SUPERCONDUCTING ELECTRONIC SPECIFIC HEATS, THE "EXPONENTIAL LAW," AND THE BARDEEN, COOPER, SCHRIEFFER THEORY

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The Bardeen, Cooper, Schrieffer[1] (BCS) theory of superconductivity evaluates the molar superconducting electronic specific heat, C_{es}, as follows:

$$C_{es}/\gamma T_c = \frac{3}{2\pi^2}\left(\frac{\epsilon_0}{kT_c}\right)\left(\frac{T_c}{T}\right)^2 [3K_1(\beta\epsilon_0) + K_3(\beta\epsilon_0)],$$

where γT_c is the electronic specific heat in the normal state at the transition temperature T_c, ϵ_0 is the half-width of the energy gap in the single particle density of states, k is the Boltzmann constant, the K's are modified Bessel functions of the second kind, and $\beta = 1/kT$. The above expression, valid under the condition $\beta\epsilon_0 \gg 1$, is actually the first term of an expression involving an infinite sum of the Bessel functions noted above for which the argument is $(n\beta\epsilon_0)$, n being an integer. However, only the first term of the sum given by the above relation need be taken into account.

If values of $\log_{10}(C_{es}/\gamma T_c)$ calculated from the above equation are plotted against T_c/T, the result is the solid curve shown in Fig. 1. For T_c/T between about 2.5 and 6, the curve may be closely

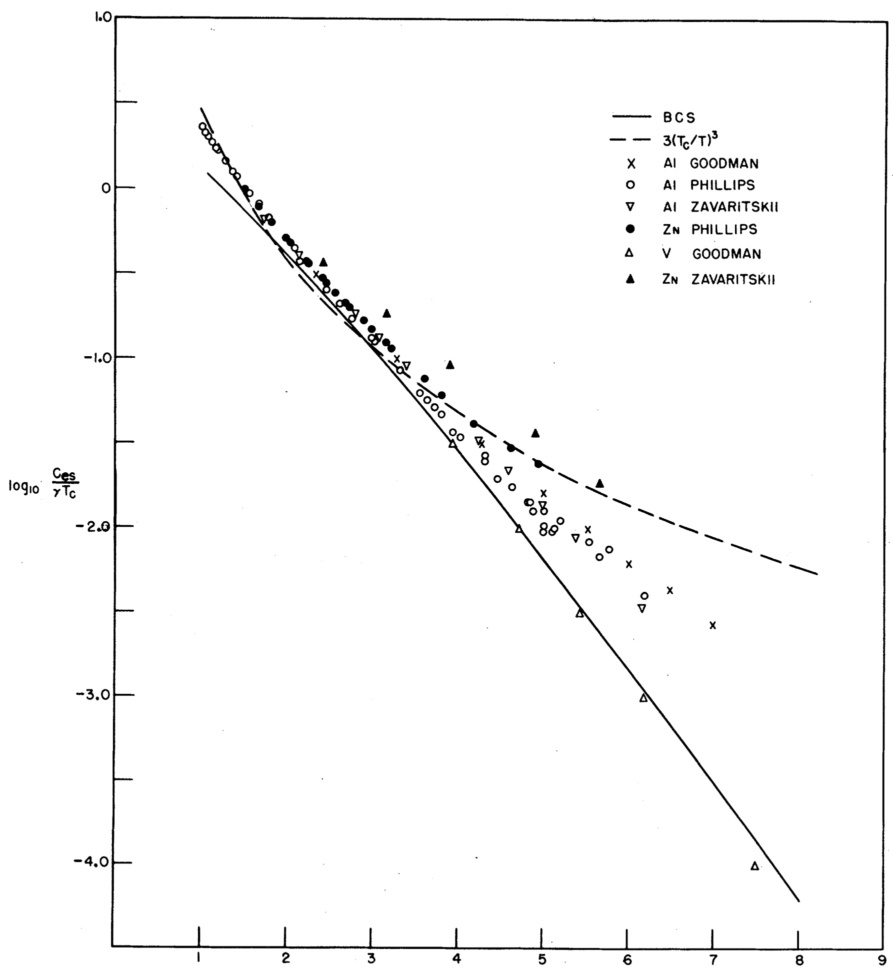

FIG. 1. The reduced superconducting electronic specific heat versus T_c/T for Al, Zn, and V, showing departure from exponential behavior at values of $T_c/T > 4$.

approximated by a straight line which satisfies the equation $C_{es}/\gamma T_c = a\exp(-bT_c/T)$, where a and b are 8.5 and -1.44, respectively. For values of $T_c/T>6$, the curve drops below this empirical line. At larger values of the abscissa, between about 7 and 11, the curve may again be approximated by a new straight line given by the same relation but with the a and b values altered to 26 and -1.62, respectively. These conclusions and their comparison with available experimental measurements have been presented previously by the author on several occasions.[2] The publication of new experimental data on Al and Zn, and conclusions based on these data, suggest that further comment may be useful.

Figure 1 presents a graph of the BCS equation, showing the slight downward curvature which gives rise to the two "exponential" laws. The first of these, beginning in the T_c/T interval beyond about 2 or 2.5, has been verified for many superconductors and constitutes a strong experimental confirmation of the theory. Most of the available data, however, do not extend much beyond $T_c/T = 4$. It is of interest to determine whether or not the general behavior of the specific heat at values of $T_c/T>6$ is also in accord with the theoretical predictions, i.e., whether it has a small downward curvature or some other behavior. In this connection, the dashed line has been drawn in the figure to show the T^3 variation predicted by Gorter-Casimir[3] two-fluid model. The experimental points in the graph are actual, as well as interpolated points taken from the measurements of Goodman,[4] Phillips,[5,6] and Zavaritskii.[7]

For vanadium the $C_{es}/\gamma T_c$ values of Goodman at $T_c/T>4$ show excellent agreement with the BCS curve. Although supporting data are absent for this region, earlier measurements[8,9] (not shown) for $T_c/T<4$ are in good agreement. Three sets of data are exhibited for Al. Inspection shows that the Zavaritskii measurements follow an exponential to $T_c/T = 6$. If exponential behavior is considered as being in agreement with theory, then these data emphasize again only the departure from the law of corresponding states. On the other hand, the aluminum data of Goodman[3] and Phillips[5] show a significant upward curvature beginning at about $T_c/T = 4$. Such a behavior suggests the existence of more states at low energies than envisioned by the theory, or the existence of states in the energy gap, or an asymmetry of the gap.

Another example of the upward curvature in the $C_{es}/\gamma T_c$ curve is afforded by measurements on Zn, although here also the situation is somewhat ambiguous. The data of Phillips,[6] confirmed at T_c/T values between 1 and 2 by Seidel and Keesom,[10] show an upward curvature starting at $T_c/T \simeq 4$. This behavior is not found in the Zavaritskii[7] data which follow an exponential. The difference between these results and those for other superconductors seems large. This is also noted by Khalatnikov and Abrikosov[11] who present a digest of data similar to Fig. 1. A further uncertainty respecting Zavaritskii's Zn measurements appears in an unfortunate discrepancy between the graph of his C_{es} data and the equation given to represent them. A final comment on the deviation of Phillips' data from an exponential seems warranted in view of the suggestion of Seidel and Keesom[12] that the difference may arise from a Schottky anomaly brought about by the interaction of the quadrupole moment of the nucleus with the crystalline field of the lattice. In this connection it may be noted that the similar deviation in the two Al curves cannot be ascribed to quadrupole coupling since Al has a face-centered cubic lattice. Hence it is possible that in Zn only a part of the difference arises from this source.

The data available on tin[4,13] have been analyzed by Biondi, Forrester, Garfunkel, and Satterthwaite.[14] They point out that although the measurements of both Goodman and Zavaritskii indicate departures from exponential behavior, the uncertainties are such that it is impossible to specify them with suitable accuracy. For this reason the tin data have been omitted.

Although a T^3 dependence for the superconducting electronic specific heat has not been observed, such behavior may be inferred for thorium from the critical magnetic field measurements of Wolcott and Hein.[15] In an effort to determine whether or not such an extreme behavior will be observed, an investigation of the heat capacity is currently under way in this laboratory.

To sum up, it appears that at T_c/T values of four or greater there is a definite departure of $C_{es}/\gamma T_c$ from exponential behavior in several of the superconductors and that the extent of the departure varies. It thus appears that a further refinement of the BCS theory is necessary to account for the experimental results.

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IMAGE OF THE FERMI SURFACE IN THE VIBRATION SPECTRUM OF A METAL*

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The lattice vibrations of the ions in a metal are partly screened by the conduction electrons. We shall see that this screening changes rather rapidly on certain surfaces in the space of phonon $\vec{q}$-vectors and that therefore on these surfaces the frequencies ω vary abruptly with $\vec{q}$. The calculations we have done give the result that $\omega(\vec{q})$ is a continuous function of $\vec{q}$ but that on the surfaces in question

$$|\mathrm{grad}_{\vec{q}}\, \omega(\vec{q})| = \infty. \tag{1}$$

The location of these surfaces is entirely determined by the shape of the electronic Fermi surface, using a simple geometrical construction.

To explain the physical origin of this effect let us first describe the conduction electrons by a free electron gas, with Fermi wave number k_F. One then finds that an embedded charge distribution,

$$\rho_{\mathrm{ext}}(\vec{r}) = \rho_0 e^{i\vec{q}\cdot\vec{r}}, \tag{2}$$

induces an electronic charge density

$$\rho_{\mathrm{el}}(\vec{r}) = -F(q)\rho_0 e^{i\vec{q}\cdot\vec{r}}, \tag{3}$$

where

$$F(q) = \frac{1}{\pi a_0 q^2}\left[1 + \frac{k_F}{q}\left(1 - \frac{q^2}{4k_F^2}\right)\ln\left|\frac{q+2k_F}{q-2k_F}\right|\right]; \tag{4}$$

here a_0 is the Bohr radius. Note that near $q = 2k_F$,

$$F(q) = \frac{1}{2\pi a_0 k_F}\left(1 + \frac{1}{2k_F}(q-2k_F)\ln|q-2k_F|\right), \tag{5}$$

and

$$\frac{dF(q)}{dq} = \frac{1}{4\pi a_0 k_F^2}\ln|q-2k_F| \approx -\infty. \tag{6}$$

The last equation shows an abrupt decrease of the ability of the electrons to screen the embedded charge distribution as soon as q exceeds $2k_F$. This is due to the fact that as long as $q < 2k_F$, $\rho_{\mathrm{ext}}(\vec{r})$ causes virtual excitations of some electrons with conservation of energy while when $q > 2k_F$ such excitations are no longer possible (see Fig. 1). Now a lattice vibration of wave vec-

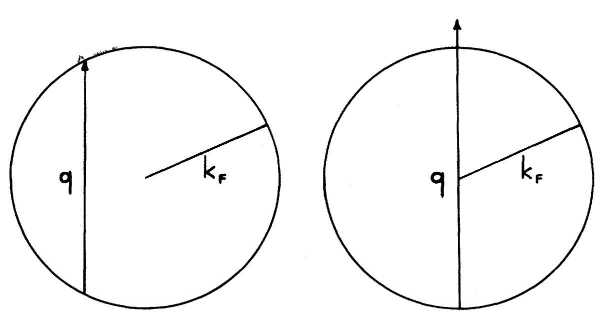

FIG. 1. Virtual excitations for $q < 2k_F$ and $q > 2k_F$.