

## Heat Capacity of Diamond at High Temperatures

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Citation: [The Journal of Chemical Physics](#) **36**, 1903 (1962); doi: 10.1063/1.1701288

View online: <http://dx.doi.org/10.1063/1.1701288>

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## Heat Capacity of Diamond at High Temperatures\*

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(Received November 2, 1961)

The enthalpy of gem diamonds has been measured from 273° to 1073°K using a "drop" method and a Bunsen ice calorimeter. The derived heat-capacity values, which are believed to be accurate to  $\pm 0.5\%$ , are used to calculate the thermal functions of diamond above 298.15°K. Values of  $C_p^\circ$  (harmonic) derived from the present investigation and recent measurements of the thermal expansion and the elastic constants of diamond are compared with theoretical treatments. Reasonably good agreement in the temperature range of this study can be obtained with a single Debye function ( $\Theta_D = 1860$ ) obtained from the measured elastic constants. Extrapolation of the data gives  $\Theta_\infty = 1880 \pm 10$ .

### INTRODUCTION

THE heat capacity of diamond has been of theoretical interest since its wide departure from the Dulong-Petit law at room temperature was noticed by Weber<sup>1</sup> in 1875. The most recent measurements at high temperatures of the heat capacity of diamond (Magnus and Holder,<sup>2</sup> 1926) differ by up to 10% from Weber's values and have been questioned because of their failure to join smoothly with values below room temperature and because of oxidation of the diamonds during their measurements.

This paper describes recent measurements of the heat capacity of diamond between 273° and 1073°K. The smoothed results are believed to be accurate to  $\pm 0.5\%$  over most of this temperature range.

### SAMPLE AND CONTAINER

The diamonds had all been cut and polished and for the most part ranged in size from about 1 to 2 mm diameter. The gems were obtained from a much larger batch of diamonds,<sup>3</sup> examination of which has indicated that more than 99% of the gems are type I with absorption in the 8 to 10 micron region and a non-graphite impurity content of 0.2 weight percent or less. It seems reasonable to assume the same purity for the diamonds used in the present study. Because it would be impractical and costly to analyze all the diamonds (several hundred) used in the heat-capacity study, no attempt was made to correct the heat-capacity data for impurities. The author believes that these impurities might contribute an error of  $+0.2\%$  in heat capacity at room temperature but would cause little error above 700°K if the error can be calculated additively.

Diamonds are susceptible to both oxidation and graphitization at high temperatures. Graphitization involves an internal rearrangement of the diamond lattice

and proceeds nearly independently of the chemical nature of the atmospheric environment. There is no evidence that graphitization is appreciable below 1170°K,<sup>4</sup> which was originally intended to be the upper limit of the heat-capacity measurements.

In order to protect the diamonds used in the present study from oxidation, they were sealed in a silver container, of about 8 cm<sup>3</sup> volume, in an atmosphere of helium at about 20 cm Hg pressure which contained no more than 5  $\mu$  Hg pressure of oxygen. Another silver container, similar to the diamond container, was evacuated and sealed. The empty container served as a *blank* in accounting for the heat content of the sample container and the heat loss during the experiments. Tests indicate that silver containers can be interchanged with little change in observed heat content.

### EXPERIMENTAL RESULTS

The heat-capacity measurements were made by the "drop" method using a Bunsen ice calorimeter. The method has been described in a previous publication.<sup>5</sup>

The results of all measurements on the diamonds and their container are given in Table I. Tests were made which indicated that 50 min exposure of the sample plus container to the furnace temperature was sufficient to achieve thermal equilibrium within the precision of the experiments.

Column 4 of Table I gives the mean heat for the empty container which served as a "blank." It can be shown<sup>6</sup> that subtraction of the "blank" heat values eliminates effects due to heat loss during the drop of the container from the furnace to the calorimeter. These values were determined by correcting the mean heats of the empty container to the actual conditions of the diamond container. An attempt was made to make the masses of the parts of the two containers identical. However, there was no way to accurately control the mass of silver in each container because of

\* From a thesis submitted in partial fulfillment for the Master of Science Degree at the University of Maryland.

<sup>1</sup> H. F. Weber, *Phil. Mag.* **49**, 161 (1875).

<sup>2</sup> A. Magnus and A. Holder, *Ann. Physik* **80**, 808 (1926).

<sup>3</sup> E. N. Bunting and A. Van Valkenburg, *Am. Mineralogist* **43**, 102 (1958).

<sup>4</sup> H. J. Grenville, *Mineralogical Mag.* **29**, 803 (1952).

<sup>5</sup> G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, *J. Research Natl. Bur. Standards* **57**, 67 (1956).

<sup>6</sup> D. C. Ginnings and R. J. Corruccini, *J. Research Natl. Bur. Standards* **38**, 593 (1947).

TABLE I. Heat measurements on the diamonds and their container.

Furnace temp $T$	Time in furnace	Measured heat <sup>a</sup> diamonds+container	Corrected heat of container	Enthalpy change of diamonds ( $H_T - H_{273.15}$ )	
				mean observed	obs-calc [Eq. (1)]
°K	min.	cal. <sup>c</sup>	cal.	cal/g atom <sup>d</sup>	cal/g atom
323.15	51	168.27	44.10	73.22	0.00
	74	168.12			
	58	168.22			
	72	168.32			
	54	168.27			
373.15	60	381.46 <sup>b</sup>	88.88	171.09	+0.03
	50	378.77			
	70	378.87			
	50	379.20			
423.15	74	629.86	134.38	292.38	-0.07
	66	629.87			
	50	630.84			
	63	629.80			
473.15	57	917.30	180.10	435.07	+0.10
	62	918.80			
	60	916.84			
	70	918.76			
	80	917.39			
523.15	60	917.26	226.77	596.21	-0.20
	73	1237.93			
	69	1236.63			
	83	1237.26			
	70	1239.50			
573.15	58	1237.14	272.93	774.10	+0.15
	66	1237.14			
	80	1586.29			
	58	1584.71			
	77	1584.63			
623.15	65	1585.56	320.50	966.22	+0.11
	60	1585.56			
	50	1960.36			
	63	1958.50			
	60	1959.32			
673.15	73	1958.97	367.68	1170.70	+0.12
	69	1957.64			
	52	1957.15			
	63	2352.39			
	60	2352.64			
773.15	62	3196.26	464.98	1609.65	-0.70
	58	3193.78			
	60	3194.42			
	63	3193.08			
	84	3192.54			
873.15	60	4094.10	563.51	2082.33	+0.12
	101	4093.77			
973.15	56	5042.05	664.70	2581.33	+0.35
	74	5040.43			
	60	5040.92			
1073.15	62	6028.22	768.39	3102.37	-0.17

<sup>a</sup> 1 calorie=4.1840 abs joules.<sup>b</sup> Rejected from mean because of inferior precision.<sup>c</sup> Total mass of diamonds=20.364 g.<sup>d</sup> Gram atomic weight=12.011 g.

TABLE II. Thermodynamic properties of diamond<sup>a</sup> at 1 atm pressure.

$T$ °K	$C_p^0$ cal/g at deg	$H_T^0 - H_0^0$ cal/g at	$(H_T^0 - H_0^0)/T$ cal/g at deg	$S_T^0 - S_0^0$ cal/g at deg	$-(G_T^0 - H_0^0)$ cal/g at	$-[(G_T^0 - H_0^0)/T]$ cal/g at deg
298.15	1.462	124.8	0.4186	0.5664	44.1	0.1478
300	1.480	127.5	0.4250	0.5755	45.1	0.1505
320	1.679	159.1	0.4972	0.6774	57.7	0.1802
340	1.878	194.7	0.5725	0.7851	72.3	0.2126
360	2.073	234.2	0.6505	0.8980	89.1	0.2475
380	2.263	277.6	0.7304	1.0152	108.2	0.2848
400	2.446	324.7	0.8116	1.1360	129.7	0.3243
420	2.621	375.3	0.8937	1.2596	153.7	0.3659
440	2.788	429.4	0.9760	1.3854	180.1	0.4094
460	2.947	486.8	1.0583	1.5129	209.1	0.4546
480	3.098	547.3	1.1402	1.6415	240.7	0.5014
500	3.242	610.7	1.2214	1.7709	274.8	0.5496
550	3.568	781.1	1.4202	2.0955	371.4	0.6754
600	3.852	966.8	1.6113	2.4184	484.3	0.8072
650	4.098	1166	1.7933	2.7367	613	0.9434
700	4.312	1376	1.966	3.048	757	1.082
750	4.497	1596	2.128	3.352	918	1.224
800	4.660	1825	2.282	3.648	1093	1.366
850	4.803	2062	2.426	3.935	1283	1.509
900	4.932	2305	2.562	4.213	1486	1.651
950	5.050	2555	2.690	4.483	1703	1.793
1000	5.162	2810	2.810	4.745	1935	1.935
1050	5.270	3071	2.925	4.999	2178	2.074
1100	5.380	3337	3.034	5.247	2434	2.213

<sup>a</sup> Gram atomic weight of diamond=12.011 g.

the method used to seal the containers. The enthalpy correction for silver was obtained from Kelley's compilation.<sup>7</sup> The largest correction was due to the different masses of silver in the two containers. Small corrections were also applied for the calorimeter heat leak, for the heat capacity of He in the sample container, and buoyancy during weighing in air. The total corrections amount to about 2% of the relative enthalpy of diamonds. The corrections are believed to be accurate to about 1%, and hence are probably the cause of insignificant uncertainty.

The mean observed enthalpy of the diamonds at  $T^\circ\text{K}$  relative to 273.15° is given in column 5 of Table I.

The Pt-Pt-10% Rh thermocouple, platinum resistance thermometer, and potentiometer standard cell used in temperature measurements were all calibrated

at the National Bureau of Standards immediately preceding the heat measurements. It is believed that temperatures were measured with an accuracy of 0.01° with the resistance thermometer and 0.1° with the thermocouple.

During the measurements at 973° it became evident that the diamond container had developed a small leak. One measurement was made at 1073° after which the container leak had greatly increased. At this point the measurements were stopped in preference to risking oxidation of the diamond surfaces. Fortunately, the diamonds lost no more than 0.0012 g during the measurements. Clearly, this had an insignificant effect on the measured enthalpy of the diamonds.

## TREATMENT OF EXPERIMENTAL DATA

### Analysis of High-Temperature Results

One measurement on the diamonds plus their container at 373° was rejected by the criterion for testing

<sup>7</sup> K. K. Kelley, "Contributions to the data on theoretical metallurgy, XIII. High temperature heat-content, heat-capacity, and entropy data for the elements and inorganic compounds," U. S. Bureau of Mines Bull. 584, U. S. Government Printing Office, Washington 25, D. C. (1960).

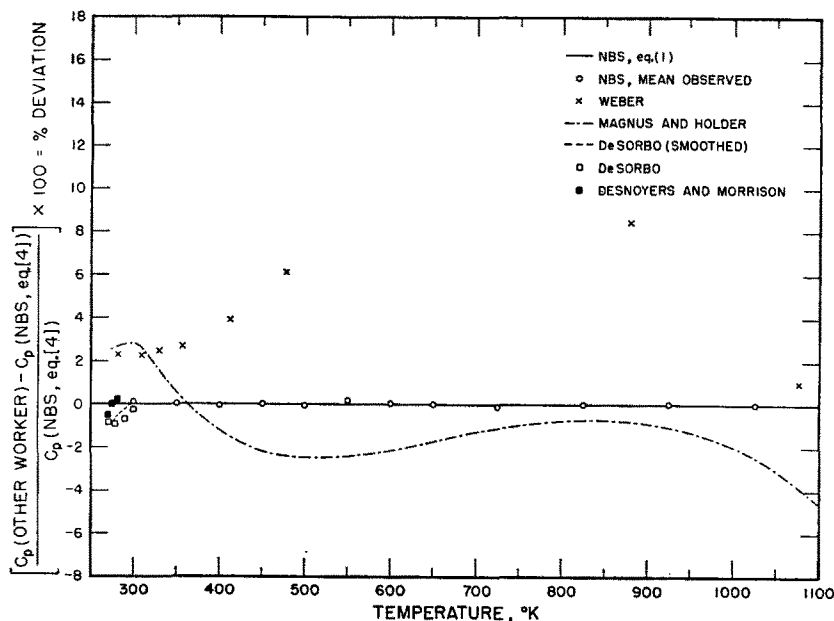


FIG. 1. Comparison of present heat-capacity measurements with those of earlier workers.

the extreme deviation from the mean<sup>8</sup> within a 98% confidence level. Experience with the ice calorimeter and furnace has shown that 2 to 5% of the experiments can be discarded on such a statistical basis.

The remaining 48 measurements have an average standard deviation from the mean observed enthalpy difference  $\Delta H$  between two successive temperatures (i.e.,  $H_{323}-H_{273}$ ,  $H_{373}-H_{323}$ , . . . etc.) of 0.38%. In calculating this figure the single value of enthalpy at 1073° was assumed to have a standard deviation of 0.30 cal mole<sup>-1</sup>, in line with the observed uncertainties at other temperatures. The standard deviation averages 0.46% for the eight temperatures measured between 273° and 673°K and 0.20% for the four temperatures above 673°. This difference occurs because the enthalpy was measured every 50° at the lower temperatures and every 100° at 773° and above. An allowance for the standard deviations of the individual empty container measurements at each temperature was included in arriving at the above figures.

An IBM 704 computer was used to fit the mean observed  $\Delta H$ 's, weighted inversely with their magnitudes to Eq. (1). This type of weighting was used since the standard deviation from the mean is roughly proportional to the magnitude of  $\Delta H$ . The constant term in Eq. (1) has been adjusted to give  $H_{273.15^\circ\text{K}} = 0.00$  cal/mole.

$$H_T - H_{273.15^\circ\text{K}} = -1.719204T + 8.483729(10^{-3})T^2 \\ - 4.93677(10^{-6})T^3 + 1.216183(10^{-9})T^4 \\ + 1.747331(10^6)T^{-1} - 1.690974(10^7)T^{-2} - 482.595. \quad (1)$$

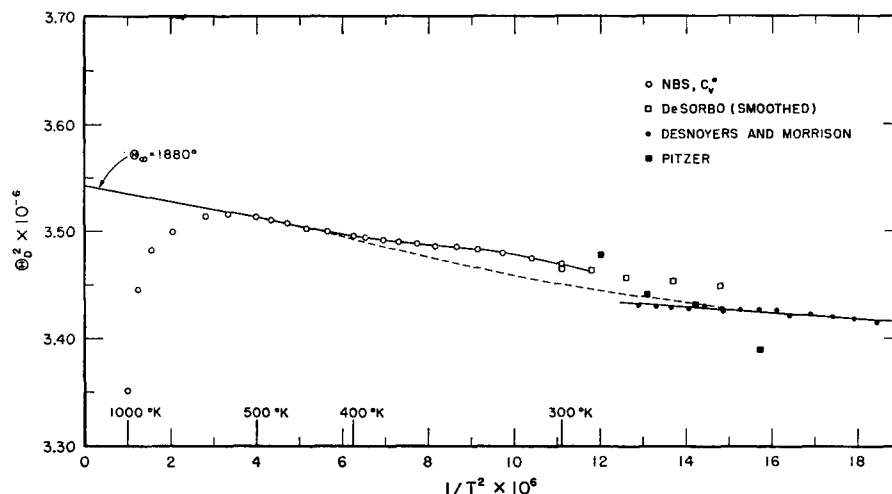
<sup>8</sup> W. J. Dixon and F. J. Massey, *Introduction to Statistical Analysis* (McGraw-Hill Book Company, Inc., New York, 1952), pp. 275 and 412.

The standard deviation of the mean observed  $\Delta H$ 's from Eq. (1) is 0.11%. The standard deviations of the mean  $\Delta H$ 's and the fit to Eq. (1) leads to an average standard deviation of the heat-capacity values, determined by differentiation of Eq. (1), of 0.4% over the whole temperature range.

Enthalpy measurements on standard sample  $\alpha$ - $\text{Al}_2\text{O}_3$  made during the diamond measurements indicated that the Bunsen ice calorimeter was giving poorer precision than usual at the time the diamond measurements were made. However the mean enthalpy values for  $\text{Al}_2\text{O}_3$  obtained at several temperatures were found to agree with smoothed reported values<sup>5</sup> within the accuracy of the latter.

Consideration of other possible causes of errors, such as those of temperature measurement, those caused by uncertain composition of the diamonds and those due to various corrections applied to bring the empty container and the sample container to the same basis, leads the author to a stated accuracy (estimated standard deviation) of the heat-capacity values obtained by differentiating Eq. (1) with respect to temperature of 0.5%. It should be noted, however, that the ice calorimeter cannot compete with the accuracy of adiabatic calorimeters in the region between 273° and about 400°K because of the low total heats involved in measurements at these temperatures. Reference to Table I indicates that the excellent precision at 323° and 373° may be fortuitous, particularly when one considers the low heat capacity of diamond at these temperatures. With this in mind, it is probably wise to assign an uncertainty closer to 1% for the heat capacity near 300°K determined from the present investigations. Low-temperature work on diamond gives further evidence for this choice.

FIG. 2. Plot of  $\Theta_D^2$  vs  $T^{-2}$  used to obtain  $\Theta_\infty$  and  $C_v^0$  (harmonic).



Equation (1) was differentiated on the 704 computer. The heat-capacity values in column 2 of Table II are a summary of the results of this differentiation.

### Comparison with Other Workers

In Figs. 1 and 2 the heat-capacity values of Table II are compared with those of previous workers in the temperature range of interest. In the "low-temperature" region, below 300°K, measurements by DeSorbo,<sup>9</sup> Desnoyers and Morrison,<sup>10</sup> and Pitzer<sup>11</sup> agree with the present study within about 1% above 270°K. The high-temperature heat-capacity values determined by Weber<sup>1</sup> and Magnus and Holder<sup>2</sup> deviate by considerable amounts from the present investigation. The measurements by Weber have received little attention since 1926 except for use in comparison with theory by Houston<sup>12</sup> in 1948. Magnus and Holder's work has been questioned by low-temperature workers<sup>10</sup> because of the failure of the data to join smoothly with low-temperature measurements, poor reproducibility of the measurements, and serious oxidation of the sample (2% of the sample was lost during the measurements).

Flubacher, Leadbetter, and Morrison<sup>13</sup> find plots of  $(\Theta_D)^2$  vs  $T^{-2}$  useful for estimating  $\Theta_\infty$ . Such curves are also extremely useful for comparing heat-capacity data in different temperature regions. In Fig. 2 such a plot compares data of the present study, corrected to  $C_v^0$ , with those of low-temperature workers<sup>9-11</sup> at their highest temperatures. Desnoyers and Morrison have assigned an accuracy of  $\pm 0.2\%$  to their work in this range. Pitzer's measurements exhibit more scatter than Desnoyers and Morrison's, but the author did not present the accuracy of his measurements. Pitzer's work deviates consistently from the other low-tempera-

ture work over the whole measured range. DeSorbo has published tables of thermodynamic functions for diamond between 25° and 300°K which Desnoyers and Morrison believe can be used above 100° without significant uncertainty.

The discrepancies in  $C_v^0$  implied by Fig. 2 are probably due to differences in the diamond samples. It would take significant impurities to account for these differences. Samples with likely chemical impurities would be expected to give higher heat capacities, such as Desnoyers and Morrison have found. No analyses for impurities were made by the low-temperature workers; however, they all used industrial diamonds which were probably less perfect than the gems used in the present high-temperature study. Differences in "degree" of lattice imperfections or graphite content could account for some of the discrepancy. Since diamond has such a high Debye characteristic temperature, thermal effects caused by imperfections would be expected to make significant contributions to the heat capacity at low temperatures. Heat-capacity measurements indicate small differences between type I and type II diamonds.<sup>14,15</sup> However, such studies have been by no means exhaustive.

### SMOOTHED THERMODYNAMIC FUNCTIONS OF DIAMOND

The values of  $C_p$  in Table II join smoothly with DeSorbo's smoothed values at 300°K. In view of this and the generally poor agreement among low-temperature workers in the vicinity of 273°K, the values of  $C_p$  obtained by differentiating Eq. (1) have been assumed correct at and above 300°K. The values of  $C_p$  were computed every 10° from 290° to 1120°K and used in a four-point numerical integration to obtain the thermodynamic functions in Table II. The values of entropy and enthalpy given by DeSorbo as modified by Des-

<sup>9</sup> W. DeSorbo, J. Chem. Phys. **21**, 876 (1953).

<sup>10</sup> J. E. Desnoyers and J. A. Morrison, Phil. Mag. **3**, 42 (1958).

<sup>11</sup> K. S. Pitzer, J. Chem. Phys. **6**, 68 (1938).

<sup>12</sup> W. V. Houston, Z. Naturforsch. **3A**, 607 (1948).

<sup>13</sup> P. Flubacher, A. J. Leadbetter, and J. A. Morrison, Phil. Mag. **4**, 273 (1959).

<sup>14</sup> R. Robertson, J. J. Fox, and A. E. Martin, Proc. Roy. Soc. (London) **A157**, 579 (1936).

<sup>15</sup> R. Berman and J. Poulter, J. Chem. Phys. **21**, 1906 (1953).

TABLE III. Heat capacity of diamond at constant volume.

$T$	$C_v^{\circ a}$	$\alpha_v^2 + a_0(\partial\alpha_v/\partial T)^b$	$\Theta_D(\text{eff})$	$C_v^{\circ}$ calc from $\Theta_D = 1860$	$C_v^{\circ}$ (harmonic)	$C_v^{\circ}$ Smith	$C_v^{\circ}$ Raman
$^{\circ}\text{K}$	cal/g at deg	$10^{-12}$	$^{\circ}\text{K}$	cal/g at deg	cal/g at deg	cal/g at deg	cal/g at deg
300	1.478	19.1	1862	1.482	1.478	1.463	1.490
400	2.439	47.4	1869	2.457	2.439	2.360	2.433
500	3.228	75.8	1874	3.254	3.227	3.139	3.211
600	3.829	105.6	1874	3.852	3.821	3.732	3.803
700	4.277	137.8	1870	4.292	4.262	4.172	4.243
800	4.610	172.9	1866	4.617	4.588	4.506	4.574
900	4.864	211.0	1856	4.860	4.835	4.760	4.820
1000	5.071	252.3	1831	5.045	5.024	4.957	5.011
1100	5.262	296.9	1762	5.189	5.170	5.111	5.157

<sup>a</sup> Experimental values.

$$^b a_0 = \int_0^T \alpha_T dT.$$

noyers and Morrison were used to determine the integration constants at 300°K. The integration was performed on the IBM 704 computer. The author believes that the thermal functions in Table II are accurate to  $\pm 0.5\%$  with the possible exception of heat capacity below 320°K.

Morrison<sup>16</sup> has recommended that the results of the present study should be adjusted between 300° and 400°K to conform with his low-temperature measurements. This would result in the dashed line in Fig. 2. This procedure would have only a slight effect on the thermal functions in Table II. However, it might be important in comparing experiment and theory between 300° and 400°K. The author of this paper did not make this correction because of the scatter of low-temperature values above 250°K. This adjustment should be borne in mind, however, when examining the next section of this paper. Additional experiments, preferably with an adiabatic calorimeter, above room temperature, will be necessary to clarify this discrepancy.

Sufficient data are now available to permit a re-examination of pressure-temperature relationships in the graphite-diamond equilibrium. The new thermal functions for diamond are close enough to earlier values<sup>7</sup> to contribute only a small change in the equilibrium curve. Recently calculated values of the thermal functions of graphite<sup>17</sup> are nearly identical to earlier ones<sup>7</sup> below 1200°K.

Berman and Simon<sup>18</sup> made calculations of the graphite-diamond equilibrium curve using the heat of

transition obtained at NBS.<sup>19,20</sup> The free energies of transition (at zero pressure) derived from the thermal tables mentioned in the previous paragraph differ from those obtained by Berman and Simon by a maximum of only 2%. There is no point in repeating the involved calculation of equilibrium pressures since uncertainties in other contributing properties introduce an uncertainty of about 5% in the calculated equilibrium pressure at 1100°K.

#### COMPARISON OF MEASURED HEAT CAPACITY WITH THEORETICAL VALUES

##### Calculation of the Harmonic Contribution to $C_v^{\circ}$

Theoretical calculations of the heat capacity of solids result in an expression for  $C_v^{\circ}$  (harmonic) (the heat capacity of the solid at the 0°K volume due to harmonic vibrations only). The heat-capacity measurements described in this paper essentially yield  $C_p^{\circ}$ , the heat capacity at zero pressure.  $C_v^{\circ}$  can be calculated from

$$C_p^{\circ} - C_v^{\circ} = V_0 T B \left[ \alpha_v^2 + \left( \int_0^T \alpha_v dT \right) \left( \frac{d\alpha_v}{dT} \right) \right], \quad (2)$$

which reduces to  $C_p^{\circ} - C_v^{\circ} = V_0 T B \alpha_v^2$  for constant thermal expansivity.<sup>21</sup> Here the symbols have the following meanings:  $V_0$  is the molar volume at 0°K,  $T$  is the absolute temperature  $^{\circ}\text{K}$ ,  $\alpha_v$  is the coefficient of volume thermal expansion,  $B$  is the bulk modulus or (compressibility)<sup>-1</sup>.

<sup>19</sup> F. D. Rossini and R. S. Jessup, J. Research Natl. Bur. Standards **21**, 491 (1938).

<sup>20</sup> E. J. Prosen, R. S. Jessup, and F. D. Rossini, J. Research Natl. Bur. Standards **33**, 447 (1944).

<sup>21</sup> J. C. Slater, *Introduction to Chemical Physics* (McGraw-Hill Book Company, Inc., New York, 1939), p. 199.

<sup>16</sup> J. A. Morrison (private communication).

<sup>17</sup> W. Evans (private communication).

<sup>18</sup> R. Berman and F. Simon, Z. Elektrochem. **59**, 333 (1955).

The thermal expansion of diamond has been measured by a number of workers. The values used here are from work by Skinner<sup>22</sup> on African gems. These values were used because they seemed to be of good precision and were given in analytic form amenable to the present calculations.

Only Adams<sup>23</sup> and Williamson<sup>24</sup> have reported measured values of the compressibility of diamond. These correspond to values of the room temperature bulk modulus  $B$  of 6.3 and 5.6 ( $10^{12}$ ) dynes  $\text{cm}^{-2}$ , respectively.

On the other hand, Huntington<sup>25</sup> and other workers in the field<sup>26</sup> have expressed confidence in the elastic constants obtained by McSkimin and Bond.<sup>27</sup> Low-temperature workers<sup>10,28</sup> have found substantiation of McSkimin and Bond's value for  $c_{44}$ . Although there has been no substantiation of their values for  $c_{11}$  and  $c_{12}$ , the excellent precision on two different diamonds recommends the use of the room temperature value,  $B=4.42$  ( $10^{12}$ ) dynes  $\text{cm}^{-2}$  in Eq. (2). Smith<sup>29</sup> has estimated that the elastic constants of diamond vary by about 0.3% per  $100^\circ$ . Insignificant error in  $C_v^0$  results from assuming the room-temperature value of  $B$  over the whole temperature range. The molar volume  $V_0$  has been taken as 3.415  $\text{cm}^3/\text{g}$  atom.

The values of  $C_v^0$  computed from Table II and the above information are given in the second column of Table III. The third column of the table gives the values of

$$\alpha_v^2 + \left( \int_0^T \alpha_v dT \right) \left( \frac{d\alpha_v}{dT} \right)$$

used in the computation. It can be seen that the largest value of  $C_p^0 - C_v^0$  occurs at  $1100^\circ\text{K}$  and is only 2.2% of  $C_p^0$ . The accuracy of  $C_p^0 - C_v^0$  is limited by the accuracy of  $\alpha_v$ . However, it is unlikely that an error greater than 0.1% is introduced in  $C_v^0$  from this source. The values of  $C_v^0$  in Table III are therefore believed accurate to about 0.5% with the possible exception mentioned earlier at  $300^\circ\text{K}$ .

Values of the Debye characteristic temperature,  $\Theta_D(\text{eff})$ , corresponding to the values of  $C_v^0$  in column 2 of Table III are given in column 4. The decrease in  $\Theta_D(\text{eff})$  above  $500^\circ$  is believed to be due to the increasing importance of anharmonic contributions to the heat capacity at high temperatures.

The harmonic contribution to the heat capacity can be estimated from Fig. 2. The curve represents the fitting of the experimental data to the Thirring expansion

which has the form

$$\Theta_D^2 = \Theta_\infty^2 \left[ 1 - A \left( \frac{\Theta_\infty}{T} \right)^2 + B \left( \frac{\Theta_\infty}{T} \right)^4 \dots \right].$$

The general technique involves assuming negligible anharmonicity over a certain temperature range and extrapolating the  $\Theta_D^2$  vs  $T^{-2}$  curve to infinite temperature (solid curve). Using this method on the present data gives  $\Theta_\infty = 1880 \pm 10^\circ$ . The dashed curve in Fig. 2 indicates a smoothed curve by which the results of Desnoyers and Morrison may be joined with the present results.

It is possible to compute the harmonic contribution to the heat capacity from the appropriate value of  $\Theta_D$  (extrapolated). The results of this computation are given in column 6 of Table III. Since all theoretical treatments have considered harmonic vibrations only, the results of theory should be compared with these values of  $C_v^0$  (harmonic). The high-temperature contributions (presumably anharmonic) can be estimated from Table III; however, it should be noted that the values obtained [ $C_v^0 - C_v^0$  (harmonic)], may be in error by 50% or more. A previous paper<sup>13</sup> has indicated that the anharmonic contribution in Si and Ge may be approximated by a linear function of  $T$ .

### Comparison of Theory and Experiment

A rough approximation to the "observed"  $C_v^0$  values was obtained using Debye's theory and the measured elastic constants.<sup>27</sup> This calculation yielded  $\Theta_D$  approximately equal to  $1860^\circ$ . The heat capacities corresponding to  $\Theta_D = 1860^\circ$  are given in column 5 of Table III. The deviations of the theoretical values are always positive and average +0.6% greater than  $C_v^0$  (harmonic) "observed." This is nearly within the stated experimental uncertainty. The real test of a heat-capacity theory occurs in the low-temperature region where the heat capacity is particularly sensitive to the frequency distribution. In the region below  $150^\circ\text{K}$  the Debye approximation fails seriously.<sup>11,29</sup>

Most treatments of the vibrational spectrum of diamond were made before the latest elastic constants<sup>27</sup> were available and hence would be expected to deviate from the values in column 6 of Table III on that account alone. Using the elastic constants of Bhagavantam and Bhimasenachar,<sup>30</sup> Smith<sup>29</sup> calculated the heat capacity of diamond assuming central and noncentral forces between nearest neighbor atoms and central forces only between next nearest neighbors. The author of the present paper has re-evaluated the heat capacity from Smith's 174 frequencies and obtained the values given from  $600^\circ$  to  $1100^\circ\text{K}$  in column 7 of Table III. The other values were obtained by Smith. These values are, on the average, about 2% lower than experiment

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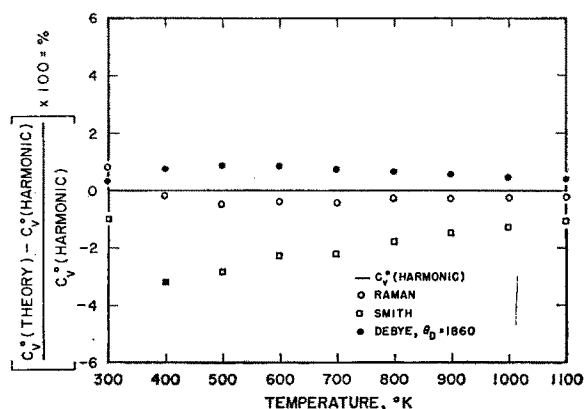


FIG. 3. Comparison of  $C_v^0$  (harmonic) from experiment with theory.

from 300° to 1100°K. Phillips<sup>31</sup> suggests that this agreement may be partly due to a fortuitous prediction by the Smith model of part of the vibrational spectrum.

The Smith theory predicts values of  $\Theta_D$  below room temperature which are significantly lower than those actually observed for diamond. Qualitatively, however, the theory does predict the general shape of the  $\Theta_D$ -vs- $T$  curve.

Raman<sup>32</sup> has used an entirely different approach to the theoretical solution of the heat capacities of crystalline solids. His approach has been criticized by some theoreticians for its failure to recognize the quasi-continuous nature of the frequency spectrum predicted by quantum mechanics and lattice dynamics.

Raman has assumed that the interactions between individual atoms in the diamond lattice can be treated by taking a "block" of 16 carbon atoms and describing the 45 normal vibrational modes between these atoms; the treatment is carried out to third neighbor atoms. In addition there are 3 normal translational modes describing the translations of the "blocks" of atoms with respect to each other. Raman treats these  $3N/16$  modes as homogeneous and isotropic and uses a Debye approximation with a cutoff at the lowest of the normal modes for the individual atoms. If some line broadening is assumed in the Raman spectrum, close coincidence with the Smith spectrum is achieved.

Raman's results deviate from  $C_v^0$  (harmonic) in Table III by +0.8% at 300°K and by an average of -0.3% between 400° and 1100°. Deviations of up to 14% from Raman's theory have been observed by Desnoyers and Morrison between 50° and 160°K. However, the general behavior of  $\Theta_D$  calculated from Raman is in agreement with experiment although it does predict too low a minimum.

In Fig. 3 the values of  $C_v^0$  (harmonic) from the

present investigation are compared with the results of the theoretical treatments discussed previously in this section.

Houston<sup>12,33</sup> attempted a calculation of the heat capacity of diamond using the Born-von Karman approach.<sup>34,35</sup> Houston's results deviate from the present experiments by 45, 9.5, and 2.4% at 300°, 500°, and 1000°, respectively. The large deviations are probably due to the use of incorrect elastic-constant data as well as the Born-von Karman assumption of central short-range forces only.

Before the shape of the frequency spectrum can be accurately defined it will be necessary to recalculate the frequency distribution from the equations of motion using McSkimin and Bond's values for the elastic constants. These elastic constants do not satisfy the Born approximations for the force constants which Smith used. It will therefore be necessary to adopt new relations between the elastic constants. Progress along these lines has been indicated.<sup>26</sup> Lax<sup>36</sup> has suggested that some long-range forces may be required to fit the data.

The importance of noncentral forces in diamond can be seen by comparing the ratios of the elastic constants with those for other materials having similar structure (Si, Ge). The indication is that the same model will not work for all materials with similar structure. Further work must be done along the lines indicated by Smith, but with a model which satisfies the requirements of the observed elastic constants.

## Summary

(1) Recent measurements of the heat capacity of diamond between 300° and 1100°K give results which are far more reliable than any previously obtained in this temperature range.

(2) The heat capacity of diamond between 250° and 400°K is still uncertain by up to 1%. Additional measurements in this range with adiabatic calorimeters will be required to remove the discrepancy.

(3)  $\Theta_\infty$  has been calculated from the data to be  $1880 \pm 10^\circ$ .

(4) The frequency spectrum of diamond requires further analysis. Raman's theory gives excellent agreement with Desnoyers and Morrison's data above 200°K, and with the present data up to 1100°. In fact, the abrupt change of sign of the deviation of Raman's values from those of the present work (Fig. 3) between 300° and 400° provides striking evidence that the "best values" of heat capacity between 250° and 400° may possibly be obtained by blending the values from the

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<sup>34</sup> M. Born and T. von Karman, Z. Physik. **13**, 297 (1912).

<sup>35</sup> M. Blackman in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, Germany, 1955), Vol. VII, 325 (1955).

<sup>36</sup> M. Lax, Phys. Rev. Letters **1**, 133 (1958).

present work with those of Desnoyers and Morrison as indicated in Fig. 2.

Such a blending will have little effect on the high-temperature thermodynamic functions or the extrapolated value for  $\Theta_{\infty}$ . However, clarification of this small discrepancy will give heat-capacity values for diamond accurate to at least 0.5% between 0° and 1100°K.

#### ACKNOWLEDGMENTS

The author wishes to thank Dr. T. B. Douglas, Dr. C. M. Herzfeld, M. L. Reilly, A. Van Valkenburg, R. K. Kirby, and Dr. J. B. Wachtman of the National Bureau of Standards and Dr. J. A. Morrison of the National Research Council (Canada) for their helpful advice during this research.

### NMR of a Glycine Single Crystal\*†

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(Received October 16, 1961)

The NMR absorption of a glycine single crystal was observed at 77° and 293°K for various orientations of the sample in the external magnetic field. On the basis of theoretical second moments computed from Van Vleck's equation it is concluded that the  $\text{NH}_3^+$  group is a regular tetrahedron whose axis lies along the C—N bond. The N—H bond distance was determined to be  $1.077 \pm 0.01$  Å.

It is concluded from the agreement between the computed and observed angular dependence of the second moments that the proposed model is correct.

#### INTRODUCTION

THE structure of glycine has been previously investigated by the methods of magnetic resonance and x-ray diffraction.<sup>1</sup> Kromhout and Moulton have concluded on the basis of the linewidth and second moments of a polycrystalline sample that the glycine molecule should be assigned a polar or zwitter-ion configuration with an N—H bond distance of  $1.074 \pm 0.014$  Å. X-ray diffraction investigations,<sup>2</sup> however, indicate that the amino group is not symmetrical and have led Marsh to assign bond distances of 0.92, 0.85, and 0.85 Å to the three hydrogen atoms in the amino group. Marsh's results also indicate that the C—H bonds are 0.91 Å, or 0.16 Å shorter than the normal C—H bond assumed by Kromhout and Moulton. Tomiie<sup>3</sup> has investigated theoretically the motion of valence shell electrons in the presence of lattice vibrations and strong chemical bonding and has concluded that under these conditions the effective center of electron density as measured by x-ray diffraction experiments will be displaced from the position of the hydrogen nucleus toward the heavy atom to which the hydrogen is attached.<sup>4</sup> It

was felt that careful NMR experiments on a glycine single crystal should determine more accurately the individual bond lengths and the orientation of the  $\text{NH}_3^+$  group in the molecule.

#### APPARATUS

A modified Pound-Knight-Watkins regenerative spectrometer similar to that described by Mays<sup>5</sup> was used in these experiments. An 8-in. electromagnet provided a magnetic field of 5 kgauss with an inhomogeneity of less than 100 mgauss over the sample. The static magnetic field was sinusoidally modulated at 88 cps by means of a small set of Helmholtz coils located within the gap. The resonance signal was fed to a lock-in detector after narrow band amplification and the derivative of the proton resonance recorded on an Esterline-Angus chart recorder. Slow scanning of the resonance over a 36-gauss range at a rate of 1.8 gauss/min was provided by an auxiliary power supply and coils wound around the magnet pole caps.

Single crystals of glycine were grown by slow evaporation from a saturated solution of Fisher reagent grade glycine in water. The samples were mounted on a 2-mm diameter Pyrex rod which ran through the center of a coaxial stainless-steel probe on which the sample coil was mounted. In this way the crystal could be rotated while immersed in liquid nitrogen. The spin lattice relaxation time was decreased by means of x-ray induced paramagnetic centers to avoid saturation at low tem-

\* This work supported by U. S. Army Research Office (Durham).

† Based in part on a thesis by W. E. Webb submitted in partial fulfillment of the requirements for the Ph.D. degree, University of Alabama.

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<sup>2</sup> R. E. Marsh, *Acta Cryst.* **11**, 654 (1957).

<sup>3</sup> Y. Tomiie, *J. Phys. Soc. Japan* **13**, 1030 (1958).

<sup>4</sup> In the case of heavy atoms the valence electrons contribute very little to the total electron charge, hence the effective center of electron density will coincide with the nuclear position.

<sup>5</sup> J. M., Mays, R. G. Schulman, and R. H. Moore, *Rev. Sci. Instr.* **29**, 300 (1958).