

## Correlation Effects on the Electronic Specific Heat of Sodium\*

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The effect of the martensitic transformation in sodium on measured values of its specific heat is analyzed. It is shown that the only important effect at low temperatures is to produce a mixture of the two phases. The measured specific heat is very closely given by the sum of the specific heats of each phase measured separately. An analysis of the various experimental measurements gives the result that the effective mass of conduction electrons in the bcc high-temperature phase is greater than 1.5 times the free electron mass while in the hcp low-temperature phase the corresponding value is less than 1.21. Using further experimental data it is estimated that the effective masses in the bcc high-temperature phase and the hcp low-temperature phase are 1.7 and 1.1 times the free electron value, respectively. These effective mass values imply that there is substantial contact of the Fermi surface in the hcp structure with the "A" faces of the Brillouin zone. The large effective mass in the bcc phase indicates a large enhancement of the specific heat of the conduction electrons in sodium by correlation and electron-phonon interaction effects. The correlation effects alone appear to increase the specific heat of a free electron gas at a density corresponding to  $r_s = 3.96$  (in units of the Bohr radius) by about 40%.

## I. INTRODUCTION

IN the last several years there has been great progress in understanding the many-body problem and the effect of correlation between particles. In particular, the properties in the high-density limit of a degenerate electron gas have been thoroughly investigated. Properties such as the specific heat, correlation energy, and plasmon energy have been calculated.<sup>1-10</sup> Yet there have been no experiments performed that can be compared directly with theory.

There have been several causes of this. The exact theory uses a model of an electron gas in a background of a uniform, "smeared out," positive charge. Any effects of a periodic lattice is missing. In practice this model is best approximated by the electrons in body-centered cubic sodium metal. The property that appears to best test the theory is the electronic specific heat of sodium at low temperatures. The correlation energy of the electron gas is only a small fraction of the total binding energy in sodium and cannot be directly measured. A measurement of the plasmon energy and lifetime as a function of wavelength is another possible check on the theory. However, in this case, the experimental difficulties of working with thin sodium films in order to measure the characteristic energy losses of high-energy electrons passing through the films does

not permit enough accuracy to give a critical check on the theory.

Measurements on the low-temperature specific heat of sodium have been made by various investigators<sup>11-16</sup> but the interpretation of these measurements in terms of an electronic specific heat that can be compared with theory has been complicated by the phase transformation that occurs in sodium at low temperatures and produces a variation in the experimental results. The purpose of this note is to show what is the effect of the phase transformation on the specific heat, and then to show that the present experimental data indicate a surprisingly large effect of correlation.

An additional difficulty in comparing theory with experiment is that the theoretical results have been expanded in a perturbation scheme about the high-density limit and give useful results for values of  $r_s < 2$ .<sup>9,17</sup> Here,  $r_s$  is the radius, in units of the Bohr radius, of a sphere that has the same volume as the average volume per electron. It thus is a measure of the density of the electron gas. The electron densities that are generally found in actual metals correspond to  $r_s > 2$ . Thus, it is seen that the theoretical results have to somehow be extrapolated in order to be compared with experiments on real solids. There is apparently some difficulty in performing this extrapolation. Pines,<sup>18</sup> and Quinn and Ferrell<sup>19</sup> give the result that the corre-

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<sup>1</sup> M. Gell-Mann and K. A. Brueckner, *Phys. Rev.* **106**, 364 (1957).

<sup>2</sup> M. Gell-Mann, *Phys. Rev.* **106**, 367 (1957).

<sup>3</sup> D. Bohm and D. Pines, *Phys. Rev.* **82**, 625 (1951).

<sup>4</sup> D. Bohm and D. Pines, *Phys. Rev.* **92**, 609 (1953).

<sup>5</sup> D. Bohm and D. Pines, *Phys. Rev.* **85**, 332 (1952).

<sup>6</sup> D. Pines, *Phys. Rev.* **92**, 626 (1953).

<sup>7</sup> K. Sawada, *Phys. Rev.* **106**, 372 (1957); K. Sawada, K. Brueckner, N. Fukada, and R. Brout, *Phys. Rev.* **108**, 515 (1957).

<sup>8</sup> J. Hubbard, *Proc. Roy. Soc. (London)* **A240**, 539 (1957); **A243**, 336 (1958).

<sup>9</sup> D. F. DuBois, *Ann. Phys.* **7**, 174 (1959); **8**, 24 (1959).

<sup>10</sup> P. Nozières and D. Pines, *Phys. Rev.* **111**, 442 (1958).

<sup>11</sup> L. M. Roberts, *Proc. Phys. Soc. (London)* **B70**, 744 (1957).

<sup>12</sup> D. H. Parkinson and J. E. Quarrington, *Proc. Phys. Soc. (London)* **A68**, 762 (1955).

<sup>13</sup> F. Simon and W. Zeidler, *Z. Phys. Chem.* **123**, 383 (1926).

<sup>14</sup> J. Rayne, *Phys. Rev.* **95**, 1428 (1954).

<sup>15</sup> R. E. Gaumer and C. V. Heer, *Phys. Rev.* **118**, 955 (1960).

The author is indebted to Dr. Gaumer and Dr. Heer for preprint copies of their paper in advance of publication.

<sup>16</sup> W. H. Lien and N. E. Phillips, *Phys. Rev.* **118**, 958 (1960).

The author is indebted to Dr. Lien and Dr. Phillips for preprint copies of their paper in advance of publication.

<sup>17</sup> R. A. Ferrell, *Phys. Rev. Letters* **1**, 443 (1958).

<sup>18</sup> D. Pines, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 408.

<sup>19</sup> J. J. Quinn and R. A. Ferrell (to be published).

lation effects *decrease* the specific heat of sodium about 10% from the value it has in the ordinary band theory calculation while a reasonable extrapolation of the results of DuBois<sup>9</sup> to  $r_s=3.96$ , the value for sodium, and the results of Fletcher and Larson<sup>20</sup> indicate an *enhancement* of the specific heat by perhaps 30% or more. It is interesting that there is not even qualitative agreement among theoreticians as to how to extrapolate the theory indicating that there is need of developing a physical insight into the effects of correlation.

## II. PHASE TRANSFORMATION

Barrett<sup>21,22</sup> discovered and investigated the fact that both sodium and lithium, in contrast to the heavier alkali metals, undergo a change in crystal structure at low temperatures. It was found that the transformation was a martensitic type occurring in Li around 80°K and in Na around 40°K. Sodium changes from a high-temperature body-centered cubic structure to a low-temperature hexagonal closed-packed structure with a  $c/a$  ratio equal to the ideal of 1.63.

A martensitic transformation<sup>23,24</sup> is a special type of transformation between two crystallographic modifications of a solid. In contrast to the nucleation and growth by diffusion type of transformation where atoms move many atomic distances, a martensitic transformation occurs by a coherent movement of many atoms the order of an atomic spacing. This movement usually consists of the combination of a shear movement between planes and a slight rearrangement within a plane. There is essentially no activation energy for a martensitic transformation and it can therefore occur at low temperatures in contrast to diffusion-type transformation. Two other important properties of this transformation for our purposes are that it can occur over a range of temperatures and when the temperature is changed that part of the material which transforms does so practically instantaneously. At the low temperatures where sodium transforms, stresses produced by strains in the medium surrounding the transforming nuclei cannot be relieved and the transformation proceeds till the induced stress energy stops further transformation. If the temperature is further lowered, the increased difference in bulk free energy between the two phases favors further transformation till the increased induced stress energy again cancels the gain in bulk free energy difference. When the temperature is so low that the bulk free energy difference no longer changes significantly with decreasing temperature, the composition of the material will no

longer appreciably change. The fraction of the material that has transformed at any given temperature depends on the past history of the sample such as the amount of cold working it has been subjected to, its purity, grain size, and surface condition. In general, at absolute zero a sample of sodium will consist of a mixture of the two phases.

If the strain produced by the transforming region (both in itself and in the surrounding untransformed medium) does not exceed the elastic limit when growth stops, the new phase region is said to be in thermoelastic equilibrium. In this case the transformed region will have a single-valued size as a function of temperature, growing and shrinking as the temperature is lowered or raised. When, however, the elastic limit is exceeded the transformation will show a temperature hysteresis, the more usual state of affairs.

One important experimental consequence of the practically instantaneous nature of the martensitic transformation is that the transformation cannot be detected by keeping the temperature constant and observing if any heat of transformation is produced as a function of time. In practice once a given temperature is reached no further transformation will occur.

Further studies of the martensitic transformations in sodium have increased our knowledge. It has been

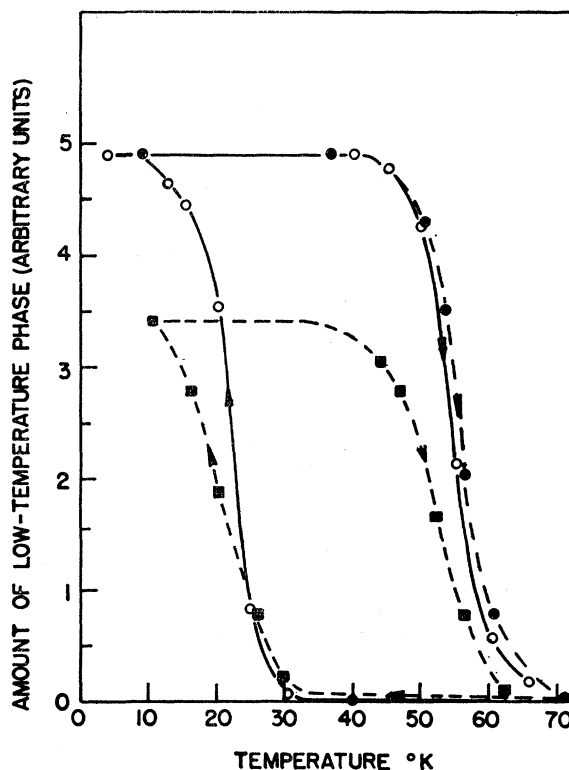


FIG. 1. Transformation curves for sodium from reference 23; O, temperature cycle after annealing at 170°K; ●, temperature cycle after annealing at 270°K; ■, subsequent temperature cycle after warming to 70°K only.

<sup>20</sup> J. G. Fletcher and D. C. Larson, *Phys. Rev.* **111**, 455 (1958).

<sup>21</sup> C. S. Barrett, *Am. Mineralogist* **33**, 749 (1948); *J. Inst. Metals* **84**, 43 (1955).

<sup>22</sup> C. S. Barrett, *Acta Cryst.* **9**, 671 (1956).

<sup>23</sup> See, for example, reviews by J. S. Bowles and C. S. Barrett, *Progr. Metal Phys.* **3**, 1 (1952); and B. A. Bilby and J. W. Christian, *The Mechanism of Phase Transformations in Metals* (Institute of Metals, London, 1956), p. 121.

<sup>24</sup> J. S. Dugdale and D. Gagan, *Proc. Roy. Soc. (London)* **A254**, 184 (1960).

estimated<sup>25</sup> that the Debye temperatures of the high- and low-temperature phases of sodium at 20°K are 153 and 160°K, respectively. Figure 1 shows the results<sup>24</sup> that were obtained on the composition-temperature curve of sodium as it undergoes its martensitic transformation. The interesting result is that when the temperature is raised from liquid helium temperatures to 30°K very little if any transformation is occurring. It appears that at these temperatures no thermoelastic behavior is occurring.<sup>24,25</sup>

### III. EFFECT OF PHASE TRANSFORMATION ON SPECIFIC HEAT

In this section some simple thermodynamic ideas will be used to estimate the effect of the phase transformation on the specific heat. The phase transformation can affect the specific heat in three different ways. (a) It changes the composition of the sample. Each phase will have a different specific heat and the measured specific heat will depend on the relative mixture of the two phases. (b) The heat of transformation that is evolved as one phase transforms into the other will add to the true specific heat producing a measured value that is larger than the actual value. This effect is proportional to the amount that is transforming at a given temperature. (c) Stresses induced in the sample will change the value of the specific heat since the specific heat is a function of stress.

It is not too hard to show that the effect (c) is not important. We estimate it as follows. Under a stress  $\tau$  the change in specific heat  $C$  is  $\Delta C = (\partial C / \partial \tau)_T \tau$ . In a solid under constant stress  $C = \partial H / \partial T$ , where  $H$  is the enthalpy of the solid. In cubic solids it can be shown that if  $\tau$  is a shear  $(\partial C / \partial \tau)_T = 0$  and an effect occurs only if the stress is a pressure. In hexagonal materials,  $C$  does depend on the shear stresses but the order of magnitude change in  $C$  can be obtained by considering the effect of pressure stresses. Under a pressure  $p$ ,

$$\Delta C = (\partial C / \partial p)_T p = (\partial^2 H / \partial p \partial T)_p = T(\partial(V\alpha_v) / \partial T)_p,$$

since  $(\partial^2 H / \partial p \partial T)_p = T(\partial^2 V / \partial T^2)_p = T(\partial(V\alpha_v) / \partial T)_p$ . Here  $\alpha_v = V^{-1}(\partial V / \partial T)_p$  is the volume thermal expansion coefficient and  $V$  is the volume. The Grüneisen relation  $V\alpha_v = \gamma\beta C$ , where  $\beta$  is the compressibility and  $\gamma$  is the Grüneisen constant, a dimensionless number around 2, then gives

$$\frac{\Delta C}{C} = \left( T \frac{1}{\beta} \frac{\partial \beta}{\partial T} + T \frac{1}{C} \frac{\partial C}{\partial T} \right) \gamma \beta p. \quad (1)$$

At low temperatures the first term in the parenthesis in (1) is much smaller than the second term. The second term at low temperatures has values between one and three. Hence at low temperatures

$$\Delta C / C \approx 5\beta p. \quad (1')$$

For pressures equal to the elastic limit,  $\beta p$  is less than

<sup>25</sup> D. L. Martin, Proc. Roy. Soc. (London) **A254**, 433 (1960).

a percent. Even if all of the sample had this stress, a highly unlikely upper limit, the percentage change in  $C$  is small. Thus we can neglect the change of specific heat produced by stresses.

Effect (b) depends on the amount transforming per unit temperature interval. If Fig. 1 is representative for all sodium samples as the experimental evidence indicates,<sup>24,25</sup> then effect (b) must be negligible as the temperature is increased between 0°K and 30°K since no transformation is occurring. Because the specific heat is usually measured when the temperature is being raised, effect (b) should not be important below 30°K. It can be argued, however, that since the transformation varies from one sample to the next, Fig. 1 may not be representative of the samples employed in some specific heat measurements. In particular, as the temperature is varied in the liquid helium range some transformation may be occurring in some samples. Even in that unlikely case we will show that the electronic value of the specific heat will not be effected by (b). That portion of the sample that is transforming must be in thermoelastic equilibrium since from Fig. 1 the hysteresis effect extends to past 30°K for that portion that has exceeded the elastic region. For the thermoelastic portion of the sample, the transformation is occurring reversibly and the heat of transformation is given by  $T\Delta S$ , where  $\Delta S$  is the difference in entropy between the two phases. At any temperature  $T$ ,  $\Delta S$  is given by  $\int_0^T (\Delta C / t) dt$ , where  $\Delta C$  is the difference in specific heat between the two phases. At liquid helium temperatures and below,  $\Delta C = AT^3 + BT$  and thus  $\Delta S = \frac{1}{3}AT^3 + BT$ . The contribution of the heat of transformation to the measured specific heat, if  $df/dT$  of the sample transforms per unit temperature change, is

$$dQ/dT = T\Delta S(df/dT) = (\frac{1}{3}AT^4 + BT^2)(df/dT).$$

One expects  $df/dT$  to be well behaved near absolute zero and thus it can be expanded in a power series in  $T$ :

$$df/dT = a + bT + \dots$$

We see that the heat of transformation does not produce a linear term in  $T$  in the specific heat and thus effect (b) cannot in any way affect the electronic specific heat. In addition, because the available experimental data indicate that no thermoelastic effect occurs with increasing temperature below 30°K, we will also assume that (b) does not affect the Debye characteristic temperature.

By the process of elimination only effect (a) can vary the measured specific heat at low temperatures. That effect (a) exists, i.e., the two different phases have different specific heats, is guaranteed by thermodynamic requirements. The low-temperature phase at 0°K must have a lower internal energy than the high-temperature phase. The high-temperature phase on the other hand must have a larger entropy at a given temperature, and thus a larger specific heat, in order that its free

TABLE I. The various experimental results on the electronic specific heat and Debye temperatures,  $\theta_D$ , for samples of sodium below 3°K. The electronic specific heat is expressed in terms of the ratio of an effective mass of the electrons,  $m^*$ , to the free electron value,  $m$ .

Investigator	$m^*/m$	$\theta_D$ (°K)	Sample preparation
Gaumer and Heer <sup>a</sup>	1.21	158	cast
Lien and Phillips <sup>b</sup>	1.33	156	cast
Roberts <sup>c</sup>	1.22±0.04	158	cast
Parkinson and Quarrington <sup>d</sup>	1.6 ±0.16	158	cut from lump

<sup>a</sup> See reference 15.

<sup>b</sup> See reference 16.

<sup>c</sup> See reference 11.

<sup>d</sup> See reference 12.

energy,  $U-TS$ , become lower at elevated temperatures. Experimental measurements<sup>25</sup> confirm this reasoning.

Effect (a) implies that the specific heat of a sample of sodium at low temperatures is given by  $C = fC_l + (1-f)C_h$ , where  $f$  is the fraction of low-temperature phase present and  $C_l$  and  $C_h$  are the specific heats of the low- and high-temperature phases, respectively,  $C_h > C_l$ . The specific heat should be well behaved at low temperatures and vary as  $\gamma T + \beta T^3$ . The only variation between various experimental results should be in the values of  $\gamma$  and  $\beta$ . We use this property in the next section to analyze the available experimental data on the specific heat of sodium.

#### IV. INTERPRETATION OF EXPERIMENTAL MEASUREMENTS

Table I summarizes the various experimental results on the low-temperature specific heat of sodium that give a value for the electronic contribution. Two other measurements have been made, one by Rayne<sup>14</sup> and another by Simon and Zeidler,<sup>13</sup> which show anomalous behavior at low temperatures. From what was said in Sec. III this anomalous behavior is probably not related to the phase transformation. All of the investigators listed in Table I found that at low temperatures the specific heat of sodium varies as  $\gamma T + \beta T^3$ . As shown in Sec. III only effect (a), the variation of the composition of the sample between the two phases, can affect  $\gamma$  and the same can be said for  $\beta$  with a little less certainty. To determine what the mixture of the two phases was in the various samples used by each investigator we use the fact that the high-temperature phase must have the larger specific heat. The results of Parkinson and Quarrington<sup>12</sup> (PQ) and Roberts<sup>11</sup> (R) are of particular interest because their measurements were made in the same laboratory, the main difference being in the method of preparation of the sample. Yet the specific heat measured by PQ was 10% higher at 1.5°K and 5% higher at 20°K than that measured by R. This difference is much larger than can be explained by errors of measurement and must be real. The sample used by PQ had more of the high-temperature phase in it than the sample of R. Another interesting obser-

vation is that R, and Gaumer and Herr<sup>15</sup> used entirely different experimental methods in measuring the specific heat, but prepared their samples in similar ways and obtained very good agreement. Thus, the difference in the experiment results appear to be only due to differences in the method of preparation of the sample.<sup>11</sup> This is consistent with our reasoning that differences in the specific heat can be caused by differences in the proportion of the two phases in the sample. The specific heat values of Lien and Phillips<sup>16</sup> are between those of PQ and R, indicating that their sample had more of the high-temperature phase than that of R but less than that of PQ.

A plot of the effective mass determined by various investigators as a function of the specific heat measured at 2°K is shown in Fig. 2. The values at 2°K are taken because that is the highest temperature where 3 of the 4 investigators have experimental points. The measurements of Lien and Phillips extended only up to 1.4°K. Their data were extrapolated to 2°K by assuming the same temperature dependence as they measured below 1.4°K. The experimental values of R and PQ for  $m^*/m$  have their estimated limits indicated. The values of Gaumer and Heer, and Lien and Phillips should be more accurate than those of R since they made measurements at lower temperatures. If our reasoning is correct and only effect (a) causes the variation, the data should be consistent with a straight line, as it is. The straight line is drawn in Fig. 2 to give most weight to the most accurate points. Since the electronic contribution to the specific heat at 2°K is less than half of the total specific heat it does not necessarily follow that the plot should be linear. There is a definite trend in the experimental values. Those samples that have more of the high-temperature phase as determined by their larger values of specific heat, also give a larger value for the effective mass of the conduction electrons. We conclude from this that the high-temperature phase has a higher value of effective mass of the conduction electrons than the low-temperature phase. We can further conclude from Fig. 2 that  $m^*/m \geq 1.5$  for the high-temperature

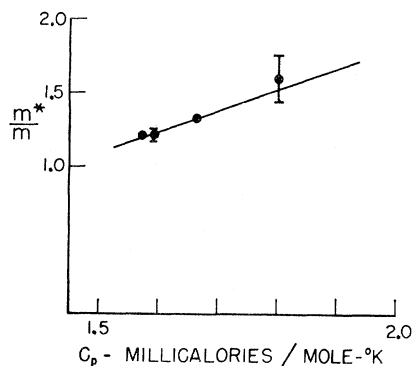


FIG. 2. Effective mass of the conduction electrons versus the total specific heat at 2°K. The values of  $m^*/m$  are the same as shown in Table I.

phase and  $m^*/m \leq 1.21$  for the low-temperature phase. The Debye characteristic temperature  $\theta_D$  does not vary appreciably from one phase to the other at very low temperatures as shown in Table I though there is an appreciable variation above 3.5°K. Figure 3 illustrates the variation of  $\theta_D$  with temperature according to the results of PQ and R.

An estimate of how much of each phase is present in the various samples of sodium can be made using the estimates of the Debye temperatures of the two phases. At 20°K the Debye temperatures of the low- and high-temperature phases are 160° and 153°K, respectively. The sample of PQ had a Debye temperature of 155°K while that of R had a Debye temperature of 158.6°K, both at 20°K. Therefore about 30% of the sample of PQ and 80% of the sample of R were in the low-temperature phase. From this we extrapolate from Fig. 2 that  $m^*/m$  for the low- and high-temperature phases are about 1.1 and 1.7, respectively.

Since there is such a large difference in the effective mass between the two phases of sodium the questions naturally arise—can this large difference be understood, and which value, if any, should be compared with the many-body theory of a dense degenerate electron gas. Experimentally it is found that the volume of the low-temperature phase is  $0.27 \pm 0.16\%$ <sup>22</sup> larger than the high-temperature phase. This small volume change in a free gas model cannot explain the large effective-mass difference between the two phases. The difference can, however, be explained by a distortion of the Fermi surface near the Brillouin zones.

The wave functions of sodium for values of the  $\mathbf{k}$  vector not too close to the Brillouin zone faces is insensitive to the crystal structure, but depends mainly on the volume per atom. The dependence on crystal structure occurs only for those values of  $\mathbf{k}$  close to the Brillouin zone faces. In the hcp low-temperature phase of sodium, if one assumes a spherical Fermi surface of radius  $k_0$ , the Brillouin zone "A" face,<sup>26</sup> which is parallel

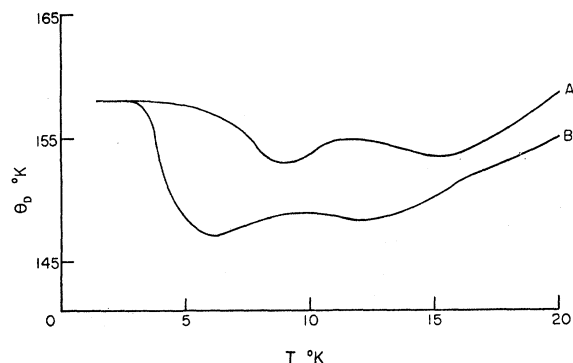


FIG. 3. The Debye temperature versus temperature for two different samples of sodium. Curve A is the results of reference 11 and curve B is the results of reference 12.

<sup>26</sup> A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1954), 2nd ed., p. 89.

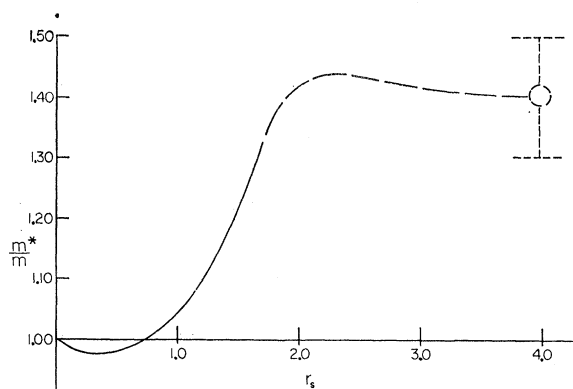


FIG. 4. The effect of correlation on the effective mass of a free electron gas as determined by the electronic specific heat. The solid curve represents the theoretical results of DuBois.<sup>9</sup> The point is the value determined from the experimental measurements of the electronic specific heat of sodium. The indicated errors are only rough estimates. The dashed curve is a possible interpolation.

to the  $c$  axis, is a distance  $1.04 k_0$  from the center of the Brillouin zone. The Brillouin zone "B" face, which is perpendicular to the  $c$  axis, is a distance  $1.11 k_0$  from the center of the Brillouin zone. In the bcc high-temperature phase of sodium the closest face is  $1.14 k_0$  from the center of the Brillouin zone. Because of the close approach of a spherical Fermi surface to the Brillouin zone "A" face of a hcp structure, it is reasonable to expect that the Fermi surface will actually be distorted from a spherical shape. The experimental values for the effective masses indicate that the Fermi surface makes a substantial contact with the "A" face in the hcp phase. The decrease in the Fermi surface area overcomes the increased effective mass in the vicinity of the contact. It is clear then that only the high-temperature bcc phase of sodium approximates a free electron gas and theory should be compared with the values of that phase alone.

## V. COMPARISON WITH THEORY AND CONCLUSIONS

Band-theory calculations, which do not include the correlations effects on the effective mass, show that the electrons in bcc sodium approximate a free electron gas. Their effective mass is almost exactly equal to the free electron value.<sup>27</sup> Any difference from the free electron value must be due to effects neglected in the ordinary band-theory calculations. One such effect, as is mentioned frequently above, is correlation effects. Another such effect is the electron-phonon interaction.<sup>19,28</sup> Estimates of the electron-phonon interaction contributions to the effective mass is that it will increase it by about 20%. The accuracy of this type of calculation

<sup>27</sup> F. S. Ham, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 127.

<sup>28</sup> M. J. Buckingham and M. R. Schafroth, *Proc. Phys. Soc. (London)* **A67**, 828 (1954); J. J. Quinn, *Bull. Am. Phys. Soc.* **5**, 199 (1960).

has been questioned since it is not clear that the electron-phonon interaction can be calculated separately from correlation effects. For lack of anything better we will nevertheless assume that the effects of correlation and electron-phonon interactions can be estimated separately. Then the experimental data that  $m^*/m=1.7$  for the bcc phase of sodium indicates that correlation alone increases the effective mass of the conduction electrons ( $r_s=3.96$ ) about 40%. This result is in disagreement with the calculations of Quinn and Ferrell,<sup>19</sup> and Pines,<sup>18</sup> but is consistent with the results of DuBois<sup>9</sup> and Fletcher and Larson.<sup>20</sup> Figure 4 shows the theoretical calculations of DuBois as the solid line and the experimental point with approximate errors from the results on bcc sodium. The dashed line is a possible interpolation between the results.

The large value of the effective mass of the electrons in bcc sodium is quite surprising. Yet, it is not at variance with the theoretical calculations of DuBois, and Fletcher and Larson, and estimates of the effect of

electron-phonon interactions. However, it would still be highly desirable to obtain further experimental measurements on the electronic specific heat of sodium. In particular, a measurement on a sample in which the transformation to the low-temperature phase has somehow been inhibited would be of great interest.

The large change in effective mass between the bcc and hcp phases is also surprising. The substantial contact of the Fermi surface to the Brillouin zone "A" face implies a fairly large energy gap at the zone face. This disagrees with the model of Cohen and Heine<sup>29</sup> for sodium. However, the contact explains why the hcp phase has the lower energy at absolute zero. The lowering of the energy levels in the vicinity of the contact lowers the total energy of the solid.

The author is indebted to Professor M. H. Cohen for a stimulating discussion and to Professor Ralph D. Myers for a critical and informative discussion.

<sup>29</sup> M. H. Cohen and V. Heine, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis Ltd., London, 1958), Vol. 7, p. 395.

## Ultrasonic Attenuation in Superconductors\*

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A general treatment of ultrasonic attenuation of both longitudinal and transverse waves in superconductors, valid for an arbitrary mean free path, is given on the basis of the Bardeen-Cooper-Schrieffer theory. The interaction between the ultrasonic waves and electrons is assumed to be given by a self-consistent electromagnetic field. Instead of the customary theory of the attenuation based on the Boltzmann equation, a different formulation is developed using the density-matrix formalism. The ratio of the attenuations in superconducting and normal metals for the longitudinal wave turns out to be approximately independent of the mean free path. The attenuation of the shear wave due to electromagnetic interaction is shown to be very small in the superconducting state.

### 1. INTRODUCTION

ULTRASONIC attenuation in metals at low temperatures, predominantly electronic in origin, has been an object of active researches in recent years, yielding valuable information on the properties of normal metals as well as superconductors.<sup>1,2</sup> Bömmel and Mackinnon<sup>3</sup> first observed the rapid fall in the attenuation below the critical temperature. While it clearly reflected the decrease of the normal component, this steep

drop could not be accounted for by the simple application of the two-fluid model and waited for the Bardeen-Cooper-Schrieffer (BCS) theory<sup>4</sup> for its satisfactory explanation. According to the latter theory the ratio,  $\alpha_s/\alpha_n$ , of the attenuations of a longitudinal sound wave in superconducting and in normal state varies with temperature as  $2f(\epsilon_0)$ , where  $f$  is the Fermi function and  $\epsilon_0$  is the temperature-dependent energy gap. The agreement between this formula and the experimental data, obtained for pure superconductors mostly in the frequency range around 50 Mc/sec, is reasonably good and is one of the strong supports of the BCS theory.<sup>5</sup> In fact this is one way of obtaining an empirical value of the

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<sup>1</sup> For general review of the subject, see R. W. Morse, *Progress in Cryogenics*, edited by K. Mendelssohn (Heywood & Company Ltd., London, 1959), Vol. I, p. 220.

<sup>2</sup> Concerning the ultrasonic attenuation in superconductors, see J. Bardeen and J. R. Schrieffer, *Progress in Low-Temperature Physics*, edited by C. J. Gorter, (North Holland Publishing Company, Amsterdam (to be published)).

<sup>3</sup> H. E. Bömmel, *Phys. Rev.* **96**, 220 (1954); L. Mackinnon, *Phys. Rev.* **98**, 1181, 1210 (1955).

<sup>4</sup> J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

<sup>5</sup> R. W. Morse and H. V. Bohm, *Phys. Rev.* **108**, 1094 (1957); R. W. Morse, H. V. Bohm, and J. D. Gavenda, *Bull. Am. Phys. Soc.* **3**, 44 and 203 (1958).