The Heat Capacity of Diamond from 70 to 300°K

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The specific heat of diamond has been measured over the temperature range 70 to 300°K, and is compared with the theoretical formula of Debye. Small but definite deviations are observed, which in both direction and order of magnitude are those to be expected when the approximations of the Debye formula are taken into consideration. The entropy of diamond at 298.1°K is 0.585±0.005 cal. per degree per mole.

THE temperature variation of the heat capacity of crystals received a satisfactory general explanation shortly after the development of quantum statistics. The papers of Einstein,[1] Born and v. Kármán,[2] and Debye[3] are particularly noteworthy, and it is the formula developed by the latter that has received most attention. Debye assumed that the frequencies of the normal modes of vibration of the crystal are distributed just as the vibration frequencies of a continuum, except that the spectrum is cut off at a certain maximum frequency (ν_D) so chosen that there are exactly the proper total number of frequencies ($3N$ if N be the total number of atoms).

TABLE I. *Molal heat capacity of diamond.*

T, °K	C_p (cal./deg.)	$(C_p/T^3) \times 10^{10}$	θ_D (Debye)
70.16	0.0224	650	1930
75.37	.0296	692	1890
81.59	.0362	667	1900
88.65	.0452	650	1930
96.68	.0592	655	1920
105.10	.0785	677	1900
113.04	.0991	686	1890
125.28	.138	703	1874
134.29	.174	719	1863
144.10	.218	730	1851
153.71	.267	736	1845
162.76	.318	740	1840
173.33	.386	743	1833
181.96	.444	739	1832
191.44	.518	740	1830
200.94	.595	735	1818
211.84	.685	722	1820
231.06	.858	694	1817
241.09	.918	653	1845
252.37	1.033	642	1840
264.31	1.137	616	1852
276.61	1.257	595	1855
287.96	1.355	568	1865

As seems likely in view of its derivation, the Debye formula only approximates the experimental data for most substances. Blackman[4] has discussed the nature of the deviations to be expected, and has shown that the specific heat curve for the vibrations of a given crystal will always approach the Debye formula at very low temperatures, but that it will be a rare and accidental occurrence if the Debye formula holds precisely over the entire temperature range.

It was the purpose of this investigation to consider the heat capacity curve for a particular substance in the light of these discussions. The choice of diamond as the subject was favored by the high symmetry of the crystal, the presence of only one kind of atom, the fact that the interatomic forces are reasonably well known and of short range, and the experimental consideration that, in a comparative sense, very low temperatures are easily attained.

EXPERIMENTAL

About twenty grams of diamonds of a grade known as "bortz" were obtained for these experiments. The stones, while imperfect, were reasonably clear and were free from foreign matter. It is believed that their heat capacity was the same as that of perfect diamonds within the experimental errors of this investigation.

The calorimeter employed in this investigation was of similar character to that described by Latimer and Greensfelder[5] but was in size just large enough to contain the diamonds. The cryostat and other equipment were the same as has been used previously. The measurements

[1] Einstein, Ann. d. Physik **22**, 180, 800 (1907); **34**, 170, 590 (1911).
[2] Born and v. Kármán, Physik. Zeits. **13**, 297 (1912).
[3] Debye, Ann. d. Physik **39**, 789 (1912).
[4] Blackman, Proc. Roy. Soc. London **A148**, 365, 384 (1935); **A149**, 117, 126 (1935).
[5] Latimer and Greensfelder, J. Am. Chem. Soc. **50**, 2202 (1928).

were of similar accuracy except at the lowest temperatures where the heat capacity of the diamonds was only about one-tenth of the heat capacity of the empty calorimeter. The error in the results may be as large as 5 percent at the lowest temperatures but rapidly diminishes to about 0.2 percent at 150°K. At the highest temperatures the errors become somewhat larger due to the rapid heat exchange by radiation. The results are listed in Table I and are presented graphically in Fig. 1, together with those of other investigators.[6]

As can be seen from Fig. 1, the results of various investigations are in reasonably good agreement with the possible exception of the data of Nernst below 100°K. That these values may be in error seems not improbable when one considers that Nernst's results at even lower temperatures show a smaller heat capacity for the filled calorimeter than for the empty.

The entropy of diamond was calculated by a graphical integration of C_p vs. log T, together with an extrapolation to the absolute zero based on the T^3 law. The results are summarized in Table II.

DISCUSSION

Columns three and four of Table I give the values of (C_p/T^3) and θ_D (Debye) respectively for the various temperatures. The heat capacity of diamond is found to be proportional to the third power of the temperature up to about 100°K, after which it rises faster than T^3 for about 75°. This increase of the heat capacity, faster even than T^3, is of course unexplainable by the Debye theory but is quite possible in

TABLE II. *The molal entropy of diamond.*

0 – 70.8°K	T^3 extrapolation	0.0077 cal./deg.
70.8–298.1°	Graphical from data	0.5776
	Entropy at 298.1°K =	0.585±.005

view of Blackman's considerations of lattices. Similarly the values of θ_D are constant at about 1910 up to 100°K, then decrease gradually to about 1820 at 200°K, after which they appear

[6] Nernst, Ann. d. Physik **36**, 395 (1911); Weber, Phil. Mag. **49**, 161 (1875); Robertson, Fox and Martin, Proc. Roy. Soc. London **A157**, 579 (1936).
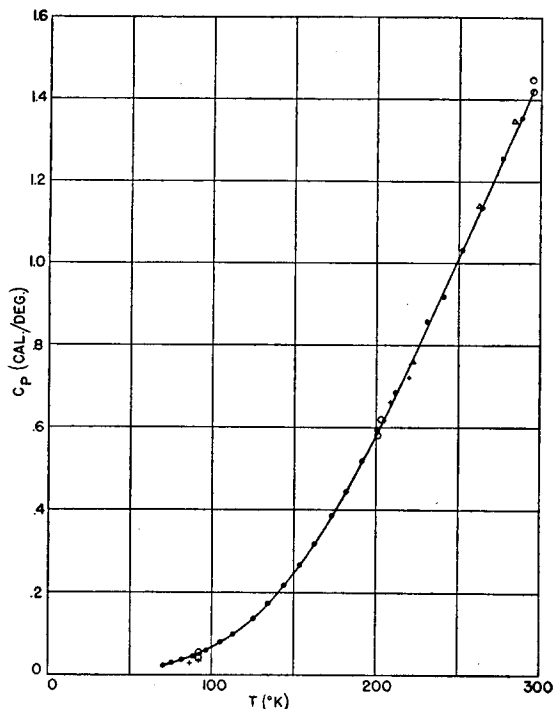

FIG. 1. The molal heat capacity of diamond in cal. per degree per mole. Solid circles, this research; crosses, Nernst; triangles, Weber; open circles, Robertson, Fox and Martin.

again to rise slightly. This variation of about 5 percent is, of course, not very great but is entirely outside the experimental error.

Some rough calculations made by the writer indicate that this variation of θ_D is entirely reasonable. These calculations followed the general methods of Blackman[4] but were specifically set up for the diamond lattice. The only forces considered were central forces between adjacent atoms and forces tending to keep the bond angles those of a tetrahedron. The ratio between the two force constants was estimated from the normal vibration frequencies of propane. The results of this calculation deviate from the experimental values by about the same amount as the Debye theory, but the deviations are in the *opposite direction*. The true distribution of vibration frequencies is thus somewhere between that given by the rough lattice calculations and that of the Debye "continuum." It is now apparent that there is nothing anomalous about the specific heat of diamond, and that the assumption[7]

[7] Simon, Sitzber. preuss. Akad. Wiss., Physik. Math. Klasse **33**, 477 (1926).

of "thermal quantum jumps" is quite unnecessary.

In conclusion it may be said that there is agreement between experimental and theoretical specific heats of crystals, within the uncertainty in the latter. This uncertainty is, nevertheless, quite large, and it is hoped that in the near future the experimental data presented above can be compared with a more precise theory.

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Order and Disorder in Binary Solid Solutions*

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A theory of order and disorder in solid solutions, based upon a direct evaluation of the crystalline partition function, is described. As in the theory of Bethe, the fluctuation in energy within states of a fixed degree of order, is taken into account. The method promises to be of use in the study of other cooperative phenomena.

I

IT has been found that the atoms of certain solid solutions, although distributed at random among the lattice sites of the crystal at high temperatures, tend to arrange themselves into an ordered structure or superlattice at low temperatures. Moreover, there exists a critical temperature, analogous to the Curie temperature in ferromagnetism, below which the ordering process first begins to set in. Experimental evidence for the existence of order in such alloys as Cu-Au and Cu-Zn is provided by x-ray analysis of their crystal structure, and by the observation of discontinuities in certain of their physical constants or in their derivatives, which occur at the critical temperature.

Bragg and Williams[1] have treated the problem of order and disorder from the theoretical standpoint. Their theory accounts for the existence of a critical temperature and provides an approximate description of the influence of order on the thermodynamic functions of binary solid solutions. In the development of the theory they assume that the energy of the crystal is determined by its degree of long range order.

It was pointed out by Bethe[2] that a given degree of order includes many crystalline configurations of different energy. Bethe developed a more elaborate theory in which the fluctuations in energy were taken into account. His theory, later extensively applied by Peierls,[3] yields results which are more nearly in accord with experiment than does the theory of Bragg and Williams.

We shall describe here an alternative theory of order and disorder, essentially equivalent to Bethe's in its degree of approximation, but somewhat less unwieldy in form. It is based upon a straightforward evaluation of the partition function of the crystal by the methods of statistical mechanics. The method of calculation bears a certain resemblance to that of the Heisenberg theory of ferromagnetism. However, the convergence difficulties, encountered by the ferromagnetism theory at low temperatures, do not arise, at least for solid solutions of rational composition. We believe that the theory may prove useful not only in the study of order and disorder in solids, but also in the treatment of cooperative phenomena in general.

II

We consider a binary solid solution containing equal numbers, N, of atoms of the components

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[1] Bragg and Williams, Proc. Roy. Soc. London **A145**, 699 (1934); **151**, 540 (1935); **152**, 231 (1935).
[2] Bethe, Proc. Roy. Soc. London **A150**, 552 (1935).
[3] Peierls, Proc. Roy. Soc. London **A154**, 207 (1936).