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The Atomic Heat of Germanium below 4°K*

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The atomic heat of germanium below 4°K has been measured with pure polycrystalline and single crystal ingots, indium and antimony doped single crystal ingots, and pure crushed material. The lattice contribution is in all cases proportional to T^3 and corresponds to a Debye temperature of (362 ± 6)°K, which agrees with the value calculated from elastic constants. From the degree to which this cubic term represents the total measured atomic heat, the estimated upper limit for the ratio of the effective carrier mass to that of free electrons is found to be in the neighborhood of unity.

I. INTRODUCTION

The atomic heat of germanium has been of special interest since Critescu and Simon[1] reported an anomalous peak in the atomic heat curve around liquid nitrogen temperatures. Recently, two measurements in the liquid hydrogen range and higher, which do not reproduce this anomaly, have been reported.[2,3] Detailed information on the vibration spectrum, such as has been obtained by Smith[4] for diamond and by Hsieh[5] for germanium (which also crystallizes in the diamond lattice) is necessary for calculation of the atomic heat in this temperature range. Blackman has shown,[6] however, that below about $\theta/50$ or $\theta/100$ (true T^3 region), where θ is the Debye temperature, it should be possible to apply the Debye theory[7] and thereby calculate θ from elastic constants. This has been done for silicon,[8] but no heat capacity data at very low temperatures have been reported for other elements which crystallize in the diamond lattice, except for two preliminary communications[9–11] of measurements on germanium in the liquid helium region. There was a large discrepancy, however, between the two results, amounting to a factor of over two in the atomic heat. Since Estermann and Friedberg[9,10] used crushed germanium in a copper calorimeter containing helium exchange gas whereas we used ingots suspended in vacuum, we have also measured crushed germanium in an effort to determine the cause of the disagreement.

We were also interested in seeing if the linear term in the atomic heat below 4°K also reported by Estermann and Friedberg[9] in one of their specimens was real. They attributed this term to the heat capacity of holes with effective mass about seven times that of free electrons, the holes being contributed by impurity atoms. We found a term corresponding to electronic specific heat in our measurements on silicon,[8,11,12] but from those results and our earlier measurements on germanium it appeared unlikely that such a term would be detectable in the latter element, because of its much larger lattice atomic heat.

II. EXPERIMENT

A. Samples

Six ingots, described in Table I, were used in these measurements. All of the ingots were prepared by Miss L. Roth of this department. The starting material was pure germanium dioxide obtained from the Eagle-Picher Company, which was reduced to the metal and then purified further. This material was then cast in vacuum to form the polycrystalline ingots. The single crystals were grown by seeding the melt (doped with Sb and In for SX III and SX IV, respectively), also in vacuum. X-ray analysis of the SX ingots performed by I. Geib of this department showed them to be single crystals. Neither of the last two ingots showed any evidence in this analysis of segregation of the impurities which had been added to the melt.

The resistivity of small samples cut from the ends of the ingots was measured, and is also given in Table I. Carrier concentrations were obtained in two ways: (a) by use of empirical relations obtained by Taylor[13] between Hall constant and resistivity of germanium at room temperature,

$$\log n_h = 15.77 - 1.23 \log\rho \qquad (1)$$

$$\log n_e = 15.54 - 1.16 \log\rho, \qquad (2)$$

where n_h is the number of holes per cm^3 in P-type germanium, n_e is the number of electrons per cm^3 in N-type, and ρ is the resistivity in ohm-cm: (b) by measurement of the Hall constant on the same samples on which the resistivity was measured. In the cases where both methods were used, the two estimates agreed fairly well.

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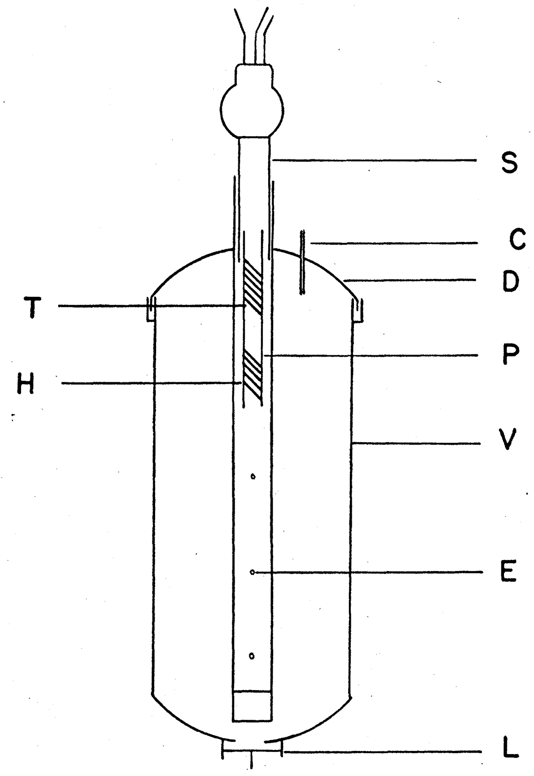

FIG. 1. Schematic drawing of container for crushed germanium.

The crushed material was prepared in a silicon carbide mortar from pure Eagle-Picher germanium. The dust was discarded and pieces from 0.1 to 3 mm were used.

B. Apparatus

The apparatus in which the heat capacity of the ingots was measured has been described previously.[8] For the second series of measurements, about 4 moles of crushed germanium was poured into a copper container (see Fig. 1). The container had a volume of 110 cm^3 and weighed 93 grams, about 3 grams of which were solder. The pouring hole was later sealed with a small lid, *L*. Into the other end, *D*, of the container, *V*, was soldered a central tube pierced with holes, *E*. Into this tube was soldered a Kovar-to-glass seal, *S*, on the wires of which was wrapped a piece of cigarette paper, *P*. The phosphor-bronze thermometer wire, *T*, and the non-inductively wound heater wire, *H*, were both wound on *P*. A 1 mm o.d. monel capillary tube, *C*, was also soldered into a hole in *D*. The container was pumped out through *C*, and its volume measured before and after filling with the crushed germanium. Volume measurements were made by comparison with a calibrated volume, using a manometer. After these measurements, this arrangement was used to fill the container with a known amount of helium gas. The capillary was then pinched off near the can, and the end tinned. Cerroseal solder (50 percent Sn, 50 percent In) was used throughout.

After filling with crushed germanium and helium exchange gas, the copper container was hung in the same vacuum can previously used to contain the ingots. The measuring procedure was then the same as has been described earlier.[8]

III. RESULTS

The results of measurements on the ingots are collected in Table II. No corrections were necessary for the heat capacity of wires and Glyptal. The method of least squares was applied to these data to calculate the coefficients in the relation,

$$C_v = \alpha T^3 + \gamma T. \qquad (3)$$

These coefficients are listed in Table III together with their standard errors, S_α and S_γ. The series of measurements with the largest standard error, those on SX II, are plotted in Fig. 2 in the form C_v/T *vs* T^2, to indicate the extent to which Eq. (3) represents the data. The line drawn is that with the coefficients given in Table III for this ingot, the solid portion covering those points which were used in calculating the coefficients.

The results of measurements on the crushed material are given in Table IV. Three separate runs were made: *A* container filled with 3.15×10^{-5} mole of helium gas (5.5 mm Hg at room temperature); *B* container filled

TABLE I. Germanium ingots.

Sample	Material	Weight (g)	Resistivity at room temperature (ohm-cm)	Carrier type and concentration, n (cm^{-3})
PX I	Pure Ge—polycrystalline	488	7.5	[a] $5\times10^{14}(P)$
PX II	Pure Ge—polycrystalline	108		[b] $1\times10^{15}(P)$
SX I	Pure Ge—single crystal	108	2.5–7	[a] $1\times10^{15}-4\times10^{14}(N)$
SX II	Pure Ge—single crystal	101	0.5–13	[a] $8\times10^{15}(N)-2\times10^{14}(P)$ [b] $4\times10^{15}(N)-2\times10^{14}(P)$
SX III	Sb-doped single crystal	128	0.003–0.05	[a] 3×10^{18} to $1\times10^{17}(N)$
SX IV	In-doped single crystal	110	0.037–0.2	[a] 3×10^{17} to $4\times10^{16}(P)$

[a] From Eqs. (1) and (2).
[b] From Hall constant.

TABLE II. Data on atomic heat of germanium ingots.

Point	T (°K)	ΔT (°K)	C_v $\frac{\text{millijoules}}{\text{mole degree}}$
PX I: 10/4/51 Points 10 through 33 used for least squares fit			
1	4.240	1.781×10^{-2}	3.169
2	4.256	1.771	3.187
3	4.267	1.735	3.254
4	3.927	2.162	2.610
5	3.943	2.091	2.698
6	3.959	2.054	2.748
7	3.654	2.677	2.107
8	3.675	2.583	2.184
9	3.695	2.536	2.225
10	3.259	3.807	1.486
11	3.298	3.661	1.545
12	3.329	3.600	1.571
13	2.893	2.416	1.072
14	2.916	2.436	1.063
15	2.937	2.360	1.098
16	2.673	3.162	0.819
17	2.730	2.990	0.866
18	2.762	2.864	0.904
19	2.441	4.091	0.633
20	2.474	3.250	0.666
21	2.484	1.631	0.664
22	2.053	2.970	0.364
23	2.090	2.847	0.380
24	2.116	2.762	0.392
25	1.883	3.720	0.291
26	1.906	1.814	0.289
27	1.920	1.708	0.307
28	1.750	2.210	0.237
29	1.770	2.136	0.245
30	1.787	2.098	0.250
31	1.541	2.804	0.187
32	1.554	2.705	0.194
33	1.582	2.748	0.191
PX I: 10/9/51 Points 1 through 21 used for least squares fit			
1	2.505	1.671×10^{-2}	0.645
2	2.510	1.629	0.662
3	2.372	1.925	0.560
4	2.380	1.920	0.561
5	2.311	2.077	0.519
6	2.324	2.085	0.517
7	1.901	3.883	0.277
8	1.921	3.747	0.287
9	1.755	4.735	0.227
10	1.791	4.549	0.237
11	1.815	4.519	0.238
12	1.638	2.920	0.182
13	1.658	2.852	0.187
14	1.675	2.698	0.197
15	1.464	4.216	0.126
16	1.491	3.864	0.138
17	1.508	3.932	0.136
18	2.728	2.417	0.860
19	2.731	2.406	0.864
20	3.150	1.614	1.288
21	3.157	1.597	1.301
22	3.627	1.110	1.873
23	3.635	1.051	1.979
24	3.645	2.086	1.994
25	3.979	0.796	2.616
26	3.989	0.798	2.608
27	4.227	1.454	2.867
28	4.239	1.440	2.896
29	4.247	1.402	2.975
PX II: 9/24/51 Points 1 through 58 used for least squares fit			
1	3.796	1.737×10^{-2}	2.419
2	3.801	1.704	2.465
3	3.903	1.592	2.639
PX II: 9/24/51—*Continued* Points 1 through 58 used for least squares fit			
4	3.929	1.545×10^{-2}	2.719
5	3.952	1.545	2.720
6	4.083	1.504	2.795
7	4.108	1.459	2.880
8	4.137	2.932	2.867
9	4.241	1.340	3.137
10	4.253	1.300	3.234
11	4.263	1.330	3.161
12	3.875	1.631	2.576
13	3.886	1.620	2.594
14	3.894	1.602	2.623
15	3.542	2.304	1.823
16	3.558	2.337	1.797
17	3.570	2.298	1.827
18	3.250	1.428	1.439
19	3.261	1.390	1.479
20	3.270	1.404	1.464
21	2.973	1.902	1.081
22	3.003	1.826	1.126
23	3.034	1.746	1.177
24	2.713	2.419	0.850
25	2.728	2.423	0.848
26	2.741	2.399	0.856
27	2.476	3.190	0.644
28	2.500	3.068	0.670
29	2.512	3.053	0.673
30	2.327	3.858	0.532
31	2.354	3.724	0.552
32	2.360	0.915	0.566
33	2.357	0.927	0.559
34	2.194	1.220	0.425
35	2.211	2.358	0.440
36	2.227	2.310	0.449
37	2.110	2.719	0.369
38	2.018	3.183	0.326
39	1.818	4.070	0.255
40	1.652	2.304	0.225
41	1.528	3.354	0.155
42	1.523	3.405	0.152
43	3.125	1.645	1.250
44	3.149	1.605	1.281
45	3.315	2.712	1.549
46	3.452	2.390	1.758
47	3.527	2.288	1.835
48	3.704	1.920	2.188
49	3.798	1.783	2.357
50	3.823	1.743	2.410
51	3.878	1.672	2.512
52	3.880	1.607	2.615
53	3.949	1.568	2.680
54	3.971	1.546	2.718
55	3.993	1.532	2.743
56	4.011	1.530	2.748
57	4.106	3.082	2.728
58	4.226	1.343	3.130
SX I: 8/27/51 Points 1 through 4 and 8 through 44 used for least squares fit			
1	2.746	3.550×10^{-2}	0.979
2	4.153	2.079	3.226
3	4.182	2.066	3.246
4	4.193	2.071	3.239
5	4.508	1.747	3.882
6	4.537	1.709	3.969
7	4.553	1.753	3.869
8	3.808	3.013	2.249
9	3.824	2.923	2.318
10	3.836	2.907	2.311
11	3.682	3.285	2.063
12	3.694	3.286	2.062

TABLE II.—*Continued.*

SX I: 8/27/51—*Continued*
Points 1 through 4 and 8 through 44 used for least squares fit

Point	T (°K)	ΔT (°K)	C_v $\frac{\text{millijoules}}{\text{mole degree}}$
13	3.696	3.297×10^{-2}	2.055
14	3.537	3.735	1.814
15	3.541	3.671	1.846
16	3.537	3.688	1.837
17	3.261	4.730	1.432
18	3.271	4.639	1.460
19	3.270	4.646	1.458
20	3.002	6.138	1.031
21	3.005	6.059	1.118
22	2.995	6.223	1.088
23	2.770	4.073	0.854
24	2.744	4.162	0.835
25	2.695	4.420	0.786
26	2.538	5.167	0.673
27	2.535	5.189	0.670
28	2.371	3.207	0.541
29	2.332	3.339	0.519
30	2.163	4.280	0.405
31	2.104	4.659	0.372
32	1.995	6.307	0.275
33	1.878	6.411	0.270
34	1.806	7.276	0.238
35	1.692	9.018	0.192
36	1.463	12.57	0.138
37	1.443	13.24	0.131
38	1.547	10.98	0.158
39	3.872	2.774	2.444
40	3.895	2.715	2.496
41	3.913	2.700	2.510
42	4.065	2.364	2.867
43	4.081	2.318	2.924
44	4.095	2.307	2.938
46	4.382	3.929	3.451
47	4.422	5.382	3.780
48	4.449	3.643	3.724
49	4.685	3.079	4.406
50	4.710	1.501	4.520
51	4.977	1.250	5.428
52	4.980	1.293	5.248

SX II: 9/12/51
Points 8 through 28 used for least squares fit

Point	T (°K)	ΔT (°K)	C_v $\frac{\text{millijoules}}{\text{mole degree}}$
1	3.491	2.223×10^{-2}	1.826
2	3.598	2.101	1.933
3	3.621	2.091	1.942
4	3.631	2.070	1.961
5	3.335	2.776	1.462
6	3.288	1.417	1.429
7	3.282	1.440	1.406
8	2.985	1.918	1.055
9	2.991	1.886	1.073
10	2.999	1.863	1.086
11	2.608	2.888	0.701
12	2.622	2.795	0.724
13	2.614	2.830	0.715
14	2.297	4.267	0.474
15	2.323	4.130	0.490
16	2.339	3.916	0.517
17	2.002	6.02	0.336
18	2.023	5.98	0.338
19	2.015	5.94	0.340
20	1.815	8.17	0.248
21	1.837	8.01	0.252
22	1.723	2.43	0.206
23	1.728	2.37	0.211
24	1.664	2.66	0.188
25	1.661	2.69	0.186
26	1.554	3.19	0.157
27	1.554	3.30	0.152
28	1.488	3.80	0.132

SX II: 9/12/51—*Continued*
Points 8 through 28 used for least squares fit

Point	T (°K)	ΔT (°K)	C_v $\frac{\text{millijoules}}{\text{mole degree}}$
29	1.484	3.82×10^{-2}	0.131
30	4.505	0.988	4.107
31	4.516	1.577	3.860
32	4.555	2.122	3.831
33	4.388	1.243	3.270
34	4.158	1.415	2.871
35	4.237	1.296	3.153

SX III: 9/19/51
Points 14 through 43 used for least squares fit

Point	T (°K)	ΔT (°K)	C_v $\frac{\text{millijoules}}{\text{mole degree}}$
1	4.236	2.280×10^{-2}	3.259
2	4.240	2.272	3.270
3	4.253	2.268	3.276
4	4.514	1.684	4.415
5	4.240	2.292	3.242
6	3.839	1.604	2.391
7	3.841	1.697	2.260
8	3.513	2.176	1.761
9	3.522	2.171	1.766
10	3.527	2.076	1.847
11	3.198	3.069	1.248
12	3.216	2.914	1.315
13	3.215	1.429	1.318
14	2.806	2.208	0.852
15	2.812	2.090	0.901
16	2.819	2.086	0.902
17	2.448	3.400	0.553
18	2.462	3.200	0.588
19	2.485	3.014	0.624
20	2.228	4.518	0.416
21	2.239	4.361	0.431
22	2.064	1.429	0.336
23	2.078	1.435	0.334
24	2.089	1.391	0.345
25	1.936	1.716	0.279
26	1.941	1.622	0.300
27	1.938	1.684	0.285
28	1.776	2.021	0.237
29	1.776	2.133	0.225
30	1.780	2.152	0.223
31	1.716	2.296	0.209
32	1.729	2.333	0.205
33	1.738	2.289	0.209
34	1.640	2.514	0.191
35	1.642	2.458	0.195
36	1.547	2.969	0.161
37	1.534	2.994	0.160
38	1.415	3.799	0.126
39	1.427	3.780	0.127
40	1.434	3.743	0.128
41	1.457	3.686	0.130
42	1.495	3.312	0.145
43	1.648	2.508	0.191

SX IV: 11/13/51
Points 1 through 29 used for least squares fit

Point	T (°K)	ΔT (°K)	C_v $\frac{\text{millijoules}}{\text{mole degree}}$
1	4.196	1.149×10^{-2}	3.143
2	4.200	1.222	2.955
3	4.205	1.217	2.968
4	3.749	1.712	2.109
5	3.754	1.714	2.106
6	3.756	1.721	2.098
7	3.548	2.046	1.764
8	3.558	2.070	1.743
9	3.562	2.093	1.724
10	3.201	2.841	1.270
11	3.223	2.719	1.327
12	3.236	2.670	1.351
13	2.869	3.863	0.934
14	2.875	3.777	0.955

TABLE II.—*Continued.*

SX IV: 11/13/51—*Continued*
Points 1 through 29 used for least squares fit

Point	T (°K)	ΔT (°K)	C_v millijoules/mole degree
15	2.874	2.730×10^{-2}	0.911
16	2.606	3.561	0.698
17	2.619	3.477	0.715
18	2.620	3.509	0.708
19	2.117	5.414	0.459
20	2.124	5.402	0.460
21	1.990	5.319	0.317
22	2.005	5.187	0.325
23	1.773	7.084	0.238
24	1.752	2.157	0.237
25	1.757	2.075	0.246
26	1.346	4.623	0.110
27	1.346	4.586	0.111
28	1.486	3.561	0.143
29	1.488	3.669	0.139

TABLE III. Atomic heat of germanium ingots. $C_v=\alpha T^3+\gamma T$. S_α and S_γ are the standard errors in α and γ.

Sample	Date	α joules/mole deg^4	S_α joules/mole deg^4	γ joules/mole deg^2	S_γ joules/mole deg^2
PX I	10/ 4/51	4.21×10^{-5}	0.05×10^{-5}	0.79×10^{-5}	0.32×10^{-5}
PX I	10/11/51	4.02	0.11	−0.19	0.62
PX II	9/24/51	4.26	0.05	−0.28	0.62
SX I	8/27/51	4.33	0.05	−0.15	0.55
SX II	9/12/51	3.95	0.17	0.39	0.92
SX III	9/15/51	3.78	0.06	0.92	0.29
SX IV	11/13/51	3.92	0.05	0.97	0.54

with the same amount of gas (11.25 mm Hg at room temperature) and 239.5 g crushed germanium; C container filled with 8.27×10^{-7} mole of helium gas (0.38 mm Hg at room temperature) and the same amount of germanium. A smooth curve was drawn through the points of set A (see Fig. 3), and this curve was then used to correct the values of sets B and C, also plotted in Fig. 3, for the heat capacity of the calorimeter and exchange gas. A further correction was made to set C to take into account the difference in amount of exchange gas for this run. The atomic heat values calculated from runs B and C are plotted in Fig. 4, together with a smooth curve representing the measurements on the ingots. It is evident that above about 3°K, there is

TABLE IV. Data on atomic heat of crushed germanium.

Set A: Cu calorimeter
December 3, 1952

Point	T (°K)	ΔT (°K)	C millijoules/degree
1	4.270	3.353×10^{-2}	14.92
2	4.292	3.758	15.11
3	3.812	1.248	10.01
4	3.819	1.226	10.19
5	3.355	1.507	8.082
6	3.367	1.505	8.077
7	2.689	1.064	5.487
8	2.693	1.047	5.582
9	1.736	1.716	3.384
10	1.716	1.727	3.357

December 5, 1952

Point	T (°K)	ΔT (°K)	C millijoules/degree
1	2.241	1.270×10^{-2}	4.440
2	2.249	1.246	4.518
3	1.751	1.654	3.379
4	1.743	1.635	3.401
5	2.686	1.488	5.684
6	2.695	1.464	5.771
7	3.011	2.053	6.881
8	3.023	2.030	6.953
9	3.512	1.587	8.879
10	3.529	1.626	8.644
11	3.956	2.459	11.43
12	3.975	2.437	11.54
13	4.147	2.083	13.52
14	4.163	2.108	13.34
15	4.274	1.946	14.45
16	4.281	1.930	14.57

Set B: Cu+Ge
December 11, 1952

Point	T (°K)	ΔT (°K)	C millijoules/degree	C_{corr} millijoules/degree	C_v millijoules/mole degree
1	2.287	1.704×10^{-2}	7.216	4.57	0.655
2	2.300	1.695	7.254	4.62	0.650
3	1.817	1.377	5.256	3.54	0.425
4	1.825	1.391	5.203	3.55	0.408
5	2.039	1.950	6.086	4.00	0.517
6	2.053	1.919	6.185	4.04	0.532
7	2.137	1.847	6.431	4.23	0.544
8	2.565	1.406	8.447	5.30	0.779
9	2.570	1.446	8.214	5.32	0.715
10	2.856	2.184	10.89	6.17	1.167
11	2.865	2.428	10.23	6.20	0.997
12	3.160	1.965	12.64	7.24	1.335
13	3.170	1.962	12.66	7.26	1.335
14	3.429	1.696	14.66	8.35	1.560
15	3.439	1.682	14.78	8.39	1.580
16	3.722	1.841	18.34	9.86	2.097
17	3.737	1.841	18.34	9.93	2.080
18	3.980	1.512	22.37	11.57	2.671
19	3.992	1.508	22.42	11.65	2.663
20	4.212	2.535	26.67	13.83	3.175
21	4.238	2.477	27.30	14.22	3.234

Set C: Cu+Ge+reduced He pressure
December 19, 1952

Point	T (°K)	ΔT (°K)	C millijoules/degree	C_{corr} millijoules/degree	C_v millijoules/mole degree
1	2.183	1.847×10^{-2}	6.298	3.96	0.554
2	2.190	1.884	6.179	3.96	0.549
3	1.800	1.671	4.210	3.09	0.277
4	1.792	1.690	4.170	3.08	0.270
5	1.985	2.249	5.167	3.47	0.415
6	1.993	2.204	5.276	3.49	0.425
7	2.185	1.851	6.284	3.94	0.579
8	2.185	1.932	6.020	3.94	0.539
9	2.185	1.932	6.020	3.94	0.539
10	2.466	2.051	7.566	4.69	0.707
11	2.472	2.111	7.351	4.71	0.653
12	2.472	2.111	7.351	4.71	0.653
13	2.857	1.533	10.13	5.87	1.053
14	2.863	1.533	10.13	5.90	1.046
15	3.205	1.773	12.64	7.06	1.380
16	3.207	1.770	12.66	7.08	1.380
17	3.488	2.099	15.73	8.23	1.855
18	3.490	2.097	15.73	8.24	1.852
19	3.815	3.391	19.48	10.07	2.327
20	3.808	1.709	19.33	10.01	2.305
21	4.140	2.655	24.86	12.82	2.977
22	4.141	2.642	24.98	12.83	3.005

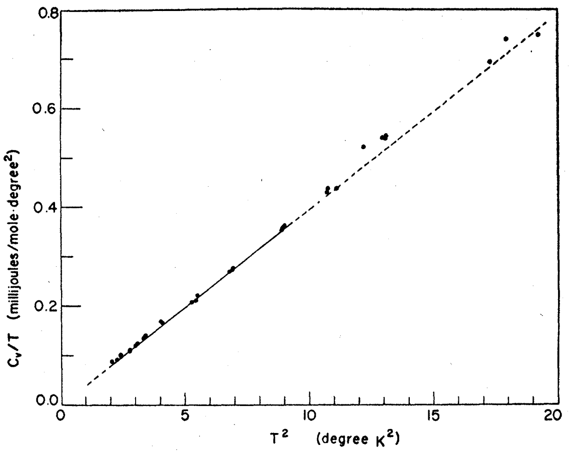

FIG. 2. Plot of C_v/T *vs* T^2 for ingot SX II. The line has the equation given in Table III: the solid portion covers the region in which points were used for the least-squares analysis.

no difference between the ingot and our crushed germanium results. Below this temperature, the points of set B are increasingly high with respect to the curve as T decreases. When the amount of helium exchange gas is decreased by a factor of 30, as was done for run C, the points again lie above the curve, but consistently below those of the run with the larger amount of exchange gas.

The difference between runs B and C and the curve representing measurements on the ingots is of the order of magnitude which would be expected if it were due to exchange gas desorbed from the small pieces of germanium during the heating periods. We estimate the area of the germanium as about 3000 cm² (particles approximated as 1-mm cubes). From the results of Dana and Kamerlingh Onnes,[14] and Keesom and Schweers,[15] respectively, we estimate 100 joules/mole for the heat of desorption and 10^{-9} mole/cm² degree for the amount desorbed. These values lead to the estimate of 10^{-5} to 10^{-4} joule/degree per mole of germanium for the heat of desorption. It thus appears that the excess heat capacity we observe below 3°K in the measurements on crushed germanium is due to desorption of exchange gas. Furthermore, as can be seen from Fig. 3 and Table IV, at the lowest temperatures about $\frac{2}{3}$ of the total heat capacity in these measurements is due to the calorimeter, so the accuracy of the crushed material measurements is not very high below 3°K. We therefore conclude that there is no significant difference between the results on the ingots and those on the crushed material.

It has been pointed out[16] that the low heat conductivity of germanium at very low temperatures might lead to the measurement of erroneously low values of the heat capacity of solid ingots, due to imperfect distribution of the heat input over the specimen. For several reasons, this does not appear to have been the case in our measurements. In the first place, the maximum diameter of our smallest ingot was 15 mm, while that of the largest was about 40 mm; the lengths varied from 60 to 100 mm. Despite this variation in size (and in shape as well, since although the single crystals were solids of revolution, their elevations were in general irregular), the measured atomic heat did not vary significantly from sample to sample, so there was no detectable dependence on size or shape. A rough calculation of the thermal relaxation time using the thermal conductivity measured by Estermann and Zimmerman[17] gives values ranging down from about 1 second at 4°K for the most unfavorable case of our largest ingot and impure material. It is therefore to be expected that good thermal equilibrium was achieved in the ingots before the first observation in the afterperiod, ten seconds after the end of the heating period. Finally, this was certainly not a problem in the measurements on the crushed germanium, but above about 3°K there is no significant difference between these results and those on the ingots. Since the heat capacity falls as rapidly as the thermal conductivity, it is unlikely that the deviations at the lowest temperatures are due to this phenomenon.

IV. DISCUSSION

The average for α, weighted by standard errors, is $(4.08\pm0.22)\times10^{-5}$ joule/mole degree⁴, which corresponds to (362 ± 6)°K for θ. This agrees well with the value 375°K, calculated by a modification[18,19] of the

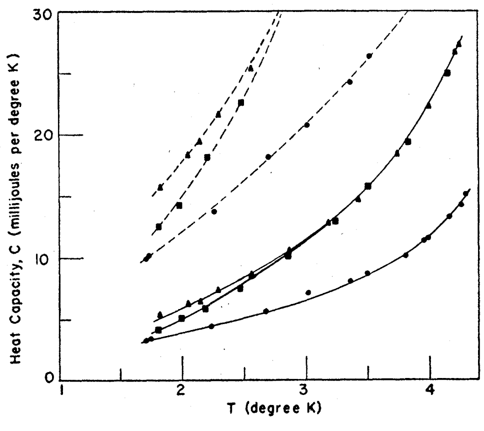

FIG. 3. Heat capacity measurements: ●—run A (container plus exchange gas); ▲—run B (container plus exchange gas and crushed germanium); ■—run C (same as B, with reduced exchange gas pressure). Solid lines refer to scale at left; dashed lines to heat capacity values multiplied by three.

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[15] W. H. Keesom and J. Schweers, Communs. Kamerlingh Onnes Lab., Univ. Leiden, No. 264c; Physica **8**, 1020 (1941).

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[19] See reference 8, Appendix II.

Hopf-Lechner method,[20] using the elastic constants of germanium recently measured by Bond and collaborators.[21] It can be seen from Fig. 2 that the true T^3 region, in which θ is constant, extends to about 4°K. This is about $\theta/100$, in agreement with Blackman's calculations.[6]

The standard error given above for $\langle\alpha\rangle_{\text{Av}}$ is larger than any listed in Table III because the latter, being calculated by the method of least squares, involve the assumption that only random errors are present. We therefore estimated our total experimental error from the observed spread of the α values of all the ingots around their average. In doing this we make the assumption that the Debye temperature of pure germanium is not changed by the addition of small amounts of impurities. On the other hand, if our estimate of the experimental error is too large, our results would indicate the presence of such an effect. The possible difference in θ values, however, is not more than a few degrees.

For a degenerate carrier gas in germanium, γ, the coefficient of the linear term in Eq. (3) will be given by

$$\gamma = 2.15\times 10^{-11}\mu n^{\frac{1}{3}} \text{ joule/mole degree}^2, \tag{4}$$

where μ is the ratio of effective carrier mass to that of free electrons and n is the number of carriers per cm^3. Hung and Gliessman[22,23] have found that for n less than about 10^{18} cm^{-3} the carrier gas will not be degenerate, so only for SX III would one expect to find a linear term in the low temperature atomic heat. Debye and Conwell[24] have shown that Hall constant and resistivity data in N-type germanium with n less than 10^{18} cm^{-3} correspond well to a value of $\frac{1}{4}$ for μ. Recently Benedict and Shockley[25] have derived the value 0.6 for μ in N-type germanium with n less than 10^{15} cm^{-3} on the basis of dielectric constant measurements in the microwave region. Since μ should be roughly independent of n, it is possible to find at least a rough estimate of γ from Eq. (4). This is 0.6–1.4$\times 10^{-5}$ for SX III so that there is good agreement with our observed value, whereas values of μ much larger than unity would seem to be excluded.[26]

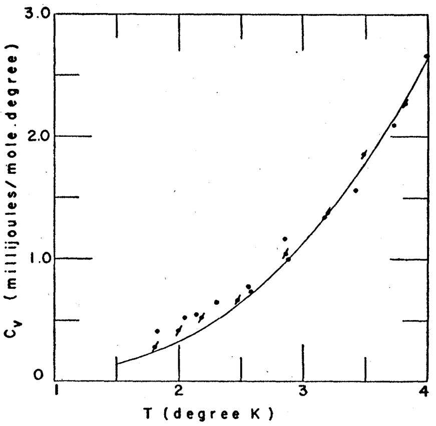

FIG. 4. Atomic heat of germanium: solid line represents results on measurements on ingots; ●—calculated from run B with crushed germanium; ⌀—calculated from run C with crushed germanium (reduced exchange gas pressure).

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[26] If the data of I. Estermann and S. A. Friedberg [Technical Report No. 4, Department of Physics, Carnegie Institute of Technology, June, 1951 (unpublished)] are analyzed by least squares, one obtains $(6.57\pm 1.21)\times 10^{-5}$ and $(5.88\pm 0.9)\times 10^{-5}$ joule/mole degree^4 for α for their pure and impure samples, respectively, and $(19.5\pm 10.3)\times 10^{-5}$ and $(75.9\pm 9.7)\times 10^{-5}$ joule/mole degree^2 for γ for the two samples. There is thus no significant difference between their values of α and ours, while an even higher value of μ than they report is required to account for the value of γ in their impure sample, if it is taken to be significant.