

## Atomic Heat of Bismuth between 1° and 4°K\*

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Between 0.96 and 2.3°K the atomic heat of a polycrystalline ingot of bismuth (99.99 percent) can be represented by:  $c = (1.213 \pm 0.006)T^3 + (0.078 \pm 0.03)T$  millijoules/mole deg. The lattice contribution, given by the cubic term, corresponds to 117°K for the low-temperature Debye  $\theta$ . Between 2.3 and 4.2°K  $\theta$  decreases to 105°K. The electronic contribution is much smaller than for normal metals.

## I. INTRODUCTION

**B**ISMUTH is unique among the metals in the variety of electric and magnetic properties for which it exhibits anomalously large effects. Among these are resistivity, Hall constant and change of resistivity in a magnetic field, diamagnetic susceptibility, magnetic anisotropy and its magnetic field dependence (de Haas-van Alphen effect). The large diamagnetism can be accounted for at least qualitatively by a theory proposed by Jones.<sup>1,2</sup>

Jones' band picture can be summarized briefly as involving an overlap between the fifth and sixth bands, the latter containing a small number of electrons and the former, a small number of holes. This structure implies that the nonlattice contribution to the atomic heat at very low temperatures will be a very small linear term. However, it was not possible to determine whether such a term is present from the measurements of Keesom and van den Ende<sup>3</sup> in the liquid helium temperature region. We have therefore, repeated these measurements, carrying them to somewhat lower temperatures, in order to determine the magnitude of this contribution to the atomic heat.

The scatter of the earlier data makes the calculation of the Debye  $\theta$  uncertain below 4°K. We were therefore also interested in determining an accurate value for  $\theta_0$ , the constant value for  $\theta$  in the "true  $T^3$  region." From the calculations of Blackman,<sup>4</sup> which show that the true  $T^3$  region extends from 0°K to  $\theta/100$  or  $\theta/50$ , and the rough values measured by Keesom and van den Ende,<sup>3</sup> this region would be expected to have its upper limit around 1° or 2°K. The variation of  $\theta$  with  $T$  immediately above the true  $T^3$  region is also of interest because of its connection with the vibration spectrum, which has not yet been calculated theoretically for the lattice in which bismuth crystallizes.

## II. EXPERIMENT

## A. Sample

The sample was a polycrystalline ingot of bismuth weighing 521.8 grams, with a stated purity of 99.99 atomic percent.<sup>5</sup> When the calorimetric measurements were completed, a piece was cut from the middle of the ingot and its resistance was measured at several temperatures from 4° to 273°K. The ratio  $R(T)/R(273^\circ\text{K})$ , where  $R$  is the resistance, is given in Table I. These values are comparable with some of the higher values found by Schubnikow and de Haas<sup>6</sup> in their measurements on a large number of single crystals of bismuth. Since our ingot was polycrystalline, it appears that it had a purity of the order which was stated. In order to check further on its purity, Mr. R. Van Veld of this department made a spectrographic analysis which could have detected metallic impurities present in concentrations as low as  $10^{-5}$ . No impurities were found.

## B. Apparatus and Procedure

The bismuth ingot was hung by nylon thread in a vacuum can. Cigarette paper was glued to the ingot with Glyptal varnish, and on it were wound a constantan heater wire and a phosphor-bronze thermometer wire.<sup>7</sup> In part of the calibrating procedure, the measurements were carried out in the manner reported previously,<sup>8</sup> except for a difference, described below.

Since it was anticipated that the linear term in the atomic heat, if present at all, would be small relative to the cubic lattice term, we added a booster pump<sup>9</sup> in the bath pumping line, so as to be able to reach lower bath temperatures. At the lowest temperature reached,

TABLE I. Resistivity ratio for bismuth sample.

$T$ (°K)	77.3	20.0	14.2	4.2
$R/R_{0^\circ\text{C}}$	0.383	0.154	0.135	0.112

\* This work was supported by Signal Corps Contract.

<sup>1</sup> H. Jones, Proc. Roy. Soc. (London) **A147**, 396 (1934).

<sup>2</sup> N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, London, 1936), p. 212.

<sup>3</sup> W. H. Keesom and J. N. van den Ende, Commun. Kamerlingh Onnes Lab. Univ. Leiden, No. 203d: Proc. Koninkl. Ned. Akad. Wetenschap. **33**, 243 (1930); Leiden Commun. 213c, Proc. Koninkl. Ned. Akad. Wetenschap. **34**, 210 (1931).

<sup>4</sup> M. Blackman, Repts. Progr. Phys. **8**, 11 (1951).

<sup>5</sup> Kindly supplied by J. Crawford of the Oak Ridge National Laboratory.

<sup>6</sup> L. Schubnikow and W. J. de Haas, Commun. Kamerlingh Onnes Lab. Univ. Leiden, No. 207c (1930): Proc. Koninkl. Ned. Akad. Wetenschap. **33**, 350 (1930).

<sup>7</sup> Kindly supplied by Dr. K. Taconis of the Kamerlingh Onnes Laboratory, University of Leiden.

<sup>8</sup> N. Pearlman and P. H. Keesom, Phys. Rev. **88**, 398 (1952).

<sup>9</sup> Distillation Products Model KB100.

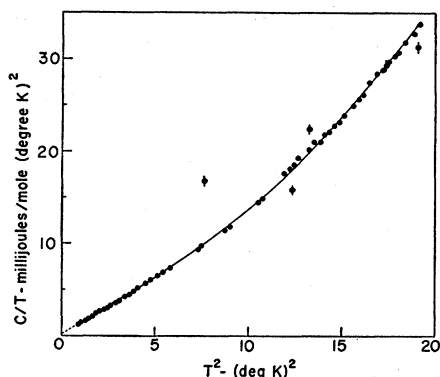


FIG. 1.  $C/T$  vs  $T^2$  for bismuth in liquid helium region. ●—our results; points with vertical line are those of Keesom and van den Ende.

0.95°K, the evaporation rate was 30 liters of helium at NTP per hour.

Because of the viscous gas flow, a pressure drop will arise in the cryostat, so that vapor pressures measured at the top of the cryostat according to our usual practice will be significantly lower than the corresponding pressures at the surface of the liquid, at the lowest temperatures. The existence of this pressure drop can be seen from the following observation. The lowest bath temperature obtainable without using the booster pump was about 1.2°K, and this temperature could also be reached with the booster pump by heating the bath. The pressure at the top of the cryostat was found to be smaller in the latter case for a given thermometer resistance, corresponding to the fact that since the gas flow was larger due to the higher evaporation rate, the pressure drop in the cryostat was greater.

The correction for this pressure drop is not easy to calculate, since it depends on the temperature distribution of the gas in the cryostat, which is not known. To overcome this difficulty, we condensed some helium in the vacuum can and measured its vapor pressure with a sloping oil manometer. The pressure drop mentioned above, between liquid surface and manometer, does not occur with this arrangement because the vapor is not being pumped away. The liquid helium film, however,

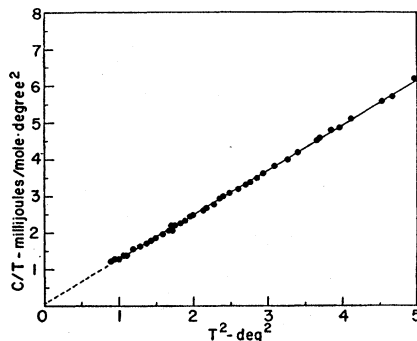


FIG. 2.  $C/T$  vs  $T^2$  for bismuth in true  $T^3$  region.

creeps up the sides of the container and the connecting tube, evaporates, and condenses at a lower point. This effect will lead to a higher measured pressure than the vapor of the liquid, but calculation shows that for our connecting tube (14-mm i.d.) the difference is negligible. Above 1.2°K the pressure measured at the top of the cryostat was equal to that inside the vacuum can. The differences below this temperature increased as the temperature was lowered, and corresponded to 0.04°K at the lowest temperature.

The thermometer resistance between 1.3° and 2°K could be represented to within 0.001°K by a parabola. This parabola also agreed with the calibration points below 1.3°K with the same accuracy, if temperatures based on vacuum can pressures were used. The parabola was therefore used below 2°K to convert resistance to temperature. Another parabola, which joined on smoothly to the first at about 2°K and represented the calibration points to within several thousandths of a degree between 2° and 4.2°K, was used in the higher-temperature interval.

### III. RESULTS

The results of our measurements are collected in Table II. From these data, we have plotted, in Fig. 1,  $C_v/T$  versus  $T^2$ , together with the points of Keesom and van den Ende<sup>3</sup> in the helium region. It can be seen that their points scatter around ours in a random fashion. Below  $T^2=5$  or  $T=2.3^{\circ}\text{K}$  a straight line can be fitted to our points. In Fig. 2 the data below  $T^2=5$  are plotted on a larger scale, again in the form of  $C_v/T$  versus  $T^2$ . The line drawn in Fig. 2 was calculated by the method of least squares; it gives for the atomic heat the expression:

$$C_v = (1.213 \pm 0.006)T^3 + (0.078 \pm 0.013)T \quad (1)$$

× millijoules/mole degree.

The errors given in Eq. (1) are standard errors, calculated on the assumption that all errors in the measurement are random. A possible source of systematic error is the vapor pressure curve, which is based on thermodynamic arguments below 1.6°K,<sup>10-12</sup> where the probable error is estimated to be  $\pm 0.003^{\circ}\text{K}$ . Taking this into account, we estimate the total standard error in the linear term to be about 0.03 millijoule/mole degree.<sup>2</sup>

### IV. DISCUSSION

#### A. Lattice Atomic Heat

From the coefficient of the cubic term in Eq. (1) we calculate the value  $(117 \pm 1)^{\circ}\text{K}$  for  $\theta_0$ , the constant value of the Debye  $\theta$  in the temperature region im-

<sup>10</sup> R. Bleaney and F. Simon, *Trans. Faraday Soc.* **35**, 1205 (1939).

<sup>11</sup> W. H. Keesom and W. P. J. Lignac, *Communs. Kamerlingh Onnes Lab. Univ. Leiden, Suppl.* 90c (1939); See also *Temperature*, AIP Symposium (Reinhold Publishing Corp., New York, 1941), p. 757.

<sup>12</sup> J. Kistemaker, *Communs. Kamerlingh-Onnes Lab., Leiden, No. 269c* (1946); *Physica* **12**, 272 (1946).

TABLE II. Data on atomic heat of bismuth.

Point	$T$ (°K)	$\Delta T$ (°K)	$C_v$ (millijoules mole deg K)	Point	$T$ (°K)	$\Delta T$ (°K)	$C_v$ (millijoules mole deg K)
27 April 1953				18 May 1953—Continued			
2	1.299	0.04877	2.982	12	1.374	0.03979	3.169
3	1.301	0.05007	2.839	13	1.363	0.03993	3.158
4	1.300	0.04978	2.817	16	1.410	0.05096	3.525
5	1.302	0.04986	2.811	17	1.434	0.04979	3.608
6	1.299	0.04877	2.849	18	1.462	0.04726	3.801
7	1.297	0.04856	2.885	19	1.469	0.04685	3.835
8	1.549	0.03009	4.586	20	1.530	0.03713	4.839
9	1.562	0.05325	4.778	21	1.572	0.03713	4.839
10	1.562	0.05305	4.758	22	1.611	0.03471	5.177
11	1.688	0.04120	6.172	23	1.659	0.06392	5.598
12	1.712	0.03997	6.236	24	1.689	0.06107	5.863
13	1.913	0.02872	8.700	25	1.710	0.05944	6.027
14	1.921	0.02821	8.792	1 June 1953			
15	2.128	0.04019	11.84	1	1.026	0.05574	1.483
16	2.159	0.03910	12.15	2	1.029	0.05716	1.446
17	2.385	0.02804	17.01	3	1.056	0.10794	1.532
18	2.409	0.05506	17.88	4	1.036	0.05844	1.415
19	2.704	0.03800	25.27	5	1.028	0.03580	1.373
20	2.731	0.03640	26.38	6	1.034	0.03596	1.366
21	2.960	0.04737	33.81	7	1.053	0.03342	1.470
22	3.009	0.04491	35.70	8	1.062	0.05400	1.531
23	3.246	0.03416	46.88	9	1.079	0.05248	1.573
24	3.282	0.03307	48.67	10	1.090	0.04947	1.671
25	3.453	0.04258	60.88	11	1.095	0.04867	1.699
26	3.497	0.04098	63.29	12	1.111	0.04728	1.749
27	3.534	0.03948	65.73	13	1.129	0.04575	1.807
28	3.576	0.03762	69.05	14	1.138	0.04401	1.879
29	3.640	0.03550	73.14	15	1.167	0.04086	2.024
30	3.679	0.03373	77.06	16	1.190	0.03881	2.131
31	3.716	0.03314	78.39	17	1.193	0.03903	2.119
32	3.751	0.03180	81.59	18	1.215	0.03688	2.242
33	3.782	0.03112	83.43	19	1.221	0.03692	2.239
34	3.817	0.02986	87.08	20	1.255	0.06853	2.437
35	3.850	0.03689	88.84	21	1.291	0.06264	2.666
36	3.888	0.03534	92.85	22	1.295	0.06209	2.690
37	3.952	0.03307	99.01	23	1.319	0.05880	2.842
38	3.989	0.03182	103.1	24	1.346	0.05506	3.036
39	4.019	0.04058	105.3	25	1.357	0.05435	3.075
40	4.060	0.03817	111.8	26	1.396	0.04943	3.381
41	4.106	0.03657	116.8	27	1.437	0.04534	3.689
42	4.146	0.03575	119.4	28	1.470	0.04264	3.923
43	4.183	0.03434	124.6	29	1.505	0.04020	4.162
44	4.220	0.03327	128.4	30	1.533	0.03727	4.492
45	4.252	0.03287	129.9	31	1.606	0.04404	5.148
46	4.287	0.03128	136.6	32	1.639	0.04096	5.535
47	4.347	0.03000	142.5	33	1.710	0.05238	6.203
48	4.376	0.02885	148.5	34	1.752	0.04836	6.719
49	4.485	0.02592	165.1	35	1.804	0.04477	7.262
50	4.507	0.02534	169.0	36	1.839	0.04203	7.736
51	4.601	0.02363	181.2	37	1.907	0.05834	8.638
52	4.635	0.04586	186.4	38	1.958	0.05368	9.388
53	4.781	0.04062	210.6	39	1.987	0.05191	9.714
54	4.819	0.03893	219.8	40	2.027	0.04878	10.336
55	5.008	0.03303	259.1	45	0.953	0.01951	1.150
56	5.036	0.03141	272.4	46	0.968	0.04097	1.206
18 May 1953				47	0.982	0.03882	1.272
8	1.344	0.04041	3.121	48	0.994	0.03790	1.303
9	1.358	0.04075	3.095	49	1.008	0.03605	1.370
10	1.371	0.04000	3.153	51	1.023	0.03659	1.350
11	1.374	0.03986	3.163				

mediately above  $\theta^\circ\text{K}$ . The variation of  $\theta$  with  $T$  at higher temperatures is given in Fig. 3, in the form of a plot of  $\theta/\theta_0$  versus  $T/\theta_0$ , in which the data of Keesom and van den Ende,<sup>3</sup> of Armstrong and Grayson-Smith,<sup>13</sup>

<sup>13</sup> L. D. Armstrong and H. Grayson-Smith, Can J. Research A27, 9 (1949).

and of Anderson<sup>14</sup> are included. These variations in  $\theta$  correspond to deviations from parabolic form of the vibration spectrum. They occur as a result of the discrete nature of real lattices, as contrasted with the continuum considered by Debye. Hence these devia-

<sup>14</sup> C. T. Anderson, J. Am. Chem. Soc. 52, 2720 (1930).

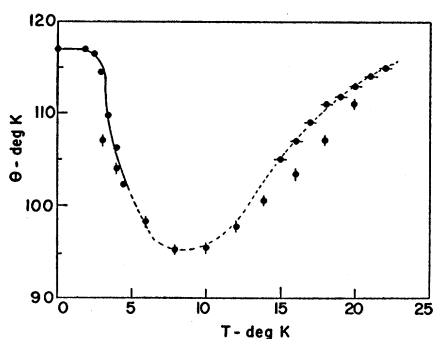


FIG. 3.  $\theta/\theta_0$  vs  $T/\theta_0$  for bismuth. ●—our results; points with vertical line, those of Keesom and van den Ende; points with horizontal line, those of Armstrong and Grayson-Smith.

tions will depend on the specific character of the interatomic forces in particular lattice.

Unfortunately, the calculation of the vibration spectrum for a lattice is a very tedious task, which has been accomplished for only a small number of lattices. Much useful information is provided by such calculations, however. For instance, it makes possible the determination of the lattice contribution to the total atomic heat of a metal so that the electronic contribution can be found by subtraction (see, e.g., the recent work of Clement and Quinell<sup>15</sup> on indium). Hence, information about the general form of vibration spectra, which can be obtained without detailed calculation on the basis of lattice theory, is of interest. Blackman has suggested<sup>16</sup> that the general form of the initial deviations from the parabolic spectrum will be the same for all three-dimensional lattices. This suggestion, which has apparently never been confirmed in the general case, is that the spectrum may be written in the form

$$g(\nu) = a_2\nu^2 + a_4\nu^4, \quad (2)$$

so that the Debye parabolic spectrum is a valid approximation at very low frequencies. This form of the spectrum has been verified by Blackman<sup>16</sup> for the simple cubic lattice and by Leighton<sup>17</sup> for the face-centered cubic lattice (f.c.c.). This was done by considering the form of the secular determinant (from which the frequencies are calculated) when its elements are approximated by expressions valid for long wavelengths.

When Eq. (2) is a good approximation for the vibration spectrum at low frequencies,  $C_v(\text{lattice})$  can be approximated by

$$C_v(\text{lattice}) = \alpha_3 T^3 + \alpha_5 T^5, \quad (3)$$

in which the  $\alpha$ 's depend on the  $a$ 's and hence on the nature of the lattice. Blackman has defined, as the "true  $T^3$  region,"<sup>16</sup> temperatures immediately above 0°K for which the second term in Eq. (3) is less than two

percent of the first. Thus  $T_3$ , the upper limit of the true  $T^3$  region, is given by

$$T_3^2 = 0.02(\alpha_3/\alpha_5). \quad (4)$$

For bismuth we find that  $(T_3/\theta_0)$  is 0.019. Blackman found<sup>16</sup> that in the simple cubic lattice  $(T_3/\theta_0)$  is 0.01, while Leighton found<sup>17</sup> that  $(T_3/\theta_0)$  is 0.021 in the f.c.c. lattice with nearest neighbor forces only, and 0.025 when the force constant for second-nearest neighbors is one-tenth that for nearest neighbors.

In order to see the extent to which Eq. (3) describes the low-temperature atomic heat of the bismuth lattice, our data are plotted in Fig. 4 in the form  $C_v(\text{lattice})/T^3$  versus  $T^2$ . It is clear that while there does appear to be a term proportional to  $T^5$  in the atomic heat, the coefficient of this term is not constant over the entire range plotted, but increases rather abruptly at a temperature which corresponds roughly to the upper limit of the true  $T^3$  region. Hence Eq. (3) is not a good approximation in this case.

Exact calculations for various spectra show (as has recently been pointed out by de Launay<sup>18</sup> in another connection) that Eq. (2) can be expected to apply over only a limited range of frequencies. Equation (3) will therefore be limited in its applicability to a restricted temperature range. The reason for this limitation is that the vibration spectra have maxima at frequencies much below the cut-off frequency, and these maxima are preceded by a frequency range in which  $g(\nu)$  may increase much faster than  $\nu^4$ . At any rate, Eq. (2) cannot apply at frequencies near the peak in the spectrum.

Although no simple expression such as Eq. (2) is available for this part of the spectrum, the position of the maximum can be estimated by the method of Katz.<sup>19</sup> He treats vibration spectra as being made up of Einstein frequencies with positive or negative weights superimposed upon a parabolic Debye spectrum. No physical basis is claimed for this mode of description; it is proposed, to quote Katz,<sup>19</sup> ". . . as a way of describing mathematically any empirical  $C(T)$  in a rapidly converging series." The positions and magnitudes of the Einstein frequencies having positive weights can be found from the dips, and of those having negative weights from the peaks, in the graph of  $\theta/\theta_0$  versus  $T/\theta_0$ , the pertinent relation being  $\nu = 5kT/h$ . Katz shows that this may be done with reasonable accuracy for  $T/\theta_0$  less than 0.1. It is then reasonable to suppose that the positions of the fictitious Einstein frequencies correspond to those of the maxima of the peaks and dips in the vibration spectra. For bismuth, the minimum in  $\theta/\theta_0 = 0.81$  at 8°K ( $T/\theta_0 = 0.068$ ) thus corresponds to a peak in the spectrum at  $\nu/\nu_{\text{max}}$  equal to 0.34. From Leighton's calculated spectra for the f.c.c. lattice we find the value 0.70 in the case of nearest-neighbor forces

<sup>15</sup> J. R. Clement and E. H. Quinell, Phys. Rev. **92**, 258 (1953).

<sup>16</sup> M. Blackman, Proc. Roy. Soc. (London) **A159**, 416 (1937).

<sup>17</sup> R. B. Leighton, Revs. Modern Phys. **20**, 165 (1948).

<sup>18</sup> J. de Launay, Phys. Rev. **93**, 661 (1954).

<sup>19</sup> E. Katz, J. Chem. Phys. **19**, 488 (1951).

only, and the value 0.65 for the case in which the second-nearest-neighbor force constant is one-tenth as large as the nearest-neighbor force constant. The latter value agrees fairly well with 0.61, the value found from the minimum in the  $\theta$  versus  $T$  curve for silver, which Leighton calculated with a somewhat smaller ratio of second-nearest-neighbor to nearest-neighbor force constants. Fine's calculation of the vibration spectrum of tungsten<sup>20</sup> (body-centered cubic lattice, b.c.c.) gives the first peak at  $\nu/\nu_{\max}$  equal to 0.57. Hence, in the bismuth vibration spectrum, the distance between the end of the low-frequency parabolic region and the first peak is only about half that in the other spectra discussed. It is likely that this circumstance is responsible for the fact that the atomic heat of bismuth makes an abrupt transition from the true  $T^3$  region to one in which its variation with  $T$  is dominated by the approach to a maximum in the vibration spectrum, without an intervening region in which the second term (and perhaps higher terms) in Eq. (2) can be seen.

As has been pointed out, it appears that the form of the vibration spectrum immediately above the low-temperature parabolic portion depends strongly on the nature of the lattice. Although all the vibration spectra calculated so far have a peak in this region, it is not inconceivable that in some cases a dip might precede this peak. Such a spectrum would, for instance, account for the behavior of the atomic heat of niobium (b.c.c.), which has been found<sup>21</sup> to increase more slowly than  $T^3$  immediately after the true  $T^3$  region.

### B. Nonlattice Atomic Heat

Since the coefficient of the linear term in Eq. (1) is only between two and three times its total standard error, it is significant only in setting an upper limit to the carrier contribution to the heat capacity. The carrier contribution depends on the density of states at the Fermi level, which can be related to the concentration of carriers and their effective masses. This relation can be written

$$\gamma T = 0.137\mu(V^2n_a)^{1/3}T \text{ millijoules/mole degree}, \quad (5)$$

where  $\mu$  is the ratio of effective carrier mass to free electron mass,  $V$  is the atomic volume (21.4 cm<sup>3</sup>/mole for bismuth), and  $n_a$  is the number of carriers per atom. From the value of  $\gamma$  in Eq. (1), we find

$$n_a\mu^3 = 4.0 \times 10^{-4}. \quad (6)$$

This expression assumes the presence of only one kind of carrier. In the case of overlapping bands such as postulated by Jones,<sup>1,2</sup> however, the thermal excitation of electrons in the sixth band will result in a shift of the Fermi level, so that the number of holes and elec-

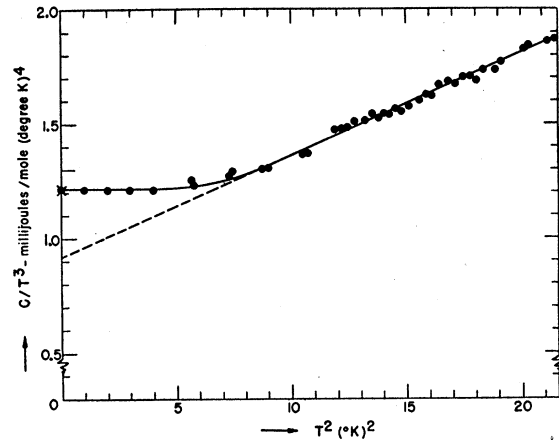


FIG. 4.  $C/T^3$  vs  $T^2$  for bismuth in liquid helium region.

trons is changed as well. This leads to an additional contribution to the heat capacity, which can be taken into account by replacing  $\mu$  in Eqs. (5) and (6) by  $\bar{\mu}$ , defined by

$$\bar{\mu} = 1.2(\mu_e + \mu_h), \quad (7)$$

where  $\mu_e$  and  $\mu_h$  are the effective mass ratios for electrons and holes, respectively. Since Jones estimated<sup>2</sup> that  $n_a$  is of the order of  $10^{-4}$ , it would follow from Eq. (6) that  $\bar{\mu}$  is of the order of unity. However, he also estimated that  $\mu_e$  is about 1/30. Although he could not make a quantitative estimate of  $\mu_h$ , data on the magnetic anisotropy led him to surmise that it is even smaller than  $\mu_e$ . If this is the case, the theoretical value of  $n_a\bar{\mu}^3$  is much smaller than the right-hand side of Eq. (6).

It should be emphasized, however, that the latter is an upper limit to the true value for bismuth, not only because it is not large compared with its standard error, but also because the possibility exists that part, or all, of the observed linear term in the atomic heat is due to impurities in the bismuth. If the impurity atoms enter the lattice substitutionally, the electrons or holes they contribute would be expected to have the small effective masses associated with this lattice. Therefore, they could not greatly increase the value of  $n_a\bar{\mu}^3$ . On the other hand, if the impurities were among those whose solubility in bismuth is very low, such as copper, tin, or iron, so that they did not enter the lattice appreciably, even small concentrations with  $\bar{\mu}$  equal to unity (or greater, as for iron) could account for the relatively large value of  $n_a\bar{\mu}^3$ . The spectrographic analysis mentioned earlier sets an approximate upper limit of  $10^{-5}$  on  $n_a$  from metallic impurities, so that it is not impossible that at least part of the value given in Eq. (6) can be accounted for in this way. A more quantitative investigation of this point would require an even purer sample, and also the attainment of lower temperatures.

We can therefore conclude only that, as far as the

<sup>20</sup> J. C. Fine, Phys. Rev. **56**, 355 (1939).

<sup>21</sup> Brown, Zemansky, and Boorse, Phys. Rev. **86**, 134 (1952).

magnitude of the non-lattice contribution to the atomic heat is concerned, Jones' theory<sup>1,2</sup> is not in disagreement with our experimental results. The complexity of the model which Adams<sup>22</sup> presents as an alternative to that of Jones makes a calculation of the expected

<sup>22</sup> E. N. Adams II, Phys. Rev. **89**, 633 (1953).

carrier contribution to the heat capacity very difficult. Such a calculation might, however, offer a useful test of its applicability.

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## Magnitude of Excitation Energy and Energy Transfer by Collision\*

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Energy transfer by collision in fluorescent solutions is found to drop sharply when the excitation energy of the solute molecule is very close to or below that of the transferring molecule. The results indicate that energy is transferred only when molecules are close to each other as in collision.

**H**IGH-ENERGY-INDUCED fluorescence in liquid solutions has been shown to be associated with a transfer of energy from an excited solvent molecule to a solute molecule.<sup>1,2</sup> We are now reporting a special instance where such energy transfer takes place between added naphthalene and various solute molecules. Naphthalene is a solid at room temperature, but it can effectively be used as a solvent for high-energy fluorescence by dissolving large amounts of it in a solvent which may by itself have only mediocre ability to transfer energy. About 300 grams per liter of naphthalene in *n*-butylphosphate is such a system.<sup>3</sup> Various highly efficient solutes (in xylene) such as  $\alpha$ ,  $\alpha'$ -binaphthyl, 2, 5-diphenyloxazole and 9, 10-diphenylanthracene were studied in this "solvent" combination. The energy transfer to the solute takes place almost exclusively from the excited naphthalene molecules; such a "solvent" combination is found to be almost as effective as xylene for the solutes mentioned. *p*- and *m*-terphenyl behave quite differently; when these substances are put into this "solvent" combination, only small fluorescence occurs, although in xylene both of these materials are highly efficient. This result is interpreted by assuming that no energy transfer takes place from naphthalene to *p*- or *m*-terphenyl. If one of these latter molecules is added to a fluorescent solution containing one of the above-mentioned solute molecules, the light output is scarcely changed. This result can be interpreted in the same way.

The explanation proposed here for this behavior is based on the assumption that the energy jump from the ground state to the first singlet state in the ter-

phenyls is slightly too great to enable frequent transfer from naphthalene. Judging by the published absorption curves of naphthalene and *m*- and *p*-terphenyl one can only say that their lowest excited states are very close.<sup>4</sup>  $\alpha$ ,  $\alpha'$ -binaphthyl, to which a very good energy transfer occurs in this "solvent" combination, also has an absorption edge close to that of naphthalene. From the absorption curves, one concludes that the lowest excitation energy for  $\alpha$ ,  $\alpha'$ -binaphthyl probably does not differ by more than 1/10 of an electron volt from the respective excitation energy of naphthalene.

The difference in behavior between the terphenyls and  $\alpha$ ,  $\alpha'$ -binaphthyl would be understandable if the absorption curve of the  $\alpha$ ,  $\alpha'$ -binaphthyl extended to longer wavelengths than those of the terphenyls. Therefore, by means of a monochromator and photomultiplier arrangement, a more complete check of the absorption curves of *m*-terphenyl and  $\alpha$ ,  $\alpha'$ -binaphthyl was made in a range where pertinent data were not previously available. (*M*-terphenyl was chosen because of its greater solubility.) The concentrations were chosen in such a way that both the *m*-terphenyl and the  $\alpha$ ,  $\alpha'$ -binaphthyl solutions had practically equal absorption at shorter wavelengths where a maximum in the absorption curve occurs. Then the relative absorption was observed at a series of longer wavelengths. These experiments showed that the absorption spectrum of  $\alpha$ ,  $\alpha'$ -binaphthyl extends to slightly longer wavelengths than that of *m*-terphenyl, which in turn shows that the lowest excitation energy of *m*-terphenyl is greater than that of  $\alpha$ ,  $\alpha'$ -binaphthyl. This supports our explanation that energy transfer to terphenyl from naphthalene does not occur because the excitation energy of terphenyl is too high. The occurrence of the small fluorescence of *m*-terphenyl in the solvent combination

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<sup>1</sup> H. Kallman and M. Furst, Phys. Rev. **79**, 857 (1950).

<sup>2</sup> M. Furst and H. Kallman, Phys. Rev. **94**, 503 (1954).

<sup>3</sup> A more complete discussion of this system will be given in a paper now in preparation.

<sup>4</sup> R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds* (John Wiley and Sons, Inc., New York, 1951).