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SPECIFIC HEAT OF BISMUTH BETWEEN 0.3 AND 4.4°K

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The specific heat of spectrally pure bismuth was measured in the temperature range 0.3 — 4.4° K. Below 1.8° K, the coefficient in the T^3 term in the formula for the temperature dependence of the specific heat is $\Theta_D = 118.5 \pm 1°$K, while the coefficient in the linear term is $\gamma = 1.6 \times 10^{-5}$ cal/deg^2-gm atom, which is an order of magnitude smaller than for most metals. The linear term is compared with the specific heat of electrons computed on the basis of the de Haas – van Alphen effect.

1. INTRODUCTION

BISMUTH has a rhombohedral lattice with two atoms per cell and a valence equal to three; consequently, the number of electrons per cell is six. Substances with an even number of electrons in the cell fill the upper band completely and are insulators. Inasmuch as bismuth always possesses metallic properties, its bands overlap and the conductivity is brought about by quasi-particles with two signs of charge — electrons and holes.

Investigation of the de Haas — van Alphen effect,[1] galvanomagnetic phenomena[2,3] and cyclotron resonance[4,5] allow us to conclude that the overlapping zone is not large and the concentration of holes and electrons $n_h = n_e \approx 10^{-5}$ electron atom^{-1}, whereas for most metals this quantity is of the order of unity. Therefore the magnitude of the linear term in the specific heat, which is related to the electron concentration, ought to be very small for bismuth, and can be determined with sufficient accuracy only for very low temperatures.

Measurements of the specific heat of bismuth have been carried out a number of times. The investigations of Keesom and van den Ende[6] were performed in the range 2 — 20° K with an accuracy of 10%. These authors found that Θ_D was not constant in the temperature range studied, but had a minimum at 9° K. They would give no judgment on the linear term of the specific heat. Keesom and Pearlman[7] measured the specific heat of bismuth in the range 1 — 4° K. The amount of impurities in the sample was estimated at 0.01%. In view of the difficulty of estimating the content of small amounts of impurities, the authors obtained data on the change in the electrical resistance of their bismuth sample as a function of temperature (Table I). The measurements showed that below 2.3° K, Θ_D is equal to 117° K. In the range 1 — 2.3° K, where the Debye law is valid, the linear specific heat term was isolated, with $\gamma = (1.9 \pm 0.7) \times 10^{-5}$ cal-deg^{-2}-gm atom^{-1}.

Ramanathan and Srinivasan[8] carried out measurements for a sample of purity 99.95% in the temperature range 1.3 — 4.1° K. The polycrystalline sample "1953" contained 0.02% Pb; 5×10^{-3}% Mn; 1×10^{-3}% Cd; 5×10^{-4}% Cu; 1×10^{-3}% Fe; As, Se, Te < 0.001%; 2×10^{-4}% Ag. The temperature of the specimen was measured by a carbon resistance thermometer, the instability of the calibration of which reduced the accuracy of the results. The temperature region in which Θ_D was established to be truly constant, was not large, which gave us no possibility of isolating the magnitude of the linear term with sufficient accuracy. Moreover, it was not evident whether one could assume that the pure bismuth will have the same values of Θ_D and γ as was obtained for these relatively contaminated samples. Therefore, the present research was undertaken with much purer metal and at much lower temperatures.

2. THE SAMPLE AND THE MEASUREMENTS

The sample investigated was a monocrystal, grown from spectrally pure bismuth,* and was several times recrystallized and outgassed in a quartz ampoule at a temperature of about 600° K in a hard vacuum. Table I allows us to judge the purity of the specimen by the magnitude of the residual resistance. The residual resistances of

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*The spectrally pure bismuth was prepared by the State Institute of rare metals.

TABLE I. Relative Resistances of Samples of Bismuth

T°K		73.3	4.2	1.5
Spectrally pure specimen	Polycrystalline	0.301	0.0251	0.0247
	Monocrystalline	0.285	0.006	0.006
Hilger Co. bismuth	Polycrystalline	0.285	0.026	—
Sample of Keesom and Pearlman[7]	"	0.383	0.112	—
Sample "1953"	"	0.68	0.56	0.425

several other specimens are listed for comparison.

The construction of the calorimeter in which the determination of the specific heat was carried out and the method of measurement were similar to those described earlier.[9] The sample, of mass 267.3 gm (1.175 gm atoms), was of cylindrical shape, with diameter 18 — 19 mm and length ~ 90 mm. The surface of the specimen was covered with a thin layer of adhesive BF-2, which was polymerized for about one hour at 120° C. A constantan heater was attached on the layer thus isolated by the same adhesive BF-2. A light copper screw with a phosphor bronze thermometer wound on it was screwed into the lower part of the cylinder. The entire thermometer, the heater, etc., had less than 0.3% of the weight of the sample. Appropriate corrections were introduced in the value of the specific heat. Above 1° K, the resistance thermometers were calibrated in terms of the vapor pressure of liquid helium in degrees of the 1955 scale. For temperatures below 1° K, the calibration was carried out in terms of the susceptibility of ferric ammonium alum (mark ChDA) compacted into a cylinder of 12 mm diameter and 40 mm length. The demagnetization factor of the salt[10] was found in order to calculate the corrections. Using the data of Kürti and Simon,[11] the magnetic temperature of an equivalent spherical sample was determined; then the magnetic temperature was reduced to the thermodynamic temperature by the method of Cooke, Meyer, and Wolf.[12] The bismuth sample and block of compressed ferric ammonium alum, which served as the cold reservoir for measurements below 1° K, were supported on nylon threads in a vacuum jacket. The heat exchange of the gases before demagnetization was brought about by an adsorbing carbon pump.[13]

3. RESULTS OF MEASUREMENT

The specific heat was measured in the temperature range 0.3 — 4.4° K. The experimental points in a plot of C/T vs. T^2 below T = 1.8° K (Fig. 1) form a straight line which determines the coefficients of the equation which describes the temperature dependence of the specific heat between 0.3 and 1.8° K:

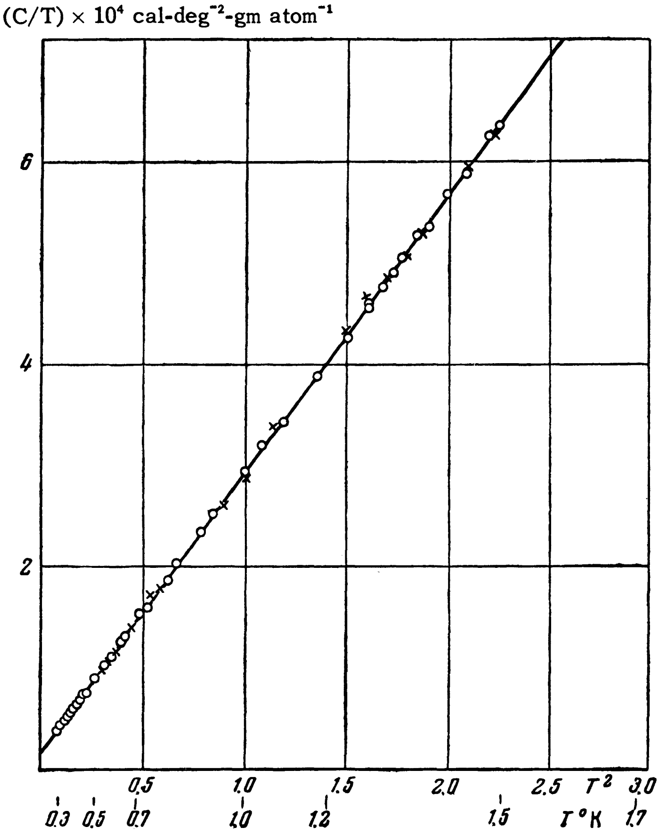

Fig. 1. C/T as a function of T^2 in the region in which the T^3 law is observed; × = measurements of 1953; o = spectrally pure sample.

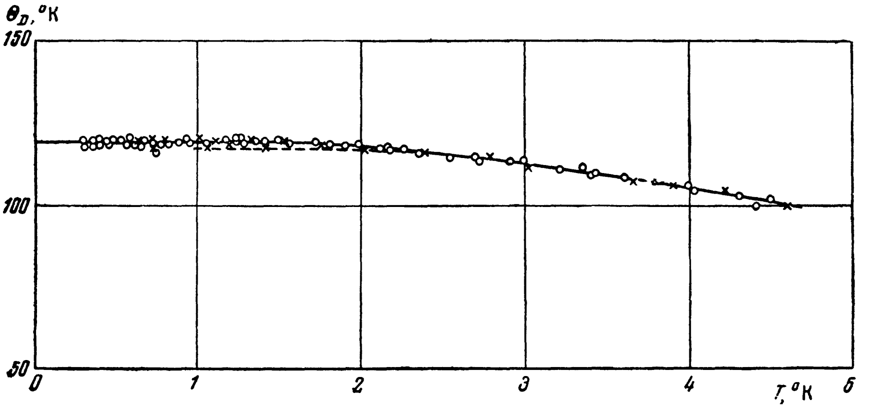

Fig. 2. Dependence of Θ_D on temperature. × = measurements of 1953; o = spectrally pure sample.

$$C = (1.6 \pm 0.1) \cdot 10^{-5} T + (2.79 \pm 0.09) \cdot 10^{-4} T^3 \text{ cal-deg}^{-1}\text{-gm atom}^{-1} \quad (1)$$

The effect of errors in measurement can be estimated by the limiting straight lines of that pencil of lines which can be drawn through the experimental points on the plot of C/T against T^2. In this way, the estimated inaccuracy of γ amounts to ± 0.1×10^{-5} cal-deg^{-2}-gm atom^{-1}. The maximum possible systematic error in the values of the specific heat for temperatures near 0.3°K did not exceed 3 — 5% in our estimate.

In the interval in which the T^3 law is satisfied, i.e., between 0.3 and 1.8°K, the Debye temperature $\Theta_D = 118.5 \pm 1$°K. The change of Θ_D at much higher temperatures is shown in Fig. 2. For bismuth, the T^3 law is satisfied for $T \leq 0.015\,\Theta_D$.

4. DISCUSSION OF RESULTS

The values obtained for Θ_D and γ can be regarded as reasonably trustworthy, since they are the results of measurements taken over an extended temperature range, which allows a thoroughly accurate separation of the magnitudes of the lattice and electronic specific heats. The purity of the investigated sample was evidently sufficient, as can be judged from the data of Table II, in which no appreciable change in the values of Θ_D and γ with purity of the metal can be observed.

TABLE II. Θ and γ of the Various Bismuth Samples

Sample	Θ_D, °K	$\gamma \cdot 10^5$, cal-deg^{-2}-gm atom^{-1}
Spectrally pure, outgassed sample	118.5±1	1.6±0.1
99.99% of Keesom and Pearlman	117±1	1.87±0.7
Sample "1953"	119±1	2±0.5
99.95% of Ramanathan and Srinavasan	120±1	1.14±1.46

In Figs. 1 and 2, we have plotted experimental points which refer to bismuth with an impurity of 0.02% of lead. No systematic variation of the results that could be related to the spectrally pure sample could be noted. The reliability with which the quantity γ has been measured, allows us to attempt to make some conclusions on the contribution of the electrons and holes to the specific heat.

The coefficient for the linear term of the specific heat is determined by the value of the mean density of electron states on the Fermi surface:

$$C_e = \gamma T = \frac{\pi^2 k^2}{3} \left(\frac{dN}{dE}\right)_{E=F_0} T. \quad (2)$$

Substituting the quantity $\gamma = 1.6 \times 10^{-5}$ cal-gm atom^{-1}-deg^{-2} found experimentally, we find that the density of states on the Fermi surface is $(dN/dE)_{E=E_0} = 2.85 \times 10^{-2}$ atom-ev. Since the second band in the energy spectrum of bismuth contains a very small number of electrons, they will be found in states close to the bottom of the band and the square law of dispersion is valid for the energy. Taking anisotropy into account (which is brought about by the real bismuth lattice), Shoenberg,[1] on the basis of experimental data on the de Haas — van Alphen effect, assumed a model for the Fermi surface containing three ellipsoids which coincide with each other upon rotation by 120°. Let us calculate the electronic specific heat for this case. The number of states for a gram atom of metal, taking into account both spin directions, $N = 2VV_p/(2\pi\hbar)^3$, where V is the atomic volume, V_p = volume bounded by the Fermi surfaces in momentum space. For the three ellipsoids considered,

$$V_p = 3\,(4\pi/3)\,p_1 p_2 p_3, \text{ where } p_i = \sqrt{2m_i E}.$$

It is easy to show that in this case we obtain the same results as for the isotropic model of Sommerfeld:

$$\left(\frac{dN}{dE}\right)_{E=E_0} = \frac{3n_a N_A}{2E_0},$$

where n_a = number of electrons per atom, E_0 = bounding Fermi energy, N_A = Avogadro's number. Then

$$\gamma = \frac{\pi^2 R}{2} \frac{n_a}{T_0}. \qquad (3)$$

In recent measurements of Shoenberg[1] on the de Haas — van Alphen effect for bismuth, the values $E_0/k = 205°K$, $n_a = 1.5 \times 10^{-5}$ electrons/atom were obtained; these are in excellent agreement with the calculations of Blackman,[14] based on earlier measurements of the de Haas — van Alphen effect ($n_a = 1.2 \times 10^{-5}$ electrons/atom, $E_0/k = 225°K$). Calculating the specific heat of the electrons from the data of Shoenberg according to Eq. (3), we find $\gamma_e = 0.072 \times 10^{-5}$ cal-gm atom^{-1}-deg^{-2}. This amounts to a small part of the experimental value obtained by us:

$$\gamma = 1.6 \ 10^{-5} \text{ cal-gm atom}^{-1}\text{-deg}^{-2}.$$

The values of the electron concentration found from galvanomagnetic measurements[2] and from cyclotron resonance[4,5] have the same order as does the quantity obtained from the de Haas — van Alphen effect of Schoenberg. Therefore we can consider that in the case of bismuth, all the conduction electrons take part in the de Haas — van Alphen effect. All this compels us to assume that the fundamental contribution to the linear term of the specific heat is made by the holes which have a significantly larger effective mass and less boundary energy than the electrons:

$$\gamma_h = \gamma - \gamma_e = 1.53 \cdot 10^{-5} \text{ cal-gm atom}^{-1}\text{-deg}^{-2},$$

where γ_h = coefficient determined by the holes, γ_e = that determined by the electrons and γ is determined experimentally from data on the specific heat.

At the present time, we can consider it established that, for bismuth, the concentration of electrons and holes is identical.[2,3,15] Taking $n_h = n_e = 1.5 \times 10^{-5}$ electrons/atom, we can determine the boundary energy of the holes from the specific heat. Substituting in Eq. (3) the value found above for $\gamma_h = 1.53 \times 10^{-5}$ cal-gm atom^{-1}-deg^{-2}, we obtain $E_0/k = T_0 = 9.65°K$, which is about 20 times smaller than the boundary energy of the electrons. Taking the mass of the holes to be isotropic, we determine it from the equation

$$\gamma_h = 3.26 \cdot 10^{-5} (m_h / m_0) \cdot n_a^{1/3} \cdot V^{2/3} \text{ cal-gm atom}^{-1}\text{-deg}^{-2}. \qquad (4)$$

It is shown that $m_h = 2.5\,m_0$, i.e., two and one-half times larger than the mass of the electron.

Thus, measurements of the specific heat of bismuth down to 0.3°K have led to a value of the coefficient in the electronic term of the specific heat $\gamma = 1.6 \times 10^{-5}$ cal-gm atom^{-1}-deg^{-2}. This value is twenty times greater than the value of γ_e for electrons computed on the basis of data on the de Haas — van Alphen effect. It can be thought that the holes determine the magnitude of the linear term of the specific heat of bismuth, for which one gets $E_0/k = 9.65°K$ and $m_h = 2.5\,m_0$.

In conclusion, the authors take the occasion to thank Academician P. L. Kapitza for his unflagging interest in the research, and also Professor N. P. Sazhin and R. A. Dul'kin for supplying the spectrally pure bismuth.

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119