag{3.4}$$

Here $h' = dh/dt$, and $\Delta U_0 (= H_0^2 V/8\pi)$ is the difference in energy between the normal and superconducting states at absolute zero.

From these equations we can draw the following conclusions:

(i) Since $\partial H_c/\partial T \leqslant 0$ (which of course implies that $\Delta S \geqslant 0$) at all temperatures below T_c[1] it follows that $h'(t) \leqslant 0$ for $t \leqslant 1$. When this inequality is combined

[9] Recent experiments[10,11] on tin, vanadium, and aluminum indicate that $h(t)$ may in fact be a universal function for *all* superconductors.

[10] Corak, Goodman, Satterthwaite and Wexler, *Report on International Conference on Low Temperature Physics* (National Center of Scientific Research and UNESCO, Paris, 1956), p. 503.

[11] B. B. Goodman, *Report on International Conference on Low Temperature Physics* (National Center of Scientific Research, and UNESCO, Paris, 1956), p. 506.

with Eqs. (3.2)–(3.4), we find that

$$\left. \begin{array}{l} \Delta \bar{K}_m \geqslant 0 \\ \Delta \bar{K}_M \leqslant 0 \\ \Delta \bar{\Phi} \leqslant 0 \end{array} \right\} \text{ for all temperatures.} \tag{3.5}$$

We can therefore conclude that (a) the mean kinetic energy of the electrons is greater in the superconducting state than in the normal state, (b) the mean kinetic energy of the ions or nuclei is less in the superconducting state in the normal state, and (c) the mean potential energy of the entire system is also less in the superconducting state than in the normal state. We shall attempt to interpret these conclusions in more detail in the next section.

(ii) Next we notice that because the superconducting transition is a second-order transition at T_c, $h(t)$ must tend to zero and $h'(t)$ must remain finite, as $t \rightarrow 1$. This implies that $\Delta \bar{K}_m$, $\Delta \bar{K}_M$, and $\Delta \bar{\Phi}$ all tend to zero as $T \rightarrow T_c$. In particular the mean kinetic energy of the electrons is the same in both states at the transition temperature.

(iii) As $T \rightarrow 0$, $\Delta S \rightarrow 0$. This follows from the third law of thermodynamics. Consequently $h' \rightarrow 0$ and $h \rightarrow 1$, as $t \rightarrow 0$. This enables us to write the three differences in a very simple form at $T = 0$. Namely,

$$\Delta \bar{K}_m = -(1+2\alpha)\Delta U_0,$$
$$\Delta \bar{K}_M = 2\alpha \Delta U_0, \tag{3.6}$$
$$\Delta \bar{\Phi} = 2\Delta U_0.$$

Since α is approximately equal to $\frac{1}{2}$, these equations tell us that all three differences are of the same order of magnitude at absolute zero. We can easily generalize this conclusion as follows.

(iv) It is known from experiment[1] that $h(t)$ varies smoothly between 1 and 0 as t varies 0 to 1; as we have remarked, it can be accurately represented by the expression $(1-t^2)$. If we bear in mind the fact that Eqs. (3.2)–(3.4) involve only the first derivative of h, we can easily see that the three differences must be of the same order of magnitude at all temperatures, except perhaps for temperatures very close to T_c.

(v) We also notice that the derivatives of all three quantities with respect to temperature tend to zero as $t \rightarrow 0$, and tend to finite limits as $t \rightarrow 1$.

(vi) Finally we have used Eqs. (3.2)–(3.4) to compute $\Delta \bar{K}_m$, $\Delta \bar{K}_M$, and $\Delta \bar{\Phi}$ as functions of t in the case of tin. It is known that the law of similarity is extremely accurately obeyed by this substance[3] and also that $\alpha = \beta = \frac{1}{2}$, within a few percent. To simplify the calculation we have assumed that $h(t)$ can be sufficiently well represented by the parabola $1 - t^2$. This is known to be inaccurate[10] but the inaccuracy is slight and will have little effect on the results.

The results of the calculations are shown in Fig. 1, where we have plotted $\Delta \bar{K}_m$, $\Delta \bar{K}_M$ and $\Delta \bar{\Phi}$, in units of ΔU_0, as functions of the reduced temperature t. For

purposes of comparison we have also plotted ΔU (in units of ΔU_0), where ΔU is the difference in internal energy between the normal and superconducting states. We see from the figure that while $\Delta \bar{K}_m$ and $\Delta \bar{\Phi}$ behave is a very similar fashion—apart from sign—$\Delta \bar{K}_M$ behaves slightly differently. The main differences are that $\Delta \bar{K}_M$ does not rise to a maximum value at an intermediate temperature and that it approaches T_c with a very much smaller slope. The fact that $\Delta \bar{K}_m$ and $\Delta \bar{\Phi}$ show maxima, at $T_c/2$ and $T_c/\sqrt{3}$, respectively, follows directly from the fact that the superconducting transition is a second order transition at T_c. For this implies that ΔS vanishes at both $T=0$ and $T=T_c$, since it is a continuous function of T it must rise to a maximum value at some intermediate temperature and this maximum is reflected in the behavior of $\Delta \bar{K}_m$ and $\Delta \bar{\Phi}$. It may be significant that $\Delta \bar{K}_M$ does not show this type of behavior. It is also worth noting that both $\Delta \bar{K}_m$ and $\Delta \bar{\Phi}$ have very large gradients at $T=T_c$; in the reduced units of Fig. 1 these slopes are ~ 15. The slope of $\Delta \bar{K}_M$ on the other hand is only 4 in the same reduced units.

In this section we have calculated what seems to us to be the most important properties of the three functions $\Delta \bar{K}_m$, $\Delta \bar{K}_M$ and $\Delta \bar{\Phi}$. In the next section we shall attempt to interpret these properties physically and thus gain some insight into the nature of the superconducting transition.

4. PHYSICAL INTERPRETATION

In the last section we derived the formal properties of $\Delta \bar{K}_m$, $\Delta \bar{K}_M$, and $\Delta \bar{\Phi}$. We shall now attempt to interpret these results physically. First however, we must make some remarks about the definitions of $\bar{K}_m$, $\bar{K}_M$, and $\bar{\Phi}$. These three quantities are essentially defined by Eqs. (2.2), (2.3), and (2.4). From these definitions we see that both $\bar{K}_m$ and $\bar{\Phi}$ contain parts which cannot possibly be involved in the superconducting transition. These parts are as follows: for $\bar{K}_m$ the kinetic energy of the electrons which form the cores of the ions in the metallic lattice, and for $\bar{\Phi}$ the potential energy of these electrons and the static potential energy of the nuclei themselves. We say that these contributions to $\bar{K}_m$ and $\bar{\Phi}$ cannot be involved in the superconducting transition simply because we have every reason to believe that the motions of the electrons in the ion cores and the static interaction energy of the nuclei are not influenced significantly by the superconducting transition. Consequently we need only consider the contribution to $\bar{K}_m$ and $\bar{\Phi}$ from those electrons that cannot be considered as being tightly bound to the nuclei. In addition to this contribution, there will of course be contributions to $\bar{\Phi}$ (and $\bar{K}_M$) from the vibrations of the ions in the lattice. We can therefore divide the electrons into two classes: (a) those which are so tightly bound to the nuclei that they cannot possibly be influenced by the small energy change[1] ($\sim 10^{-3}$ cal/mole) involved in the superconducting

transition and (b) the remainder, some or all of which may be influenced by the transition. We believe this division to be well justified.

Next we give a simple qualitative analysis of the normal state of a superconductor. In this state the specific heat, C_n, can be written in the form

$$C_n = \gamma T + a(T/\theta)^3, \qquad (4.1)$$

where γ, a, and θ are constants, independent of the temperature. The first term γT has the form one would expect[12] if there are electrons in the lattice which are very nearly free from the influence of any potential fields. Furthermore γ is known,[3] from measurements of the dependence of H_c on M, to be independent of M. Consequently we can interpret this term as arising from the motions of *nearly free* electrons moving in a *static* lattice. It should be pointed out, however, that for most superconductors γ departs fairly markedly from its "free electron" value and hence we cannot suppose that the electrons are *completely* free. The remaining term $a(T/\theta)^3$ also has a very natural interpretation for it is of the well-known Debye T^3 form and can at once be interpreted as arising from the low-frequency vibrations of the ions in the lattice. This interpretation is confirmed by the fact that provided $T < \theta/50$, θ is a true constant; as would be predicted from the theory of lattice vibrations. On the basis of this analysis, we conclude that the thermal properties of a superconductor in its *normal* state can be accurately accounted for on the assumption that there are two independent assemblies contributing—an assembly of nearly free electrons moving in a static lattice and an assembly of low-frequency lattice vibrations. We should perhaps emphasize that from the experimental data on the specific heat in the normal state there is no evidence for any coupling between these assemblies.

Let us now use this qualitative description to estimate the order of magnitude of $\bar{K}_m$, $\bar{K}_M$, and $\bar{\Phi}$ in the normal state. It will become clear that quite rough estimates will suffice for our purpose. Firstly $\bar{K}_m$; this quantity is clearly of the same order of magnitude as the Fermi energy of the metal in the normal state. (It is not of course equal to it because the Fermi energy contains contributions from the potential energy of interaction with the static lattice.) It will therefore be of the order of 10^4 cal/mole.[12] Next $\bar{K}_M$; this will simply be one-half the zero point energy of the lattice vibrations and will be of the order $\frac{1}{2}R\theta$; that is, about 10^2 cal/mole.[13] Finally $\bar{\Phi}$; this quantity is the sum of three different contributions, as shown by Eq. (2.4). It will, however, be of the order of E_0, the energy at the bottom of the conduction band, that is, it will be of the order of -10^4 cal/mole,[13] or rather less.

We are now ready to examine the magnitudes of

[12] R. H. Fowler, *Statistical Mechanics* (Cambridge University Press, Cambridge 1950), second edition, Chap. XI.
[13] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), Chap. III and Chap. X.

$\Delta \bar{K}_m$, $\Delta \bar{K}_M$, and $\Delta \bar{\Phi}$, and for simplicity we shall confine ourselves to the absolute zero. This involves no loss of generality because we have seen that these quantities vary quite slowly with temperature. From Eq. (3.6), we see that they are all roughly equal to ΔU_0, and a typical value for this quantity is 10^{-3} cal/mole. We therefore see that all these differences are extremely small compared to the values of the quantities in the normal state. In other words, $\bar{K}_m$, $\bar{K}_M$, and $\bar{\Phi}$ only change by very small amounts in the superconducting transition. There is an obvious and natural explanation of this fact in the case of the kinetic energy of the electrons, namely that only a small number of electrons in the immediate neighborhood of the Fermi surface are influenced by the transition. It is tempting to try to make the conclusion more quantitative, but any attempt of this nature must overcome the fundamental difficulty that we have a given quantity of kinetic energy ($\sim \Delta U_0 \sim 10^{-3}$ cal/mole) to share among an unknown number of electrons each of which changes its energy by an uncertain amount in the course of the transition. Clearly it is impossible to resolve this difficulty without further information. In view of this the best one can do is to try to guess what natural quantities of energy might be involved in the transition. The most obvious natural quantity would appear to be kT_c, and we do in fact find that if we suppose that the electrons in a layer at the top of the Fermi surface of depth kT_c increase their kinetic energy by an amount kT_c, then the total change in the kinetic energy of the system is just of the order ΔU_0. However, even if we cannot resolve this question in a rigourous manner, we can at least assert that if we assume the existence in the normal state of a Fermi-like distribution in momentum space, then we have a natural mechanism present to reduce $\Delta \bar{K}_m$ to roughly the right order of magnitude.

It is clear that since the energy of the electrons in the Fermi distribution is partly kinetic and partly potential energy, the general argument we have just presented will also suffice to explain the very small value of $\Delta \bar{\Phi}$ as compared with $\bar{\Phi}$.

We next turn to $\Delta \bar{K}_M$. Here no such simple and natural explanation of the magnitude of $\Delta \bar{K}_M$ appears to be possible. One might suppose, for instance, that only a comparatively narrow band of vibration frequencies are involved or that all the vibration frequencies are altered slightly in some simple fashion. Neither of these arguments is, however, at all convincing at the moment. It is worth noting that the temperature dependence of $\Delta \bar{K}_M$ is significantly different from that of $\Delta \bar{K}_m$ and $\Delta \bar{\Phi}$ and that the ratio $\Delta \bar{K}_M/\bar{K}_M$ is many times larger than either $\Delta \bar{K}_m/\bar{K}_m$ or $\Delta \bar{\Phi}/\bar{\Phi}$. This latter fact clearly indicates that at least part of the lattice assembly is relatively strongly influenced by the transition.

It is interesting to look a little more closely at the ratios $\Delta \bar{K}_m/\bar{K}_m$, $\Delta \bar{K}_M/\bar{K}_M$, and $\Delta \bar{\Phi}/\bar{\Phi}$. These ratios have magnitudes of about 10^{-8}, 10^{-5}, and 10^{-8}, whereas $\Delta \bar{K}_m$, $\Delta \bar{K}_M$, and $\Delta \bar{\Phi}$ are all of the same order of magnitude. In other words, the change in any one of these quantities seems to be unrelated to the magnitude of the quantity in the normal state. The inequality of $\bar{K}_m$, $\bar{K}_M$, and $\bar{\Phi}$ in the normal state is of course, easily understood because $\bar{K}_m$ and $\bar{\Phi}$ are quantities relating to the electron assembly whereas $\bar{K}_M$ is related to the lattice assembly, and these two assemblies are supposed to be essentially independent. On the other hand, the equality in magnitude of $\Delta \bar{K}_m$, $\Delta \bar{K}_M$, and $\Delta \bar{\Phi}$ strongly suggests that those parts of the two assemblies that *are* involved in the transition must be very intimately linked together. This suggestion receives support from the fact that $\Delta \bar{K}_m$ depends very strongly, through a factor M^{-1}, on the mass of the ions in the lattice, while $\Delta \bar{K}_M$ depends equally strongly, through γ on the mass of the electrons. This dependence is completely different from the dependence of $\bar{K}_m$ and $\bar{K}_M$ in the normal state.

We can summarize our conclusions by saying that we believe that only very small parts of the electron and lattice assemblies are involved in the superconducting transition but that the parts which are involved are linked together in a very intimate fashion. This last statement is in agreement with the theoretical ideas put forward by Frohlich[14] and Bardeen.[15] Indeed our calculation of the magnitude, and dependence on m, of $\Delta \bar{K}_M$ shows that the lattice vibrations are appreciably influenced by the superconducting transition. The fact that we have shown that $\Delta \bar{K}_m \geq 0$ at all temperatures lends considerable support to the energy gap "models" that have been put forward[16] as a basis for understanding the superconducting state. However, we should point out that it would be equally consistent with our calculations to suppose that the available momentum states just above the Fermi surface are merely more widely separated in the superconducting state.

Finally we examine the formal equations (2.25), (2.26), and (2.27). The immediate interpretation of these equations is that the distribution functions σ_e, σ_N, ρ_e, ρ_N, and ρ_{Ne} are all distorted by the superconducting transition. We think it is important to make this rather formal, but rather general statement, because it may be possible to design experiments to try to study this distortion. From the discussion given above, the average distortion of any one of these functions will be extremely small. However, some or all of them may be very markedly distorted, for particular values of their arguments. For instance, we might suspect that σ_e will be quite different in the neighborhood of the Fermi surface in the superconducting state. Indeed we would suspect that it may be nonzero, at absolute zero, even for values of **p** which correspond to

[14] H. Frohlich, Phys. Rev. **79**, 845 (1950).
[15] J. Bardeen, Phys. Rev. **80**, 567 (1950).
[16] J. Bardeen, Phys. Rev. **97**, 1724 (1955).

energy states above the Fermi surface in the normal metal. If this type of behavior is typical of the distortion to be expected in the other distribution functions, then it may be possible to examine their behavior experimentally.

5. CONCLUSIONS

In conclusion, we would like to make two remarks about the methods used in this paper.

First it should be noticed that we have used, in Eqs. (2.10) to (2.12), all the available information on the dependence of ΔG on T, P, and M. Moreover it is very hard to see how the dependence of ΔG on any other microscopic variables can be found experimentally. Consequently we do not see any direct or obvious extensions of the techniques we have used.

Secondly we wish to discuss the difference $\Delta\Phi$. This difference is the sum of three terms; namely the difference in the potential energy of the nuclei, the potential energy of the electrons, and the interaction potential energy between the electron and nuclei. It is therefore tempting to try to split it up into these three constituent parts in order to study them separately. Unfortunately the present techniques do not enable us to do this. These techniques rest, essentially, on differentiating ΔG with respect to various variables (e.g., T, P, and M). Consequently we can split up $\Delta\bar{\Phi}$ only if we can find three variables that are characteristic of each of the three parts. This is clearly impossible because the only characteristic variable these potential energies depend on is $(Ze)^2$, and they all depend on this variable in essentially the same way. It may, however, be possible to find some other method to split up $\Delta\bar{\Phi}$.

6. ACKNOWLEDGMENTS

APPENDIX

In this appendix we derive Eq. (2.9) of the text. We start from the well-known equations,[17]

$$Q = \sum_V \sum_l \exp[-\beta[E_l(V) + PV]], \quad \text{(A.1)}$$

$$G(T,P) = -kT \log Q. \quad \text{(A.2)}$$

Here $E_l(V)$ is the lth energy level of the system for a volume V, P is the pressure, $\beta = 1/kT$, and k is Boltzmann's constant. The summations in Eq. (A.1) are over all accessible energy states and over all volumes V.

The energy levels, $E_l(V)$, are the eigenvalues of the Hamiltonian given by Eq. (2.1); if $\psi_l(R,r)$ are the eigenfunctions of this Hamiltonian, then

$$H\psi_l = E_l\psi_l; \quad \psi_l \equiv 0 \quad \text{on the surface of } V. \quad \text{(A.3)}$$

If we differentiate Eq. (A.3) with respect to the mass M, multiply both sides of the resulting equation by ψ_l^*, and integrate, we get

$$\partial E_l/\partial M = \int_V \psi_l^*(\partial H/\partial M)\psi_l dV. \quad \text{(A.4)}$$

Consequently,

$$-M\partial E_l/\partial M = (K_M)_{ll}, \quad \text{(A.5)}$$

where K_M is the kinetic energy operator defined by Eq. (2.3). Combining Eqs. (A.5), (A.2), and (A.1), we have at once that

$$-M\left(\frac{\partial G}{\partial M}\right)_{T,P} = \sum_V \sum_l (K_M)_{ll}$$

$$\times \exp[-\beta(E_l + PV)]/Q,$$

$$= \bar{K}_M, \quad \text{(A.6)}$$

and this is the desired result.

[17] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1939), Chap. VI.