

THE SPECIFIC HEATS OF CRYSTALS

Part II. The Case of Diamond

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IN a lecture on the diamond published in the September issue of these *Proceedings* (Vol. 44, 1956, p. 99), the vibrations of the diamond structure were discussed in detail and the results of spectroscopic investigations on the nature of the vibration spectrum were also set forth. The results contained in that paper furnish us with all the material necessary for a complete theoretical evaluation of the specific heat of diamond over the entire range of temperatures for which experimental data are available. We shall now proceed to make such an evaluation and compare it with the results of the published measurements on the specific heat of diamond.

Table I gives a list of the nine characteristic frequencies of the diamond structure expressed in wave-numbers (cm.^{-1}), their respective degeneracies and the geometric description of the corresponding modes of vibration. The frequencies shown in the last column of the table were evaluated with the aid of the equations of motion and a set of force constants and were also independently confirmed by the results of spectroscopic investigation by several

TABLE I
Vibration Spectrum of Diamond

No.	Degeneracy	Description of the mode	Frequency in cm.^{-1}
I ..	3	Oscillation of the two interpenetrating lattices against each other	1332
II ..	8	Tangential oscillation of the octahedral planes	1250
III ..	6	Tangential oscillation of the cubic planes	1239
IV ..	4	Normal oscillation of the octahedral planes	1149
V & VI ..	(3+3)	Normal oscillation of the cubic planes	1088
VII ..	4	Normal oscillation of the octahedral planes	1008
VIII ..	6	Tangential oscillation of the cubic planes	740
IX ..	8	Tangential oscillation of the octahedral planes	621

different techniques. It is a simple matter with the aid of the table to calculate the contributions to the specific heat arising from the nine modes of internal vibration of the diamond structure. The lowest frequency appearing in the table expressed in wave-numbers, *viz.*, 621 cm.⁻¹ may also be properly assumed to be the upper limit of frequency in the continuous spectrum of the vibrations arising from the translations of the super-cell of the crystal structure, as explained in Part I of the present paper.

The contribution to the specific heat arising from the continuous part of the vibration spectrum can be readily evaluated on this basis with the aid of the tabulated values of the relevant functions available in "Landolt-Bornstein". Table II below shows the results of such computations. The contributions to the atomic heat arising respectively from the discrete spectrum and from the continuous spectrum are shown separately for a series of temperatures ranging from 15° to 1100° on the absolute scale. The sum of the two contributions is also tabulated.

TABLE II
Theoretical Computation of the Atomic Heat of Diamond
(Calories per gram-atom per degree)

Absolute Temperature T°	Discrete Frequencies	Continuous Spectrum	Total	Absolute Temperature T°	Discrete Frequencies	Continuous Spectrum	Total
15	..	0.00014	0.00014	200	0.4069	0.1631	0.5700
20	..	0.00033	0.00033	225	0.5894	0.1895	0.7789
25	..	0.00064	0.00064	250	0.7844	0.2124	0.9968
30	..	0.0011	0.0011	275	1.0137	0.2319	1.2456
40	..	0.0026	0.0026	300	1.2418	0.2486	1.4904
50	..	0.0051	0.0051	350	1.700	0.275	1.975
60	..	0.0088	0.0088	400	2.139	0.294	2.433
70	0.0005	0.0140	0.0145	450	2.538	0.308	2.846
80	0.002	0.0207	0.0227	500	2.892	0.319	3.211
90	0.0056	0.0290	0.0346	600	3.469	0.334	3.803
100	0.0128	0.0388	0.0516	700	3.899	0.344	4.243
120	0.0419	0.0619	0.1038	800	4.224	0.350	4.574
140	0.0957	0.0877	0.1834	900	4.465	0.355	4.820
160	0.1758	0.114	0.2898	1000	4.653	0.358	5.011
175	0.2517	0.1333	0.3850	1100	4.797	0.360	5.157

The values of the atomic heats of diamond listed in Table II are exhibited in graphical form in Fig. 1. At temperatures below 70° absolute, the curve appears to touch the axis since the very low values of the specific heats in this region cannot be represented on the scale of the graph. The values in this region are, however, of great interest, since, as will be seen from

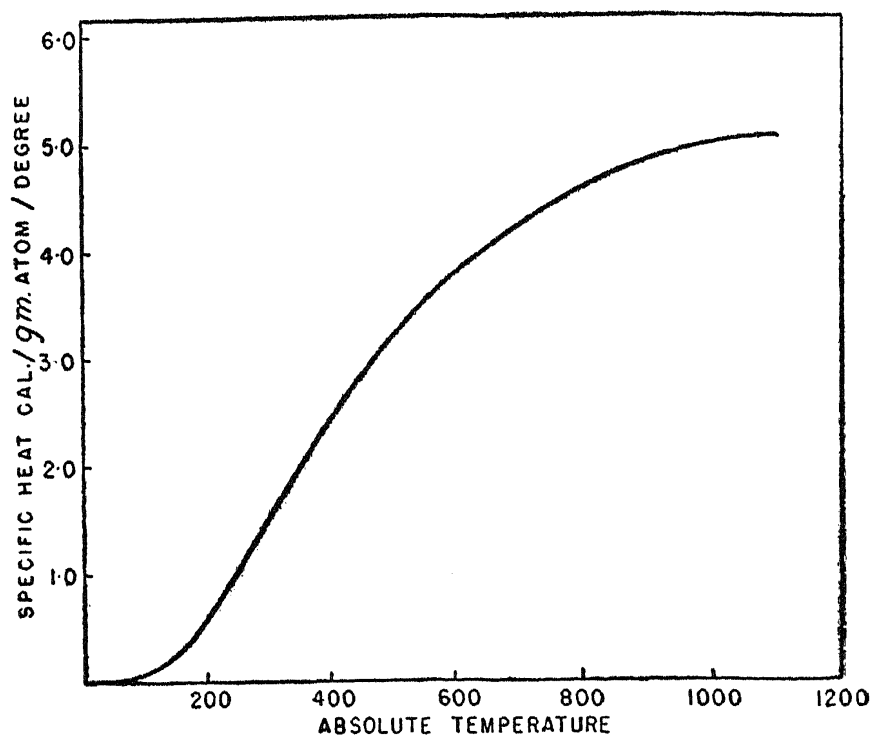


FIG. 1. The atomic heats of diamond calculated from the spectroscopic data.

Table II, they arise exclusively from the contribution of the continuous spectrum of frequencies which represents only 3 out of the 48 degrees of atomic freedom of movement of the crystal. Accordingly, the theoretical curve for this part of the temperature range has been drawn with a greatly enlarged scale for the ordinates in Fig. 2 below. Fortunately also, the specific heat of diamond in this region of temperature has been the subject of detailed investigation by Warren DeSorbo (*Journal of Chemical Physics*, Vol. 21, 1953, p. 876) and his experimental results for this very interesting region are plotted in the diagram. A gratifying agreement between theory and observation will be noticed.

The specific heat of diamond in the range of absolute temperatures from 70° to 300° was determined by K. S. Pitzer (*Journal of Chemical Physics*, Vol. 6, 1938, p. 68). The measurements by DeSorbo also cover this range. A careful inter-comparison between them shows that Pitzer's values are distinctly higher than those of DeSorbo throughout this range and that they also exhibit a scatter which is distinctly larger than the results of DeSorbo. DeSorbo's work is of later date and his data form a continuous sequence over a wider range of temperatures. For these reasons, it was felt that a comparison between theory and experiment would be more appropriately made with the results of DeSorbo. Fig. 3 below shows such comparison and here again a very satisfactory agreement emerges.

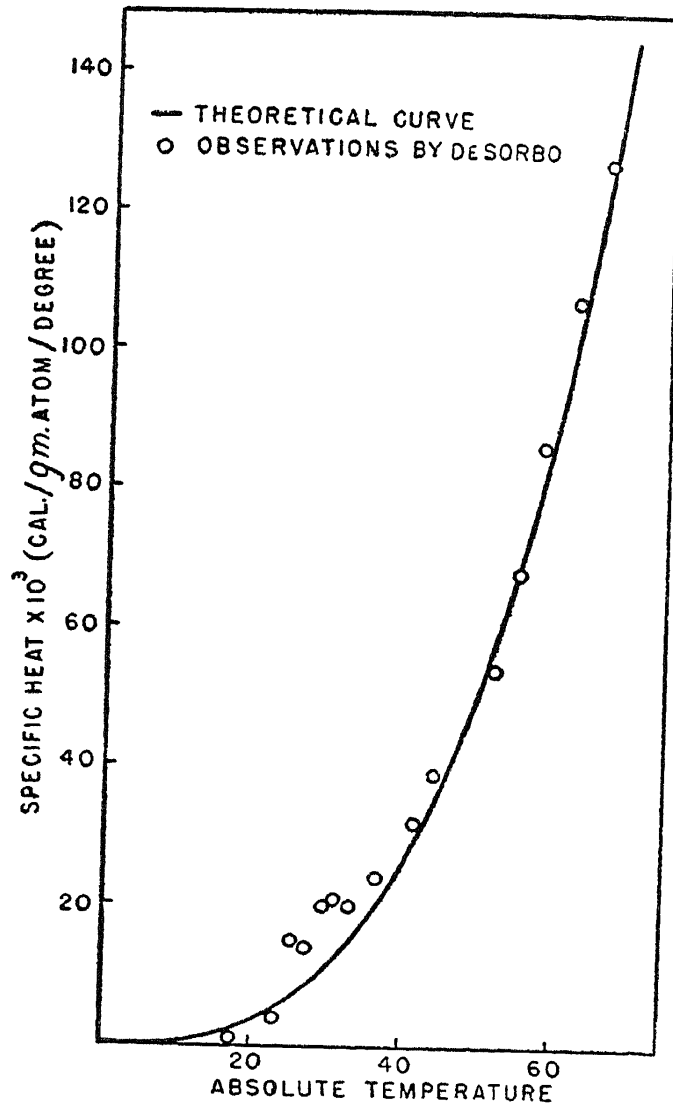


FIG. 2. Comparison between theory and experiment at very low temperatures.

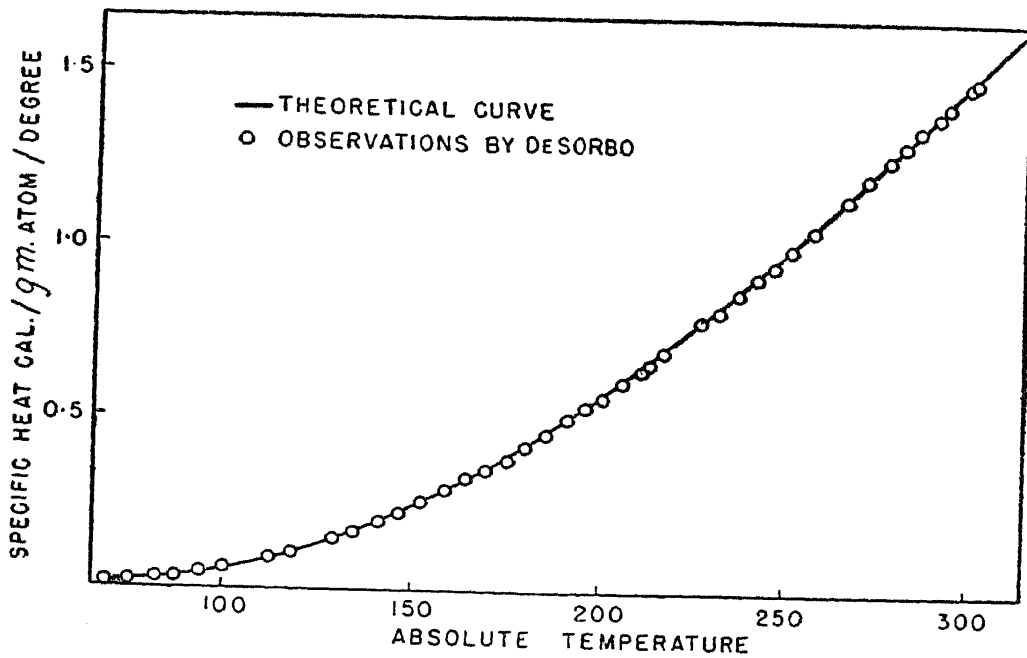


FIG. 3. Comparison of theory and experiment below room temperature.

Finally, Fig. 4 exhibits a comparison between the theoretical values and the experimental data in the temperature range from 300° to 1100° absolute covered by the determinations of Magnus and Hodler (*Annalen Der Physik*, Vol. 80, 1926, p. 808). The observed discrepancies throughout the range do not exceed two per cent. and in most cases are much less. The agreement should therefore be considered as satisfactory.

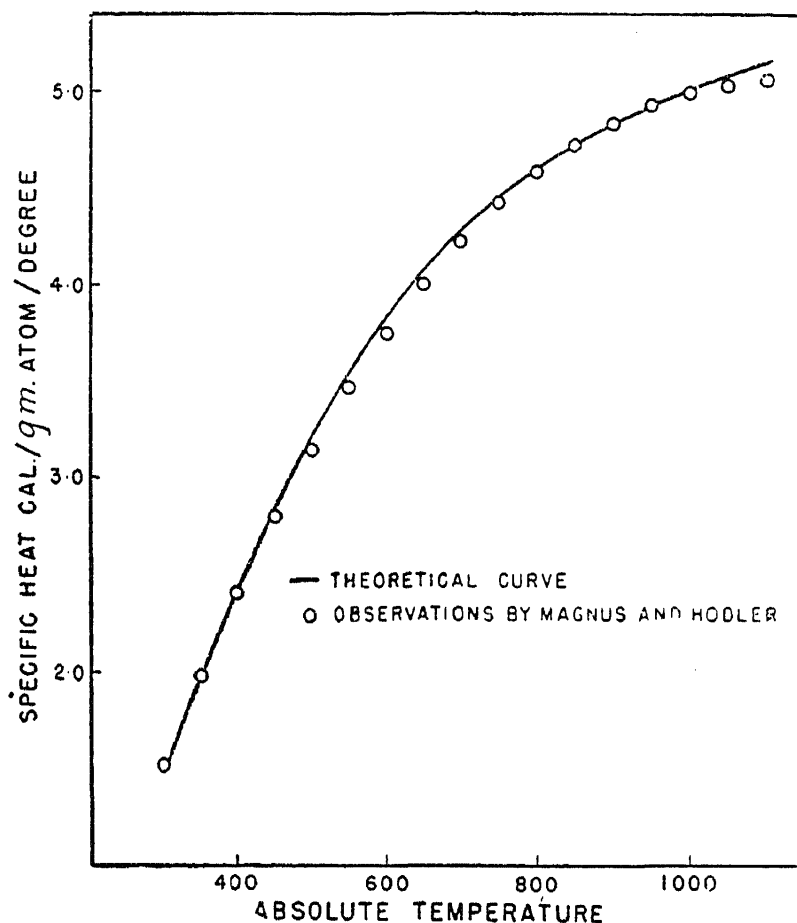


FIG. 4. Comparison between theory and experiment at high temperatures.

SUMMARY

The specific heat of diamond in the temperature range between 15° and 1100° absolute has been computed theoretically, making use of the nine spectroscopically determined vibration frequencies of the diamond structure as well as their known degeneracies, and further taking the lowest of these nine frequencies to be the upper limit of frequency in the residual continuous spectrum as explained in Part I of the paper. The results are compared with the experimental observations of DeSorbo from 15° to 300° absolute and of Magnus and Hodler from 300° to 1100° absolute. A highly satisfactory agreement between theory and experiment emerges.