

THE HEAT CAPACITY OF DIAMOND BETWEEN 0 AND 1000° K.

BY SIR C. V. RAMAN

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1. INTRODUCTION

THE evaluation of the heat capacity of diamond on the basis of the theory of specific heats of crystals advanced by the author formed the subject of a recent publication¹ in these *Proceedings*. Since then, fresh experimental determinations have been reported which go down to temperatures at which the value of C_p for diamond is as low as 0.0001, in other words only a fifty-thousandth part of its value 5.0 at 1000° K. which is itself smaller than the theoretical maximum of 5.96 for a monatomic solid. We proceed here to consider the new experimental results. The theoretical evaluation already published succeeds in explaining the change of C_p with temperature over the whole of this enormous range of values in a highly satisfactory manner, but with certain reservations made necessary by the fact that the theoretical calculations are based on the spectroscopic behaviour of ideal diamonds, whereas the reported determinations have been made with material which is very far indeed from being ideal. To exhibit the closeness of the agreement which is observed over practically the entire temperature range as well as the minor differences which are noticeable in certain limited parts of it, the data have been plotted on adequate scales alongside of the theoretical values in a series of graphs which are reproduced in the present paper. The cause of the small differences which appear in the temperature range between 50 and 150° K. is discussed and it is shown that they are explicable in terms of the differences in the spectroscopic behaviour of ideal and non-ideal diamonds.

Diamond illustrates in a most striking manner the fundamental relationship between the specific heats of crystals and their spectroscopic behaviour. Being an elementary solid crystallising in the cubic system with an exceptionally simple structure, the characteristic modes of atomic vibration which determine both the thermal behaviour and the spectroscopic properties of diamond can be described in geometric terms without any reference to the magnitude of the interatomic force constants. Considerations of a general nature enable us to go further and arrange these modes in a scale of descending frequency, thereby greatly facilitating their identification.

Diamond being a transparent solid, the modes and frequencies of atomic vibration in it are also accessible to observation by a variety of spectroscopic methods. It is found possible to determine these frequencies with precision and compare them with the theoretically computed values. Thus theory and experiment agree to give us a complete and detailed picture of the atomic vibration spectrum of diamond. It thereby becomes possible to evaluate the heat capacity of the crystal in a completely independent fashion involving no assumptions of any sort. The agreement which emerges between the results of such evaluation and the experimental data is a convincing demonstration of the correctness of the theoretical approach.

2. THE VIBRATION SPECTRUM OF DIAMOND

The crystal structure of diamond consists of two distinct sets of atoms of carbon which appear separately in layers parallel to the faces of the octahedron and the cube respectively. The normal modes of atomic vibration of the structure can be readily described in terms of this arrangement. The principal mode of vibration is an oscillation of the two sets of atoms with respect to each other along any one of the three cubic axes and has therefore a degeneracy of 3. The atoms present in the layers parallel to the octahedral faces may oscillate with respect to each other either normally or transversely to themselves with degeneracies of four and eight respectively; but since the adjacent non-equivalent layers may oscillate either in the same or opposite phases, we have two such sets of modes. Likewise, we have two sets of modes in which the layers of atoms parallel to the cube faces oscillate normally or transversely to themselves with degeneracies of three and six respectively. Thus, we have 9 distinct normal modes with degeneracies of 3, 4, 4, 8, 8, 3, 3, 6 and 6 respectively, making a total of 45 modes in all. Considering the set of 16 atoms contained in a volume element which is twice as large in each direction as the unit cell of the crystal structure, the total number of atomic degrees of freedom of this group is 48. The 45 modes of vibration described above may be regarded as the *modes of internal vibration of this group*, while the three degrees of freedom left over represent *its three translations*.

In a lecture on the diamond delivered at Zurich, Freiburg and Bonn in July 1956, and subsequently published in these *Proceedings*² it was shown in detail how the frequencies of the nine normal modes described above may be evaluated and checked against the frequency shifts observed in the scattering of light by diamond when it is traversed by the λ 2536.5 radiations of the mercury arc. We shall content ourselves here with reproducing below as Fig. 1 a chart showing the nine frequencies and their respective degeneracies.

The two modes of oscillation normal to the cubic planes have an identical frequency of 1088 cm^{-1} . They have accordingly been shown as a single frequency with a degeneracy of 6.

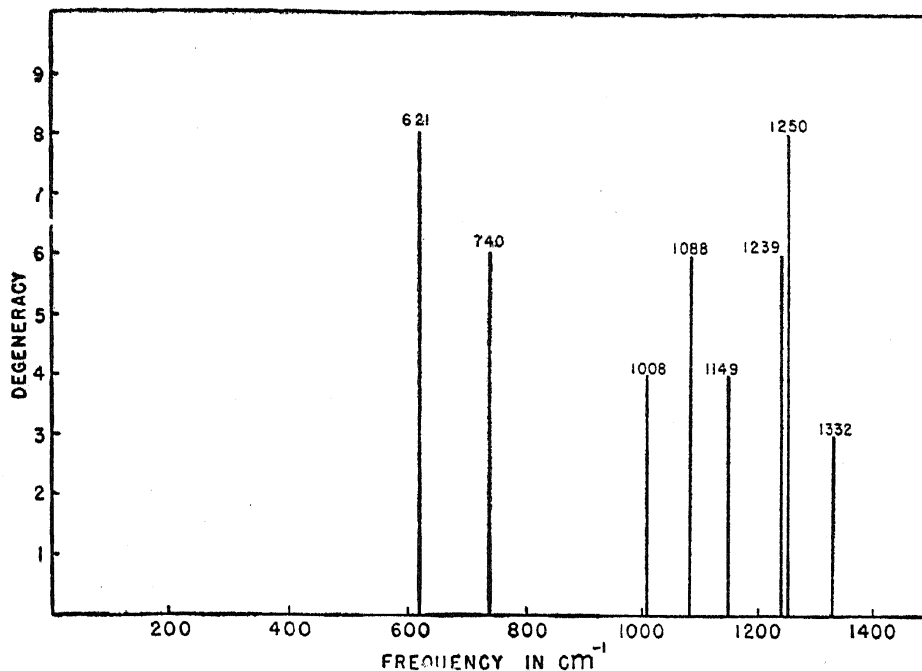


FIG. 1. Chart of the Vibration Spectrum of Diamond.

To complete the picture, we require to know how the three translatory movements of the 16-atom group manifest themselves in the vibration spectrum of the crystal. It is obvious that they would appear as internal vibrations in volume elements of larger size than the 16-atom group and therefore having lower frequencies. In dealing with vibrations of this nature, it is permissible to ignore the discrete atomic structure of the material. The larger the size of a volume element is, the lower would be the frequencies of its internal vibration. Considering volume elements of all possible sizes as the oscillators, their frequencies of internal vibration would evidently range from the lowest possible value $\nu = 0$ to an upper limit ν_L which may be taken equal to the lowest of the frequencies of vibration appearing in the chart (Fig. 1). The manner in which the disposable degrees of freedom of atomic movement are distributed over this range of frequencies is indicated by a simple argument. The number of volume elements of any specified dimension included in the crystal and hence also the number of degrees of freedom represented by their translations diminish in inverse proportion to the cube of the linear dimensions, while the frequencies of their internal vibration would vary inversely as the first power of the same. Hence the number of degrees of freedom appearing as internal vibrations of the volume

elements and having frequencies between 0 and ν would be proportional to ν^3 . By differentiation, we obtain the result that the number of degrees of freedom appearing between frequencies ν and $\nu + d\nu$, in other words, the number of oscillators in the crystal having frequencies in that range would be proportional to $3\nu^2 d\nu$. The constant of proportionality may be deduced at once from the consideration that on integration between zero and the upper limit ν_L , we should obtain as the total number of oscillators three times the number of 16-atom groups comprised in the crystal.

3. THE HEAT CAPACITY OF DIAMOND

Having thus ascertained the nature of the complete vibration spectrum of diamond, we proceed to make use of the theory of Einstein and obtain an expression for the heat content of the crystal as a function of the temperature. This appears as a sum of two quantities; the first is a summation of the average energies of the individual oscillators having the discrete frequencies shown in the chart (Fig. 1) multiplied by their respective degeneracies and by the total number of 16-atom groups contained in the crystal. The second part is a summation of the average energies of vibration of the oscillators of larger sizes having various frequencies from 0 to ν_L , and this takes the form of an integral between these limits of frequency. The details of the calculations have already been given in the earlier paper and it is therefore sufficient to reproduce here the final results here in tabular form.

TABLE I

Theoretical Computation of the Atomic Heat of Diamond

(Calories per gram-atom per degree)

Absolute Temperature	Discrete Frequencies	Residual Spectrum	Total	Absolute Temperature	Discrete Frequencies	Residual 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	4.24	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

It will be seen that the contribution from the set of discrete frequencies becomes negligible at temperatures below 60° Abs. At and below that temperature, the residual spectrum of frequencies alone is responsible for the entire heat capacity of the crystal. At higher temperatures, however, the contribution of the spectrum of discrete frequencies rapidly increases and ultimately becomes responsible for all except 1/16th part of the specific heat.

In order to exhibit the over-all success of the theory in explaining the thermal behaviour of diamond, the figures for the atomic heat shown in Table I have been plotted as a curve (Fig. 2) on a scale which is adequate

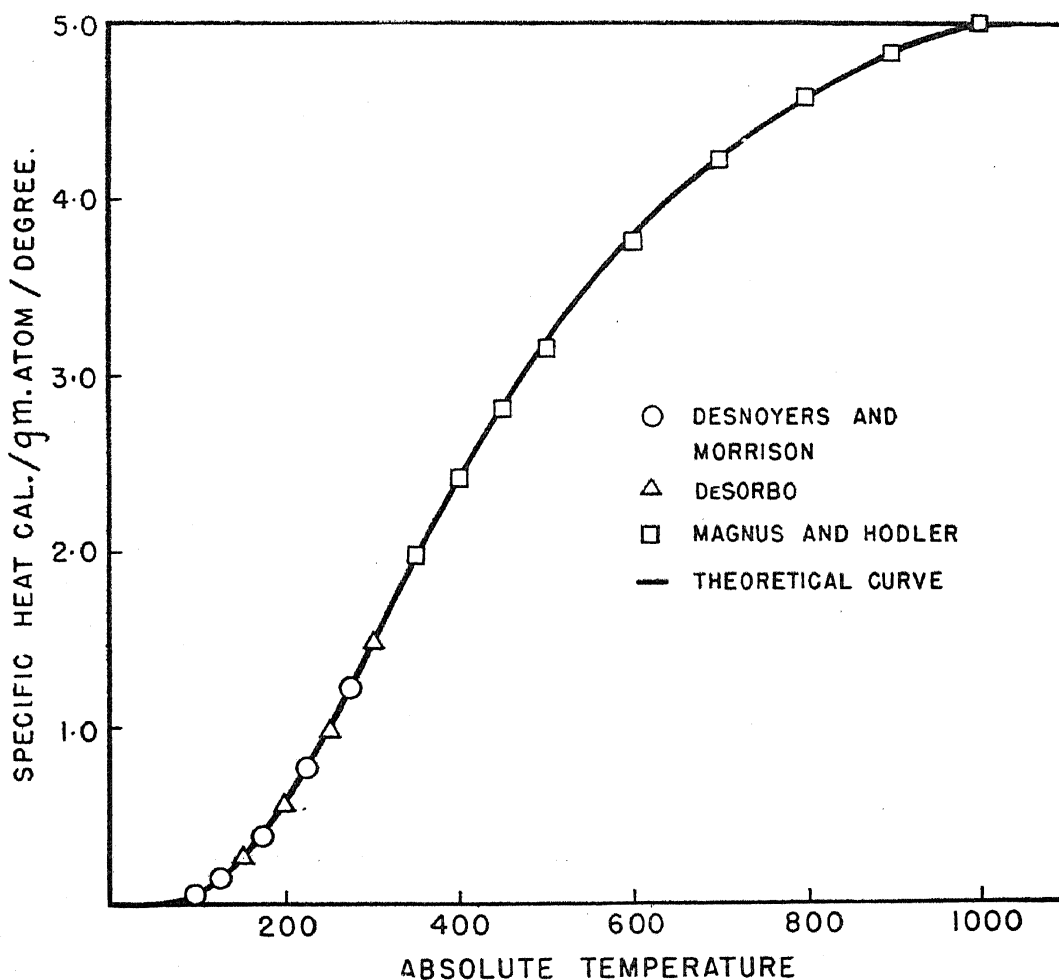


FIG. 2. Specific Heat of Diamond from 0 to 1000°.

to represent the data except in the region where it runs nearly parallel to the axis of temperature. In the temperature range between 300 and 1000° K., the values determined by Magnus and Hodler have been used, while in the

lower ranges, the data of DeSorbo as well as those reported by Desnoyers and Morrison have been put in. It will be seen that no deviations between theory and experiment which are at all significant are noticeable on the scale of the graph.

For temperatures below 300°, the determinations by Pitzer, DeSorbo and by Desnoyers and Morrison are available, but since the two latter sets of determinations are in good agreement, they have been plotted in a graph covering the temperature range between 160 and 300° K. (Fig. 3). The

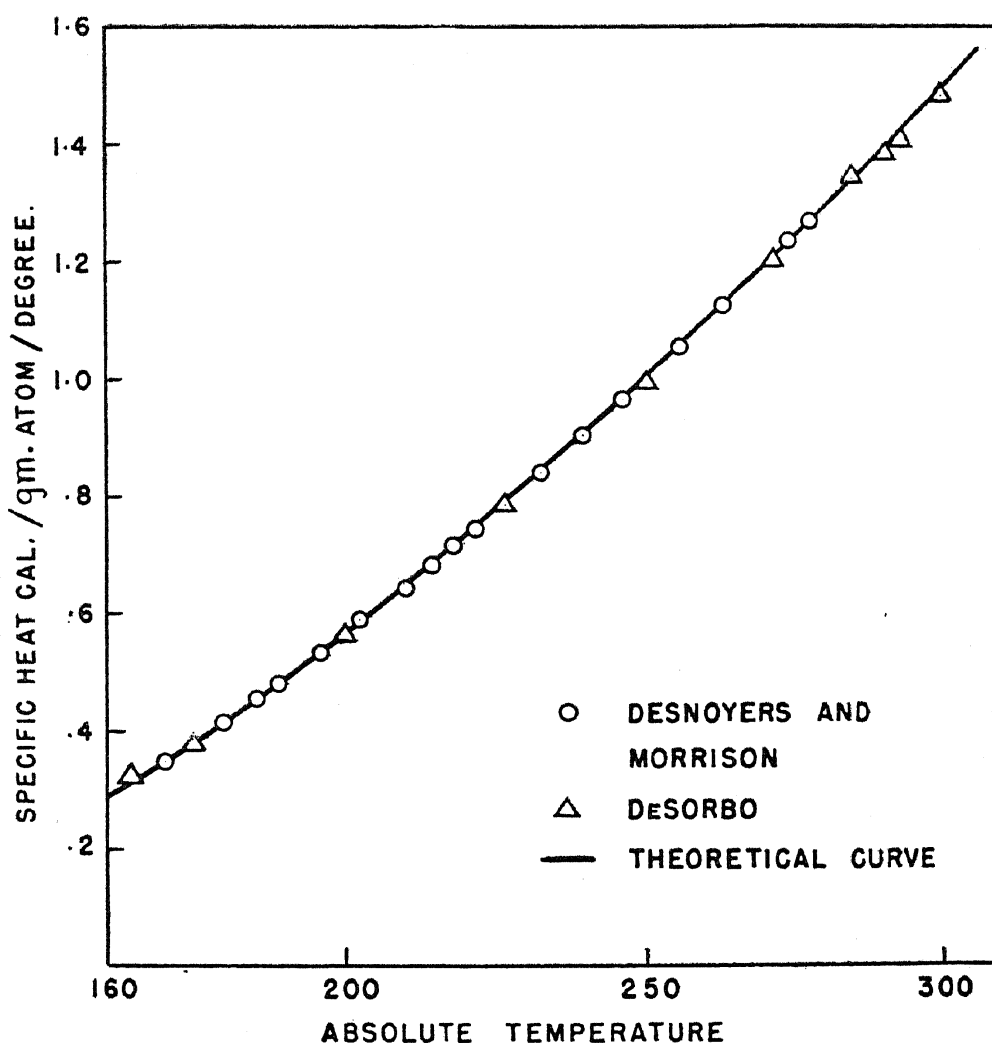


FIG. 3. Specific Heat of Diamond from 160 to 300°.

scale on which this figure has been drawn is adequate to disclose any systematic deviations between theory and experiment, had such existed. No such deviations are noticeable and hence it is evident that throughout the range of temperature in which the spectrum of discrete frequencies is principally

responsible for the heat capacity of diamond (160 to 1000° K.), the theory is in very satisfactory accord with the facts.

We shall next consider the very lowest temperatures where the value of C_p retreats into the third or fourth decimal place. The theoretical curve for this region has been drawn in Fig. 4, an adequately large scale being used for the ordinates, and the data reported by DeSorbo and by Desnoyers and Morrison have been plotted alongside of it. At the lowest temperatures the values of DeSorbo exhibit a distinct scatter, many of them lying above the theoretical curve. On the other hand, the more recent data of Desnoyers and Morrison lie smoothly on the curve up to 50°. The agreement between theory and experiment in this range made apparent by the graph must be considered highly satisfactory.

In the temperature range between 50° and 60° K., the experimental values plotted in Fig. 4 lie above the theoretical curve, the magnitude of the differences being a few units in the fourth place of decimals. From Fig. 5 which

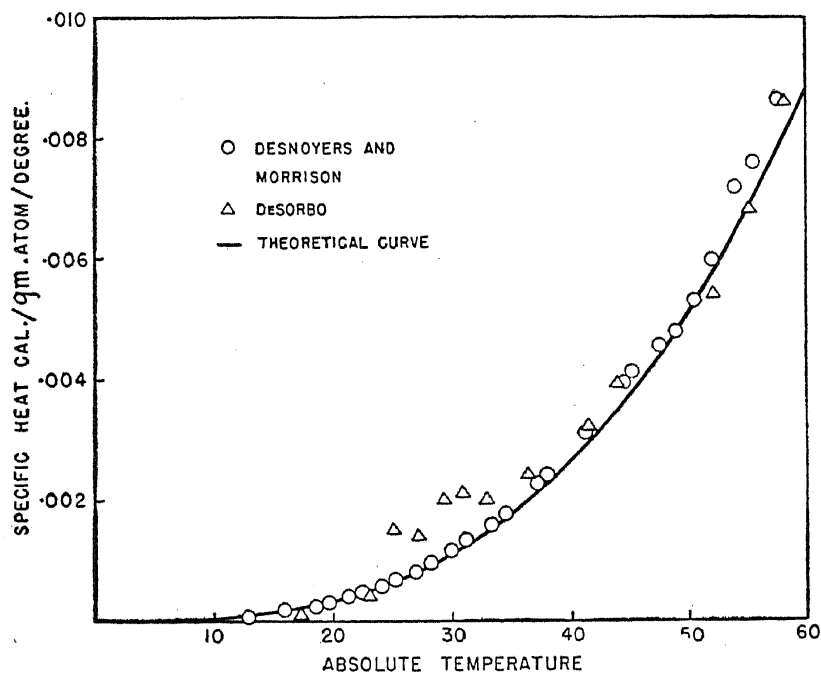


FIG. 4. Specific Heat of Diamond from 0 to 60°.

represents a comparison between theory and experiment in the range between 60 and 160° K. it will be seen that such differences become distinctly more pronounced at higher temperatures, reaching a maximum value of 0.007 at about 100°; they steadily diminish again at higher temperatures and finally cease to be noticeable on the graphs beyond 150° K. Since the value of the specific heat at 100° K. is itself very low, being only 0.059, the difference

between theory and experiment expressed as a percentage of the specific heat is 12%, but to express the difference in this way exaggerates its significance. Since, however, the discrepancy is real, we shall consider and comment upon its origin.

4. SPECTROSCOPIC BEHAVIOUR OF NON-IDEAL DIAMONDS

An explanation of the differences which are noticeable between theory and observation in the values of C_p in the range between 50 and 150° K. is not far to seek. The theoretical calculations refer to the case of an ideal crystal. They could therefore be expected to show a complete agreement with the experimentally determined specific heats if only the latter had also been made with ideal diamonds. Actually, however, determinations of specific heat require fairly large masses of material and it is therefore inevitable that they are made with diamonds of an inferior sort. It may be noted that DeSorbo used 80 grams of fragmented bort. He noticed that some of the crystals exhibited colour and also that about 20% of the material was fluorescent. Desnoyers and Morrison report that the sample used by them consisted approximately of 160 grams of industrial diamonds, their average dimensions being about 3 mm. They also remark that most of their diamonds were lightly coloured, either yellow, brown or green but that none contained inclusions. It is evident from these descriptions that we are concerned here with the class of diamond that exhibits its non-ideality of crystal structure in a visible manner, in other words, shows colour in daylight and luminescence under ultra-violet illumination.

The spectroscopic behaviour of diamonds of all sorts has been investigated by a variety of methods over a period of many years by the author and his collaborators. It will suffice here to refer to the results reported in a paper by Miss Anna Mani³ recording a detailed study of the fluorescence and absorption spectra of twenty-two diamonds of various sorts. When the crystals are cooled down to liquid air temperature, these spectra sharpen notably, and it then becomes possible to analyse them in detail. Inter-comparison of the fluorescence and absorption spectra enables the frequencies representing electronic transitions to be identified and distinguished from those due to the vibrational transitions appearing in combination with them. The result emerges clearly that the spectroscopic behaviour of diamonds which are colourless as seen by daylight and of those which exhibit various shades of brown, yellow or green is strikingly different. Diamonds of the former sort exhibit a blue fluorescence and the atomic vibration spectrum deduced from studies thereof is generally similar to that shown in the chart

reproduced above as Fig. 1 in the text. On the other hand, diamonds exhibiting visible tints by daylight fluoresce with a greenish yellow colour, the analysis of the spectrum of which discloses many features both in the electronic and atomic vibration spectra which are absent in the blue luminescence of

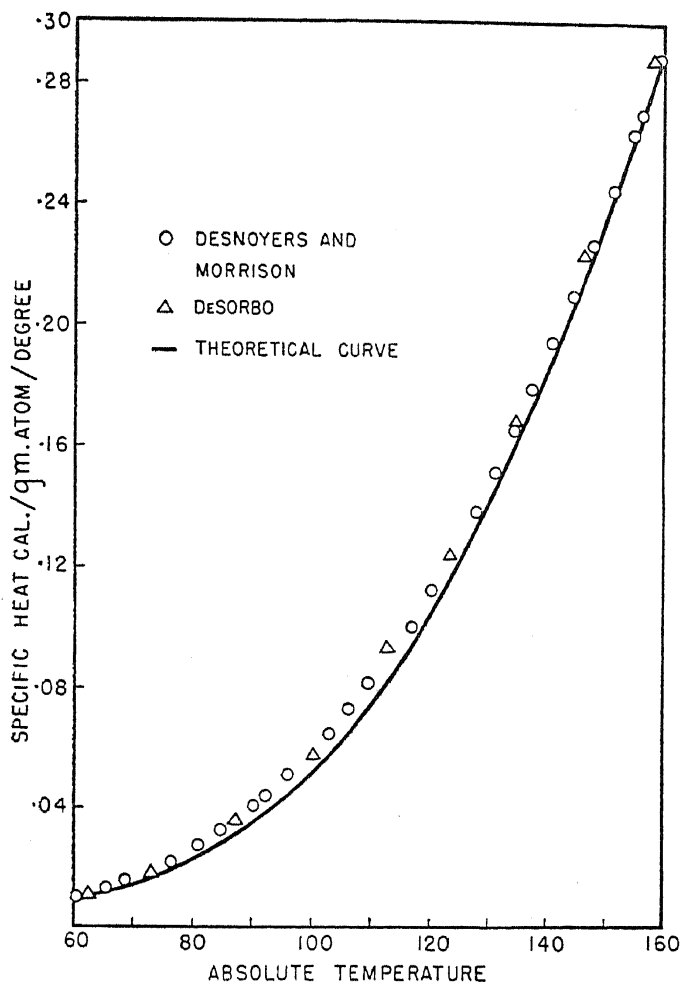


Fig. 5. Specific Heat of Diamond from 60 to 160°.

colourless diamonds. The most prominent of the additional features in the vibration spectrum is a band stretching from 257 to 443 cm.^{-1} with its peak at 359 cm.^{-1}

It is clear from the facts recited above that the atomic vibration spectrum of non-ideal diamonds differs notably from that of the ideal material. The difference arises chiefly in the region of the residual spectrum of frequencies and may be described as an enhancement of its strength in the region of frequencies about 359 cm.^{-1} . Since the total number of atomic degrees of freedom is invariant, such enhancement would necessarily involve a diminu-

tion in the strength of the residual spectrum at higher frequencies between 359 cm.^{-1} and the upper limit of 621 cm.^{-1} . A change in the character of the residual spectrum of the nature indicated would evidently result in altering the specific heat of the crystal. The Einstein function for a frequency of 359 cm.^{-1} has a negligible value at temperatures below 50° K. It increases most rapidly in the temperature range in the vicinity of 100° , and at higher temperatures tends more slowly towards its limiting value. The change in the character of the residual spectrum would thus result in an increase of the specific heat of non-ideal diamonds which would be vanishingly small at very low and at very high temperatures and would be most prominent at about 100° K. This describes what is actually observed.

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SUMMARY

The evaluation of the heat capacity of diamond on the basis of the theory of specific heats advanced by the author is discussed and the results are compared graphically with the latest available experimental data. A striking over-all agreement emerges over the whole of the temperature range between 0 to 1000° K. The experimental values are however slightly in excess of the theoretical ones in the limited range between 50 and 150° K. , the difference in the value of C_p being a maximum of 0.007 at about 100° K. and ceasing to be noticeable both below 50° K. and above 150° K. This small excess is explained as a consequence of the use in the experimental determinations of industrial diamonds whose spectroscopic behaviour is observably different from that of the ideal material.

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