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Nuclear Quadrupole and Electronic Heat Capacities of Bismuth*

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The heat capacity of bismuth has been measured from 0.1 to 2.0°K and found to be represented by $C=2.8\times10^{-7}T^{-2}+2.1\times10^{-5}T+1944(T/\theta)^3$ joules/mole deg with $\theta=120.4-0.6T^2$. The T^{-2} term in the heat capacity is assumed to be associated with the alignment of the nuclear electric quadrupole moment in the electric field gradient of the crystal and is used to obtain the value 25 Mc/sec for the quadrupole coupling constant. The linear term is used, together with known parameters for the electrons in the conduction band, to obtain an average effective mass for the holes in the valence band of 0.9 times the free electron mass.

I. INTRODUCTION

MEASUREMENT of the electronic heat capacity of a metal permits a direct evaluation of the total density of states at the Fermi level from the relation[1]

$$\gamma=\tfrac{1}{3}\pi^2k^2n'(E_F), \tag{1}$$

in which γ is the coefficient of the linear term in the electronic heat capacity, k is Boltzmann's constant, and $n'(E_F)$ is the number of states per unit range of energy at the Fermi energy E_F. For bismuth the electronic heat capacity is unusually small relative to the lattice heat capacity, $(12/5)\pi^4k(T/\theta)^3$. At the lowest temperatures accessible with liquid helium, the electronic term is only a few percent of the total and an accurate measure of γ can be obtained only at temperatures well below 1°K.

In addition to the electronic and lattice heat capacities, a contribution from the alignment of the nuclear electric quadrupole moment in the electric field gradient of the crystal can be expected to be important at temperatures of the order of 0.1°K. Keesom and Bryant[2] have observed a heat capacity of this type at somewhat higher temperatures in rhenium, which has an unusually large quadrupole moment. When the nucleus is in an axially symmetric field gradient, the orientation dependent part of the nuclear energy is given by[3]

$$E_m=\frac{e^2qQ}{4I(2I-1)}[3m^2-I(I+1)], \tag{2}$$

in which m is the projection of the nuclear spin, I, on the symmetry axis, e is the electron charge, Q is the scalar quadrupole moment of the nucleus, and q is the largest component of the electric field gradient tensor in the principal axis system. An energy level system of this type produces a Schottky-type heat capacity anomaly with a maximum at a temperature determined largely by e^2qQ, the quadrupole coupling constant. Naturally occurring bismuth consists of a single isotope, Bi^{209}, which has a spin $I=9/2$ and a quadrupole moment $Q=-0.4\times10^{-24}$ cm^2.[4] By analogy with the field gradients existing in gallium[5] and indium[6] for which the pure quadrupole resonance spectra have been observed, and in rhenium[2] for which e^2qQ has been measured calorimetrically, the temperature of the maximum in the heat capacity can be estimated to be of the order of magnitude of 10^{-3}°K. At temperatures above the maximum the nuclear quadrupole heat capacity, C_Q, can be expanded in a power series in T^{-1} with coefficients determined by the spacing of the energy levels. The first two terms in the expansion, calculated from (2) by standard statistical methods,

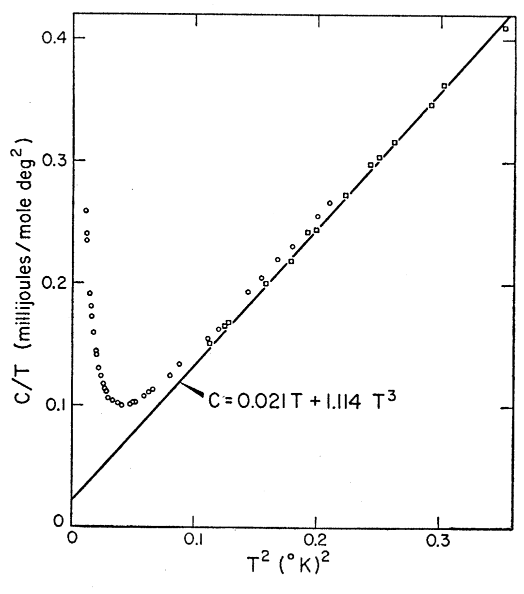

FIG. 1. Total heat capacity plotted as C/T vs T^2, for the lower temperature points. The straight line was chosen to fit points between $T^2=0.2$ and $T^2=1.0$ on an extension of this plot.

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[1] A. H. Wilson, *Theory of Metals* (Cambridge University Press, New York, 1953), 2nd ed., p. 144.

[2] P. H. Keesom and C. A. Bryant, Phys. Rev. Letters 2, 260 (1959).

[3] See, for example, T. P. Das and E. L. Hahn, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, New York, 1957), Suppl. 1.

[4] For references see D. Strominger, J. M. Hollander, and G. T. Seaborg, Revs. Modern Phys. **30**, 585 (1958).

[5] W. D. Knight, R. R. Hewitt, and M. Pomerantz, Phys. Rev. **104**, 271 (1956).

[6] R. R. Hewitt and W. D. Knight, Phys. Rev. Letters **3**, 18 (1959).

are:

$$\frac{C_Q}{R}=\frac{1}{80}\,\frac{(2I+2)(2I+3)}{2I(2I-1)}\left(\frac{e^2qQ}{kT}\right)^2-\frac{1}{1120}\,\frac{(2I-3)(2I+2)(2I+3)(2I+5)}{(2I)^2(2I-1)^2}\left(\frac{e^2qQ}{kT}\right)^3, \qquad (3)$$

in which R is the gas constant. The result is valid for both integral and half-integral spins.

At temperatures high enough for the second term in (3) to be negligible, but low enough to be in the T^3 region of the lattice heat capacity, the total heat capacity is given by

$$C=AT^{-2}+\gamma T+(12/5)\pi^4R(T/\theta_0)^3. \qquad (4)$$

In the above equation, θ_0 is the Debye characteristic temperature of the lattice at 0°K and A is obtained from the coefficient of T^{-2} in (3).

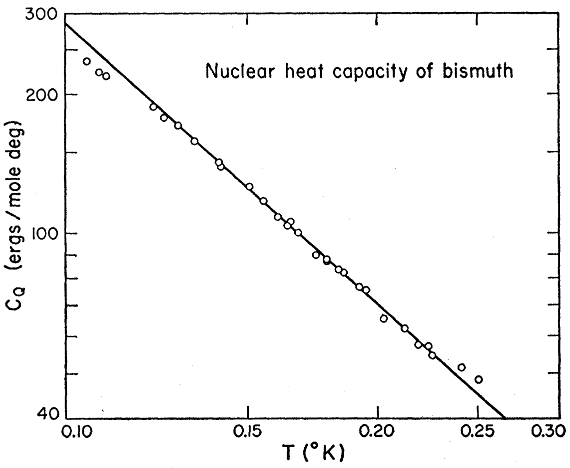

FIG. 2. The nuclear quadrupole heat capacity plotted as $\log C_Q$ vs $\log T$. The line has a slope of -2.

II. EXPERIMENTAL RESULTS

The measurements were made on a polycrystalline sample with a grain size of about 1 cm. The original material was 99.999% pure containing $2\times10^{-4}\%$ each of copper, silver, and lead and less than $10^{-4}\%$ of iron. After being cast in vacuum in a high purity graphite mold, the final sample was found to have a residual resistance ratio $\rho_{1.5°}/\rho_{298°}=0.015$.

The method used in the measurements has already been described[7] and will not be repeated here except to point out that temperature measurements below 1.1°K were based on an extrapolation from higher temperatures of a Curie-Weiss law for the susceptibility of copper potassium sulfate. The temperature scale, as defined in this way, is believed to introduce errors which increase with decreasing temperature, amounting to 3% of the measured heat capacity at 0.3°K and 15% at 0.1°K.

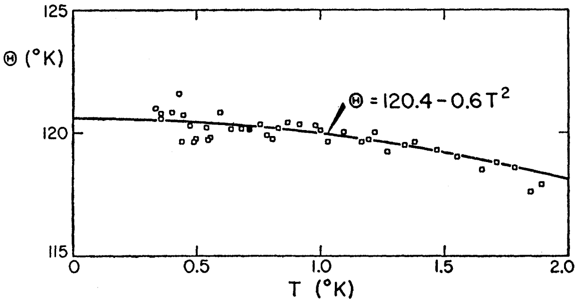

FIG. 3. The apparent Debye temperature as a function of temperature.

Two separate sets of heat capacity measurements were made covering the ranges 0.1 to 0.45°K and 0.35 to 2.0°K. The different sets are distinguished from each other in the figures and can be seen to differ by slightly more than the scatter of the individual points in the region common to both. This is presumably due to errors in the choice of constants for extrapolation of the Curie-Weiss law.

The constants γ and θ_0 were determined by plotting C/T versus T^2 and fitting the points for T^2 between 0.2 and 1.0 deg^2 with a straight line. Figure 1 shows the low-temperature end of this plot. The resulting values are $\gamma=0.021\times10^{-3}$ joule/mole deg^2 and $\theta_0=120.4$°K. The nuclear quadrupole heat capacity, C_Q, was taken to be the difference between the individual points below 0.25°K and the straight line of Fig. 1. Figure 2 demonstrates the proportionality of C_Q to T^{-2}, and Fig. 3 shows the apparent Debye temperature for the higher temperature points.

III. DISCUSSION

1. Nuclear Quadrupole Heat Capacity

The rhombohedral unit cell of bismuth contains two atoms, each located on the triad axis. Thus, the environment of each atom has a threefold symmetry axis and the quadrupole coupling constant, together with the nuclear spin, completely determines the energy level pattern and the nuclear quadrupole heat capacity, C_Q.

The proportionality of C_Q to T^{-2} shows that the second term of (3) is negligible at the temperatures of the experiment and permits an evaluation of the quadrupole coupling constant. It is found that $e^2qQ/k=1.22\times10^{-3}$°K or, in terms of the associated frequency, 25 Mc/sec. From this it follows that the second term in (3) is in fact about 0.1% of C_Q at 0.1°K. The magnitude of the field gradient in the direction of the symmetry axis is given by $q=1.83\times10^{24}$ cm^{-3}.

2. Electronic Heat Capacity

As pointed out above, the electronic heat capacity amounts to only a few percent of the total at liquid

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[7] N. E. Phillips, Phys. Rev. **114**, 676 (1959).

helium temperatures and measurements above 1°K cannot be expected to give reliable values of γ. Measurements to 0.3°K have been made by Kalinkina and Strelkov[8] who find $\gamma = 0.067\times10^{-3}$ joule/mole deg^2 compared with the present value of 0.021×10^{-3}. The electronic heat capacity is only about 15% of the total at 0.3°K but the measurements at lower temperatures in the present work do not necessarily give a more accurate value of γ because of the increasing importance of the nuclear term. Part of the discrepancy is apparently produced by the nuclear heat capacity, which is comparable to the electronic heat capacity even at 0.3°K, and which could not be taken into account by Kalinkina and Strelkov in the analysis of their data. There remains a discrepancy by a factor of two for which several explanations seem possible. There may be a real difference between the samples. It is known that in bismuth the valence band is almost exactly filled and, under these conditions, the density of states at the Fermi level would be expected to be extremely sensitive to the presence of impurities. In residual resistivity the present polycrystalline sample is intermediate between the polycrystalline and single crystal forms of the material used by Kalinkina and Strelkov. A second possibility is that the difference is related to the use of different paramagnetic salts for temperature determinations: copper potassium sulfate in this work, and iron ammonium sulfate in the experiments of Kalinkina and Strelkov. Measured temperature differences can be very sensitive to errors in the temperature scale and the use of different salts can lead to appreciably different results even when the available corrections to thermodynamic temperatures are used.[9]

Jones[10] has proposed a model for the electronic structure of bismuth in which a Brillouin zone capable of holding five electrons per atom is almost filled, leaving a small number of holes and an equal number of electrons in the next zone. The portions of the Fermi surface in the conduction band consists of three sets of ellipsoids arranged to preserve the symmetry of the crystal. A study of the de Haas-van Alphen effect by Shoenberg[11] has shown that one set of ellipsoids can be represented by

$$2m_0E_e/\hbar^2 = \alpha_{11}k_x^2 + \alpha_{22}k_y^2 + \alpha_{33}k_z^2 + 2\alpha_{23}k_yk_z, \tag{5}$$

if the x and z directions are chosen to be along a diad axis and the triad axis, respectively. E_e is the Fermi energy of the electrons, m_0 the free electron mass, α_{ij} the components of the reciprocal mass tensor in units m_0^{-1} and $\mathbf{k}$ is the wave number vector. The other ellipsoids are related to the first by 120° rotations about the triad axis. Abeles and Meiboom[12] were able to interpret their measurements of galvanomagnetic effects in bismuth by including an ellipsoid of revolution for the holes. If E_h is the Fermi energy of the holes and β_{ii} their reciprocal mass components, the Fermi surface for the holes is

$$2m_0E_h/\hbar^2 = \beta_{11}k_x^2 + \beta_{11}k_y^2 + \beta_{33}k_z^2. \tag{6}$$

A contribution from the electrons has been observed in the de Haas-van Alphen effect,[11,13,14] galvanomagnetic effects,[12] cyclotron resonance,[15–17] ultrasonic attenuation[18] and the anomalous skin effect[19] with the result that the parameters in (5) are relatively well known and can be used to estimate the contribution of the electrons, γ_e, to γ. The contribution of the holes to γ is then $\gamma_h = \gamma - \gamma_e$ and can be used to calculate the Fermi energy of the holes and an average effective mass which, in combination with the mobilities of the holes, gives the values of β_{11} and β_{33}.

For a single ellipsoidal energy surface the density of states is given by

$$\begin{aligned} n'(E_e) &= (8\pi V/h^3)(2E_e)^{\frac{1}{2}}m_0^{\frac{3}{2}}(\alpha_{11}'\alpha_{22}'\alpha_{33}')^{-\frac{1}{2}} \\ &= (8\pi V/h^3)(2E_e)^{\frac{1}{2}}(m_{11}'m_{22}'m_{33}')^{\frac{1}{2}}, \end{aligned} \tag{7}$$

where V is the molar volume, the α_{ii}' are components of the reciprocal mass tensor in the principal axis system and the m_{ii}' are the corresponding effective masses. If Shoenberg's values of the effective masses, $m_{11}/m_0 = 2.4\times10^{-3}$, $m_{22}/m_0 = 2.5$, $m_{33}/m_0 = 0.05$, $m_{23}/m_0 = -0.25$, and Fermi energy, $E_e = 0.0177$ ev, are used with (1) and (7) remembering that there are three ellipsoids for the electrons, we obtain $\gamma_e = 0.0027\times10^{-3}$ joule/mole deg.^{2} This accounts for only about one tenth of the measured electronic heat capacity. The contribution of the holes, obtained by subtraction, is $\gamma_h = 0.018\times10^{-3}$ joule/mole deg^2. The density of holes is related to their Fermi energy and density of states by

$$E_h = 3n_hN/2n'(E_h), \tag{8}$$

where N is the Avogadro number and n_h is the number of holes per atom. Taking n_h equal to the number of electrons per atom[20] calculated from Shoenberg's data, the Fermi energy of the holes is $E_h = 0.0027$ ev and the overlap of the valence and conduction bands is $E_e + E_h = 0.020$ ev. A value of 0.73 m_0 is then obtained for the average effective mass of the holes, $m_0(\beta_{11}^2\beta_{33})^{-\frac{1}{3}}$, by application of (7) with E_e and α_{ii}' replaced by E_h and β_{ii}, respectively. Heine[20] has estimated an average

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[11] D. Shoenberg, Proc. Roy. Soc. (London) **A170**, 341 (1939).

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[16] J. E. Aubrey and R. G. Chambers, J. Phys. Chem. Solids **3**, 128 (1957).

[17] J. K. Galt et al., Phys. Rev. **114**, 1396 (1959).

[18] D. H. Reneker, Phys. Rev. **115**, 303 (1959).

[19] G. E. Smith, Phys. Rev. **115**, 1561 (1959).

[20] For a discussion of this point see: V. Heine, Proc. Phys. Soc. (London) **A69**, 505, 513 (1956).

effective mass of $1.5m_0$ from a consideration of the effect of alloying on the de Haas-van Alphen periods and Galt et al.[17] obtained an average effective mass of $0.16m_0$ from cyclotron resonance experiments. If the relaxation time for the holes is assumed isotropic, the ratio of the reciprocal mass components β_{33}/β_{11} is the ratio of the mobilities and the data of Abeles and Meiboom give $\beta_{33}/\beta_{11}=0.27$. In combination with the above estimate of $\beta_{11}^2\beta_{33}$ this leads to the values $\beta_{11}=2.1$ and $\beta_{33}=0.58$. These values of β_{11} and β_{33} may be compared with the values 1.7 and 0.13, respectively, obtained from anomalous skin effect experiments,[19] and 14.7 and 1.07 from cyclotron resonance experiments.[17]

As a result of inadequacies in the theory and the combinations in which the various quantities appear in the theoretical expressions, the de Haas-van Alphen experiments give some of the parameters for the electrons more accurately than others. Aubrey and Chambers[16] have suggested that α_{11}, α_{22}, α_{33}, and α_{23} be taken as 168, 2.0, 100, and -10, respectively, to give better agreement with the galvanomagnetic and cyclotron resonance experiments and at the same time preserve unchanged the ratios most accurately determined in the de Haas-van Alphen experiments. With these values of the α_{ij} the parameters for the holes become: $E_h=0.0016$ ev and the average effective mass is $0.90\ m_0$.

3. Lattice Heat Capacity

Over the temperature range of the measurements the lattice heat capacity is $C_L=(12/5)\pi^4R(T/\theta)^3$ with θ given by $\theta=120.4-0.6T^2$ to within a scatter of about 1%. This is in good agreement with other measurements. Kalkinkina and Strelkov[8] found $\theta_0=118.5\pm1$ and approximately the same curvature of θ vs T. From measurements above 1°K Ramanathan and Srinivasan[21] found $\theta_0=120$°K and Keesom and Pearlman[22] report an average θ of 117°K between 1.0 and 2.3°K.

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[21] K. G. Ramanathan and T. M. Srinivasan, Phys. Rev. **99**, 442 (1955).

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Note added in proof.—R. R. Hewitt and W. D. Knight (private communication) have found two quadrupole resonance absorption frequencies which are consistent with the above value of the nuclear quadrupole heat capacity.

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Spin Resonance of Charge Carriers in Graphite

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The observations reported here of the electron spin resonance in quite perfect single crystals of graphite clearly establish that the resonance arises from mobile charge carriers. The line shape is of the Dysonian form which is characteristic of conduction electron spin resonance in metals. The intensity of the spin resonance agrees, both in absolute magnitude and in temperature dependence, with values calculated from the band model of graphite by McClure. The g value of the resonance shows a remarkably large anisotropy which depends strongly on temperature and on the position of the Fermi level with respect to the band edge. At room temperature in pure graphite, g varies from 2.0026 ± 0.0002 to 2.0495 ± 0.0002 as the magnetic field is shifted from perpendicular to parallel to the c axis. The g-value anisotropy increases with decreasing temperature; $g_{\parallel}$ becomes 2.127 at 77°K while $g_{\perp}$ remains constant. The line width of the resonance is a few gauss ($T_2=2.0\times10^{-8}$ sec) which is extremely narrow in comparison with the field shifts caused by changes of anisotropy with temperature. This indicates that for conduction states in graphite, the g value is a strong function of the wave vector and that the line is narrowed by an averaging process in k space. This averaging is similar to that which occurs in motional and exchange narrowing.

I. INTRODUCTION

THE purpose of these experiments was to determine the nature of the unpaired spins which give rise to the electron spin resonance in graphite.[1,2] The investigation leads us to conclude that the spin resonance in pure, relatively perfect, single crystals is due to the mobile charge carriers. Both electrons and holes are thought to contribute to a single resonance line whose shape is described by Dyson's theory[3] of conduction electron spin resonance and whose intensity agrees with the band theoretical result of J. W. McClure. The resonance shows a remarkably large g-value anisotropy which exhibits a dependence upon temperature and Fermi level similar to that predicted by Elliott.[4] The band structure of graphite proposed by Wallace[5] and elaborated by Slonczewski, Nozières, and others[6,7] contains a degenerate band edge. This is just the situation which, on Elliott's theory, would give rise to the

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[6] J. C. Slonczewski and P. R. Weiss, Phys. Rev. **109**, 272 (1958).

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