# The infra-red absorption by diamond and its significance—Part X. Evaluation of the specific heat

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## 1. Introduction

Einstein in his classic paper of 1907 introducing the quantum theory of specific heats showed that the thermal energy content of all material bodies depends in a fundamental way on the vibration frequencies of their atomic constituents in the region of the infra-red. Crystalline solids were included within the scope of his theory and the case of diamond was specially considered by him in the paper. The very striking changes which appear in the specific heat of diamond with alterations in temperature had been discovered by H F Weber in the year 1875 and Einstein made use of Weber's data to illustrate and support his theory. Assuming that the atoms in diamond had a single characteristic frequency of vibration corresponding to an infra-red wavelength of 11 $\mu$, Einstein showed that the general trend of the specific heat changes observed by Weber could be accounted for.

In the preceding parts of this memoir, it has been shown that the structure of diamond has eight specific frequencies of free vibration lying in the wavelength range between 7·5 $\mu$ and 16 $\mu$. The spectrographic record of infra-red absorption by diamond enables us to recognise these frequencies and determine them with the necessary precision. It is, therefore, appropriate that we devote the concluding part of this memoir to showing that on the basis of the spectroscopically determined frequencies, and without introducing any other data or any arbitrary constants, the entire course of the variation of the specific heat of diamond over the temperature range from the absolute zero upwards to 1000° K can be computed. A comparison will also be made of the results of the computation with the latest available data on the thermal energy content of diamond.

## 2. The theory of Einstein

We may usefully here sketch the theory of the specific heats of crystals as envisaged by Einstein. He begins by showing that the acceptance of Planck's

radiation formula leads to the consequence that the energy of a resonator capable of absorbing or emitting radiation with a specific frequency could only increase or diminish by quanta proportional to that frequency. A procedure which enables this principle to be used for the evaluation of the thermal energy of crystals is then outlined. The thermal energy is identified with the mechanical energy of vibration of an immense number of *individual* oscillators distributed over the volume of the crystal. The total number of these oscillators is assumed to be the same as thrice the number of atoms comprised in the crystal. It is further assumed that the oscillators can be grouped into sets, each set comprising a great number of individual oscillators characterised by a common frequency of vibration. The individual oscillators in each set occupy the various energy levels allowed by the quantum hypothesis for the particular frequency. The numbers occupying these levels are in the relative proportions determined by the respective energies and by the temperature as indicated by the principle of Boltzmann. The average energy of an oscillator in each of the sets is then evaluated. Summing up over all the oscillators in each of the sets, and then over all the sets, Einstein obtained an explicit formula for the thermal energy of the crystal as a function of the temperature.

It is evident that there is adequate justification for the various steps in the foregoing argument. A crystal is an assembly of a great number of similar and similarly situated groups of atoms, the modes and frequencies of vibration of which would necessarily all be identical. The total number of degrees of dynamical freedom of the entire system may therefore be divided up into sets, each set representing a great number of individual oscillators having a common frequency. Since these oscillators are interconnected, they can exchange energy with each other and thereby constitute a system in thermodynamic equilibrium of which the behaviour could be statistically described in terms of Boltzmann's principle. The argument implies that the atomic vibration spectrum of a crystal would exhibit a set of frequencies, their number being the same as the number of sets of oscillators which are the carriers of the thermal energy. By virtue of Boltzmann's principle, the distribution of this energy over the volume of the crystal would exhibit fluctuations both in space and in time, the magnitude of the fluctuations being the greater, the higher the frequency of the oscillators under consideration.

## 3. The spectrum of free vibrations

The modes of free vibration of the structure of diamond were determined and described in the sixth part of this memoir. In the subsequent parts of this memoir, the characteristic frequencies of vibration as found from the spectroscopic records were assigned to their respective modes on the basis of a theoretical evaluation of the frequencies and confirmed by a comparison of the activities

theoretically to be expected with the activities actually found. We are thus on firm ground in listing the modes, their frequencies and their respective degeneracies as shown in table 1 and making the entries in the table the basis for the evaluation of the thermal energy of diamond as a function of the temperature.

**Table 1.** Modes, degeneracies and frequencies

| Mode | Description | Degeneracy | Frequency (cm$^{-1}$) |
|---|---|---|---|
| I | Oscillation of the two lattices in opposite phases | 3 | 1332 |
| II | Oscillation of the octahedral layers tangentially in opposite phases | 8 | 1273 |
| III | Oscillation of the cubic layers tangentially in opposite phases | 6 | 1219 |
| IV | Oscillation of the octahedral layers normally in the same phase | 4 | 1176 |
| V & VI | Oscillation of the cubic layers normally in the same or opposite phases | 3 + 3 | 1087 |
| VII | Oscillation of the octahedral layers normally in opposite phases | 4 | 1010 |
| VIII | Oscillation of the cubic layers tangentially in the same phase | 6 | 746 |
| IX | Oscillation of the octahedral layers tangentially in the same phase | 8 | 624 |
| | Translations | 3 | 624 → 0 |
| | Total | 48 | — |

The 48 degrees of freedom represented in table 1 are the degrees of freedom of movement of the 16-atom group which is the dynamic unit in the structure of diamond, viz., two groups of eight atoms each located respectively at the corners of the unit cells of two interpenetrating rhombohedral lattices. All except three of these degrees of freedom are represented by discrete modes and frequencies of vibration. The three degrees left out are the three translations of the 16-atom group. They are represented in table 1 as a continuous spectrum of frequencies stretching down to zero. We shall now proceed to justify and explain this entry in greater detail.

The translations of an atomic group within a crystal would necessarily tend to displace neighbouring atomic groups and hence would set up forces resisting the movement. We are therefore led to conclude that the degrees of freedom which do not appear as internal vibrations of our dynamic units would manifest themselves as internal vibrations in elementary volumes of larger dimensions. The larger such an element of volume is, the lower would be the limit of its possible

frequencies of vibration. Hence, the translations of our atomic groups would be associated with vibrational movements in the crystal whose frequencies extend from the upper limit set by the frequencies of their internal vibration down to very low values. In other words, the vibration spectrum of diamond with its discrete set of frequencies would be supplemented by a residual spectrum which is continuous and extends down to zero frequency.

We have now to determine how the modes of vibration referred to above are distributed with respect to frequency in the residual spectrum. Low frequencies arise from internal vibrations in volume elements of large size. The number of such elements included within the crystal diminishes rapidly with increase of their linear dimensions. It follows that the density of the vibrational modes in the residual spectrum would fall off quickly as their frequency diminishes.

## 4. The characters of the residual spectrum

The considerations set forth above may be put into a quantitative form. Consider an element of volume whose linear dimensions are $m$ times as great as that of our 16-atom group. The number of such groups included in the crystal being denoted by N, the number of elementary volumes whose linear dimensions are $m$ times greater would be $N/m^3$. The larger $m$ is, the lower would be the frequencies of internal vibration in the element under consideration. We denote by $v_m$, the lowest of these frequencies. If $m$ be replaced by $n$, the corresponding number of volume elements would be $N/n^3$ and the lower limit of frequency would be denoted by $v_n$. Thus the part of the vibration spectrum included between $v_m$ and $v_n$ may be ascribed to $3N(1/m^3 - 1/n^3)$ oscillators. It is evident that $v_m$ and $v_n$ would depend on the linear dimensions of the oscillators, and if we assume that $v_m = f/m$, and $v_n = f/n$, where $f$ is a quantity having the dimensions of a frequency, we find that the spectral region between $v_m$ and $v_n$ would be associated with $3N(v_m^3 - v_n^3)/f^3$ oscillators. In the limit as $m$ approaches $n$, we may write $v_m - v_n = dv$ and $(v_m^3 - v_n^3) = 3v^2 dv$. Thus, the 3N available degrees of freedom would be distributed over the spectrum as indicated by the quantity $3N \cdot 3v^2 dv/f^3$. Integrating this over the entire range of the continuous spectrum, we should regain 3N. Thus, we find $f$ to be the upper limit of the continuous spectrum, its lower limit being zero.

The law of distribution of frequencies in the residual spectrum thus determined rests on the assumption that the frequencies of vibration of the volume elements considered are inversely proportional to their linear dimensions. This assumption is certainly valid when the oscillators are of sufficiently large dimensions. But it should be remarked that the distribution formula deduced on the basis of the assumption shows quite clearly that the great majority of the oscillators which contribute sensibly to the thermal energy are not much larger in size than our 16-atom groups. A further remark which should also be made is that we do not distinguish between the different possible modes of vibration of the volume

elements, as for example, whether the vibrations are of the compressional or of the distortional type.

We have next to determine the value which should be assumed to be the upper limit of frequency in the residual spectrum. Since the spectrum owes its origin to the translatory movements of our 16-atom groups, the highest frequency appearing in it cannot exceed the lowest of the discrete frequencies of internal vibration of those groups which is $624 \, cm^{-1}$. We may, therefore, provisionally assume $624 \, cm^{-1}$ to be also the upper limit at which the frequency distribution derived on the basis of our assumptions abruptly terminates. It is clear that the entire procedure is a simplification adopted to enable us to evaluate the atomic heat of diamond over the entire range of temperature in terms of well known functions of which the tabulated values are available. We shall later consider the amendments needed to bring it into closer accord with the facts.

## 5. The experimental data

The graph depicting the variation of the atomic heat of diamond with temperature consists of three parts. The first part appears in the low temperature range between 0° and 100° K. In this range, the atomic heat is very small, being only a few units in the second decimal place. In the second range which lies between 100° and 300° K the atomic heat rises steeply, reaching a value of about 1·5 at room temperature. The third part of the range extends from 300° K to the highest temperatures for which the experimental data are available. It is to be noted that even at 1000° K, the atomic heat is only about 5, in other words distinctly smaller than the theoretical limit of 5·94.

The measurements of H F Weber already referred to (*Philos. Mag.* **49**, 161 (1875)) showed clearly that the atomic heat of diamond falls off rapidly as the temperature is lowered, and that *per contra*, it increases as the temperature is raised but not so quickly, the graph of the variation showing a point of inflexion at about 400° K. More complete and accurate data than those of Weber in the temperature range from 275° K to 1000° K are available from the determinations by Magnus and Hodler (*Ann. Phys. (Leipzig)*, **80**, 808 (1926)). In the lower ranges of temperature, measurements have been made by K S Pitzer (*J. Chem. Phys.* **6**, 68 (1938)), by De Sorbo (*ibid.*, **21**, 876 (1953)), and most recently by Desnoyers and Morrison (*Philos. Mag.*, **3**, 42 (1958)). In the temperature range between 100° K and 300° K the measurements by these authors are in fair agreement with each other. But in the low temperature range between 0° K and 100° K where the atomic heat is very low and the measurements are therefore more difficult, there are considerable discrepancies between them. In the comparison between theory and experiment which will be made in the present memoir, we shall make use exclusively of the data of Desnoyers and Morrison, as these cover the entire range between 0° K and 278° K at short intervals. For the higher temperatures, the data

reported by Magnus and Hodler are utilized. The experimental data of these authors are presented in a summarised form in tables 2 and 3 below.

**Table 2.** Interpolated experimental values of atomic heats by Desnoyers and Morrison.

| Temperature | 20° K | 30° K | 40° K | 50° K | 60° K | 70° K | 80° K | 90° K | 100° K |
|---|---|---|---|---|---|---|---|---|---|
| Atomic heat | 0·00034 | 0·00117 | 0·00285 | 0·00564 | 0·01004 | 0·01676 | 0·02635 | 0·04030 | 0·05832 |

| Temperature | 120° K | 140° K | 160° K | 180° K | 200° K | 220° K | 240° K | 260° K |
|---|---|---|---|---|---|---|---|---|
| Atomic heat | 0·1115 | 0·1893 | 0·2915 | 0·4172 | 0·5624 | 0·7271 | 0·9050 | 1·0957 |

**Table 3.** Experimental values of atomic heats by Magnus and Hodler.

| Temperature | 300° K | 400° K | 500° K | 600° K | 700° K | 800° K | 900° K | 1000° K |
|---|---|---|---|---|---|---|---|---|
| Atomic heat | 1·522 | 2·417 | 3.162 | 3·771 | 4·255 | 4·625 | 4·890 | 5·059 |

It is obvious that the data covering such a great range of temperature and presenting such enormous variations in the quantity measured offer a most stringent test for the theory. As has been already remarked, the evaluation of the atomic heats is based entirely on the spectroscopically determined vibration frequencies, and no use is made of any other data or arbitrary constants. It is not possible to present the comparison between the results of the theoretical computation and the experimental data with the aid of only a single graph. In the lowest part of the temperature range, such a graph would be nearly coincident with the axis along which the temperature is plotted. Even in the second part of the temperature range, the ordinates would have to be presented on a large scale for a satisfactory comparison to be possible. Accordingly, the comparison is here made in three separate figures. Figure 1 below exhibits the over-all agreement between theory and experiment, the data for the entire range of temperatures being represented on a suitable scale. In figure 2, the data for the temperature range between 0° K and 160° K are presented, a much larger scale being adopted for the ordinates. In figure 3, the temperature range between 160° K and 300° K is similarly covered, but with the ordinates drawn on a less highly enlarged scale.

## 6. Computation of the atomic heats

The procedure adopted for the evaluation of the atomic heat will be evident from tables 4, 5 and 6 where the calculations are shown in detail. The Einstein functions which give the atomic heat in terms of the characteristic frequencies and the absolute temperature are multiplied by their respective degeneracies and divided by 48. These are entered in the tables. The contribution of the residual
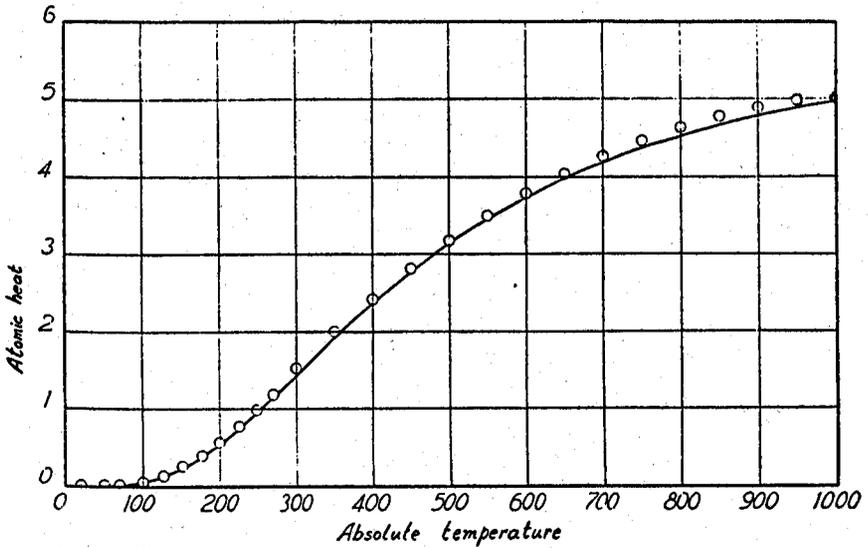
**Figure 1.** Comparison of calculated and observed atomic heats.
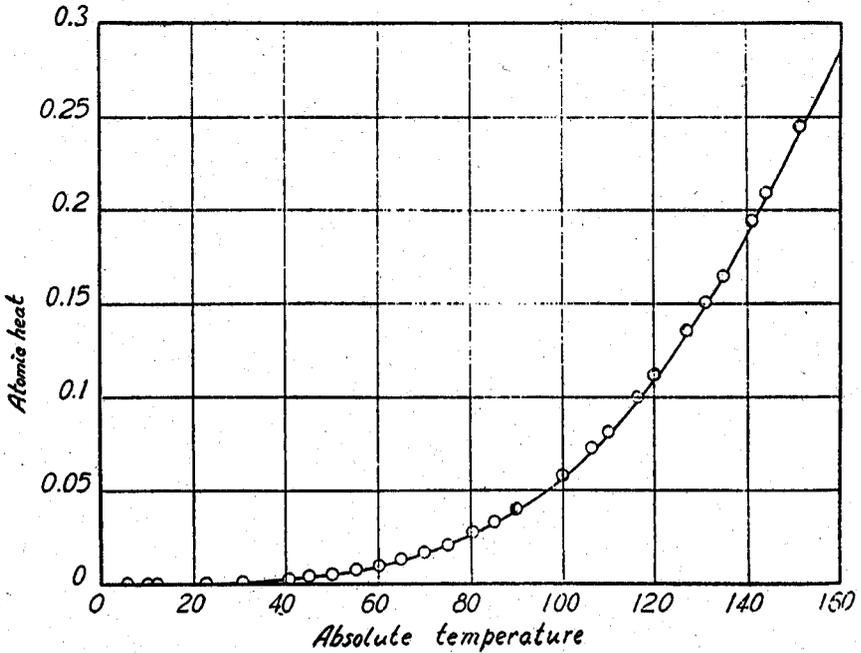Calculated atomic heats————. Experimental data ○○○○.



**Figure 2.** Comparison of calculated and observed atomic heats.
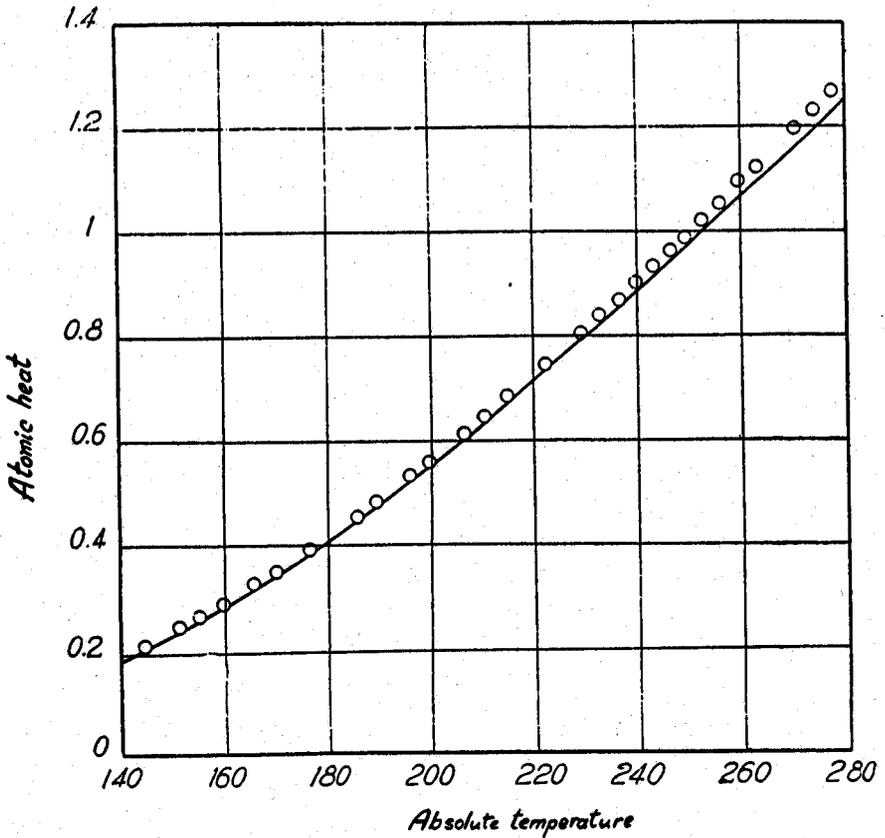Calculated atomic heats————. Experimental data ○ ○ ○ ○.

Figure 3. Comparison of calculated and observed atomic heats.
Calculated atomic heats————. Experimental data ○○○○.

spectrum to the atomic heat at the respective temperatures is entered below those of the discrete frequencies. This contribution is obtained by an integration of the Einstein function multiplied by the weight-factor given by the distribution law over the whole range of frequencies appearing in the residual spectrum. The final result is divided by 48 as in the case of the discrete frequencies. It is then added to the contribution of the discrete frequencies of vibration to the atomic heat at each of the temperatures listed in the table.

It will be seen from tables 4, 5 and 6 that in the lowest part of the temperature range between 0° K and 100° K the atomic heat is determined entirely or principally by the contribution of the residual spectrum of frequencies, the discrete frequencies being altogether too high to be thermally excited. In the second part of the temperature range between 100° K and 300° K the energy of vibration associated with the discrete frequencies rapidly mounts up with rising

**Table 4.** Computation of the atomic heats.

|  | 20° K | 30° K | 40° K | 50° K | 60° K | 70° K | 80° K | 90° K | 100° K |
|---|---|---|---|---|---|---|---|---|---|
| $3E_1(1332)$ | — | — | — | — | — | — | — | — | — |
| $8E_2(1273)$ | — | — | — | — | — | — | — | — | — |
| $6E_3(1219)$ | — | — | — | — | — | — | — | — | — |
| $4E_4(1176)$ | — | — | — | — | — | — | — | — | — |
| $3E_5(1087)$ | — | — | — | — | — | — | — | — | — |
| $3E_6(1087)$ | — | — | — | — | — | — | — | — | — |
| $4E_7(1010)$ | — | — | — | — | — | — | — | — | — |
| $6E_8(746)$ | — | — | — | — | — | — | 0·0002 | 0·0006 | 0·0016 |
| $8E_9(624)$ | — | — | — | — | — | 0·0004 | 0·0014 | 0·0041 | 0·0092 |
| $3D(624)$ | 0·0003 | 0·0011 | 0·0025 | 0·0048 | 0·0084 | 0·0132 | 0·0195 | 0·0273 | 0·0367 |
| Atomic heat | 0·0003 | 0·0011 | 0·0025 | 0·0048 | 0·0084 | 0·0136 | 0·0211 | 0·0320 | 0·0475 |

**Table 5.** Computation of the atomic heats.

|  | 120° K | 140° K | 160° K | 180° K | 200° K | 220° K | 240° K | 260° K | 280° K |
|---|---|---|---|---|---|---|---|---|---|
| $3E_1(1332)$ | — | 0·0001 | 0·0003 | 0·0009 | 0·0021 | 0·0043 | 0·0074 | 0·0118 | 0·0174 |
| $8E_2(1273)$ | — | 0·0003 | 0·0012 | 0·0035 | 0·0079 | 0·0153 | 0·0259 | 0·0402 | 0·0578 |
| $6E_3(1219)$ | 0·0001 | 0·0004 | 0·0014 | 0·0036 | 0·0082 | 0·0151 | 0·0248 | 0·0373 | 0·0527 |
| $4E_4(1176)$ | 0·0001 | 0·0004 | 0·0013 | 0·0033 | 0·0069 | 0·0121 | 0·0200 | 0·0295 | 0·0408 |
| $3E_5(1087)$ | 0·0001 | 0·0006 | 0·0018 | 0·0043 | 0·0084 | 0·0143 | 0·0220 | 0·0312 | 0·0419 |
| $3E_6(1087)$ | 0·0001 | 0·0006 | 0·0018 | 0·0043 | 0·0084 | 0·0143 | 0·0220 | 0·0312 | 0·0419 |
| $4E_7(1010)$ | 0·0003 | 0·0015 | 0·0042 | 0·0092 | 0·0170 | 0·0275 | 0·0405 | 0·0554 | 0·0721 |
| $6E_8(746)$ | 0·0071 | 0·0190 | 0·0384 | 0·0646 | 0·0966 | 0·1311 | 0·1684 | 0·2042 | 0·2402 |
| $8E_9(624)$ | 0·0289 | 0·0632 | 0·1094 | 0·1634 | 0·2219 | 0·2799 | 0·3374 | 0·3905 | 0·4401 |
| $3D(624)$ | 0·0587 | 0·0838 | 0·1096 | 0·1347 | 0·1584 | 0·1796 | 0·1992 | 0·2162 | 0·2313 |
| Atomic heat | 0·0954 | 0·1699 | 0·2694 | 0·3918 | 0·5358 | 0·6935 | 0·8676 | 1·0475 | 1·2362 |

**Table 6.** Computation of the atomic heats.

|  | 300° K | 400° K | 500° K | 600° K | 700° K | 800° K | 900° K | 1000° K |
|---|---|---|---|---|---|---|---|---|
| $3E_1(1332)$ | 0.0240 | 0·0692 | 0·1201 | 0·1658 | 0·2029 | 0·2327 | 0·2560 | 0·2747 |
| $8E_2(1273)$ | 0·0782 | 0·2104 | 0·3516 | 0·4713 | 0·5703 | 0·6460 | 0·7054 | 0·7501 |
| $6E_3(1219)$ | 0·0700 | 0·1764 | 0·2844 | 0·3760 | 0·4465 | 0·5017 | 0·5426 | 0·5757 |
| $4E_4(1176)$ | 0·0536 | 0·1371 | 0·2020 | 0·2617 | 0·3080 | 0·3436 | 0·3696 | 0·3902 |
| $3E_5(1087)$ | 0·0530 | 0·1157 | 0·1712 | 0·2147 | 0·2466 | 0·2713 | 0·2895 | 0·3029 |
| $3E_6(1087)$ | 0·0530 | 0·1157 | 0·1712 | 0·2147 | 0·2466 | 0·2713 | 0·2895 | 0·3029 |
| $4E_7(1010)$ | 0·0896 | 0·1785 | 0·2518 | 0·3069 | 0·3482 | 0·3773 | 0·3986 | 0·4159 |
| $6E_7(746)$ | 0·2746 | 0·4159 | 0·5086 | 0·5709 | 0·6119 | 0·6398 | 0·6589 | 0·6764 |
| $8E_9(624)$ | 0·4862 | 0·6552 | 0·7589 | 0·8219 | 0·8643 | 0·8924 | 0·9128 | 0·9269 |
| $3D(624)$ | 0·2449 | 0·2911 | 0·3173 | 0·3326 | 0·3426 | 0·3491 | 0·3540 | 0·3573 |
| Atomic heat | 1·4271 | 2·3652 | 3·1371 | 3·7365 | 4·1879 | 4·5252 | 4·7769 | 4·9730 |

temperature, while on the other hand, the contribution of the residual spectrum increases less rapidly; it progressively approaches its limiting value which is 1/16th of the theoretical limit for the total atomic heat.

We may here make some remarks on the comparison between the results of theory and experiment exhibited in figure 1. While there is an excellent overall agreement, divergences of a few per cent appear at temperature above 600°. The origin of these discrepancies is not far to seek. The characteristic frequencies used are those determined with the diamond held at room temperature. The changes in these frequencies which manifest themselves as the temperature is raised are small but are by no means negligible. For example, the highest frequency which is 1332 cm$^{-1}$ at ordinary temperatures goes down to 1318 cm$^{-1}$ at 1000°. The change is evidently associated with the thermal expansion of the crystal and it is to be expected that all the characteristic frequencies would likewise be diminished by small percentages. The atomic heats if calculated on the basis of the diminished frequencies would necessarily be greater. In view, however, of the uncertain accuracy of the experimental data at a higher temperatures, this matter will not be further pursued here.

## 7. The low temperature specific heats

A comparison of the figures in tables 2 and 4 shows that at the very lowest temperatures, the computed and observed atomic heats are in good agreement with each other. Disagreements however appear at higher temperatures, the calculated values being distinctly smaller than the observed ones. The percentage

Table 7. Re-computation of theoretical atomic heats.

| Temperature | 20° K | 30° K | 40° K | 50° K | 60° K | 70° K | 80° K | 90° K | 100° K |
|---|---|---|---|---|---|---|---|---|---|
| 3D(575) | 0·0004 | 0·0014 | 0·0032 | 0·0062 | 0·0106 | 0·0168 | 0·0247 | 0·0343 | 0·0456 |
| Atomic heat | 0·0004 | 0·0014 | 0·0032 | 0·0062 | 0·0106 | 0·0172 | 0·0263 | 0·0390 | 0·0564 |

| Temperature | 120° K | 140° K | 160° K | 180° K | 200° K | 220° K | 240° K | 260° K | 280° K |
|---|---|---|---|---|---|---|---|---|---|
| 3D(575) | 0·0713 | 0·0992 | 0·1270 | 0·1530 | 0·1769 | 0·1981 | 0·2162 | 0·2326 | 0·2467 |
| Atomic heat | 0·1081 | 0·1853 | 0·2868 | 0·4101 | 0·5543 | 0·7123 | 0·8846 | 1·0639 | 1·2516 |

| Temperature | 300° K | 400° K | 500° K | 600° K | 700° K | 800° K | 900° K | 1000° K |
|---|---|---|---|---|---|---|---|---|
| 3D(575) | 0·2592 | 0·3017 | 0·3246 | 0·3383 | 0·3468 | 0·3525 | 0·3566 | 0·3594 |
| Atomic heat | 1·4414 | 2·3758 | 3·1444 | 3·7422 | 4·1921 | 4·5286 | 4·7795 | 4·9751 |

differences are greatest at about 100° K and become smaller at higher temperatures. It is evident that these discrepancies arise from the assumption made in our calculations that the upper limit of frequency in the residual spectrum is the same as the lowest of the discrete frequencies of vibration, viz., 624 cm$^{-1}$. That a somewhat smaller value for the limit should be assumed as the basis of the calculation is indicated by various considerations, including especially the evidence furnished by studies on the blue luminescence spectra of diamond held at liquid-air temperatures. The vibration spectrum of diamond manifests itself in these spectra in combination with the electronic transition giving rise to the luminescence and it is noticed that there is a large and sudden drop in its intensity at a point distant about 575 cm$^{-1}$ from the electronic transition. There is some justification therefore for taking 575 cm$^{-1}$ instead of 624 cm$^{-1}$ as the upper limit of frequency in the residual spectrum.

In figures 2 and 3, a comparison is made of the experimental data with the theoretical computed atomic heats in the lower ranges of temperature, viz., from 0° to 160° A and from 140° to 280° A, the observational values being those of Desnoyers and Morrison, and the theoretical values being those recalculated taking 575 cm$^{-1}$ to be the upper limit of frequency in the residual spectrum, as shown in table 7. The agreement now obtained between the calculated and observed atomic heats is satisfactory. It is especially good in figure 2.