

EVALUATION OF THE SPECIFIC HEAT OF DIAMOND FROM ITS RAMAN FREQUENCIES

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1. INTRODUCTION

THE case of diamond has played a historic role in the development of the theory of specific heats of crystalline solids. Weber in 1875 discovered that the specific heat of diamond shows large variations with temperature, falling off and tending towards small values when the temperature is lowered and on the other hand increasing when it is raised, and tending towards the limiting value given by Dulong and Petit's law, above $1,000^{\circ}\text{C}$. The specific heat of diamond has been further investigated by various authors in more recent times. It will suffice here to mention the work of Magnus and Hodler (1926) which covers the range $273^{\circ}\text{--}1,100^{\circ}\text{K}$ at intervals of 50° and that of Pitzer (1938) who made a series of determinations in the low temperature range between 70°K and 300°K .

In his celebrated paper introducing the quantum theory of specific heats, Einstein (1907) showed that Weber's data are in fair accord with a specific heat curve calculated on the assumption that the carbon atoms in diamond have a single vibration frequency corresponding to an infra-red wavelength of 11μ . Subsequently, when more precise experimental data became available, other attempts were made to fit them into a specific heat formula based on different assumptions regarding the nature of the vibration spectrum of diamond. It cannot be said that any of these theories has been really successful in explaining the observed facts. The best-known amongst these theories is that due to Debye. Pitzer found that the variations of the specific heat in the range of temperatures examined by him could not be fitted into a single expression of the Debye type. He calculated the "characteristic temperatures" from the observed specific heat at 70.16° , 125.28° and 231.06°K and found them as 1930° , 1874° and 1817°K respectively. Reversing the process and calculating the specific heat from these different values, it will be seen from the figures in Table I below that the calculated and observed specific heats differ from each other by as much as 10% to 20%.

To possess real significance, a specific heat formula should be based on *independent* knowledge of the vibration spectrum of the substance under study. Fortunately, in the case of diamond, such knowledge has come to hand from spectroscopic investigations by several different methods. The most precise data are those derived from Raman effect studies. It is proposed in the present paper to present calculations of the specific heat of diamond made on the basis of the spectroscopically known vibration frequencies of the structure of the crystal.

TABLE I

| Temp.° K | Calc. C_v $\theta = 1930$ | Calc. C_v $\theta = 1874$ | Calc. C_v $\theta = 1817$ | Observed C_v |
|----------|--------------------------------|--------------------------------|--------------------------------|-------------------|
| 70.16 | 0.0224 | 0.0244 | 0.0268 | 0.0224 |
| 125.28 | 0.127 | 0.138 | 0.152 | 0.138 |
| 231.06 | 0.738 | 0.796 | 0.858 | 0.858 |

2. THE VIBRATION SPECTRUM OF DIAMOND

Many investigations have been made on the Raman effect in diamond. It will suffice here to mention the early work of C. Ramaswamy (1930) and the latest investigations of R. S. Krishnan (1947) and P. S. Narayanan (1951). C. Ramaswamy discovered the first order spectrum which consists of a single intense sharp line of frequency shift 1332 cm.^{-1} , while the latter authors have found a series of intense and sharp lines and interpreted them as the overtones and combinations of the fundamental vibration frequencies. The basis for this interpretation is the theory of lattice dynamics put forward by Sir C. V. Raman (1943, 1947). Exact expressions for the frequencies of the modes of vibration indicated by the theory have been found and evaluated by K. G. Ramanathan (1947). They give data in satisfactory accord with the experimentally observed frequencies. These are eight in number and have the following values expressed in wave numbers; their respective degeneracies indicated by the theory are shown enclosed in brackets.

$$1332 (3), 1250 (8), 1232 (6), 1149 (4), \\ 1088 (6), 1008 (4), 752 (6), 620 (8).$$

Totalling the numbers appearing within brackets, we account for 45 out of the 48 degrees of freedom of the 16 atoms contained in eight contiguous cells of the crystal structure. The remaining three degrees of freedom refer respectively to the three translations of the group of 16 atoms and are identifiable with the movements of the volume element containing this group and associated with vibrations of the elastic solid type.

If N be the number of atoms in the atomic volume V of the crystal, the degrees of freedom associated with the elastic modes of vibration are thus $\frac{3N}{16}$ in number. We assume these to be equally distributed over the three classes of elastic wave-patterns possible in a crystal. It is necessary to determine how these degrees of freedom are distributed over the possible frequency range in each case. The modes of stationary elastic vibration as well as their frequencies would evidently depend upon the velocities of wave-propagation in different directions. For the purpose of our calculations, we shall assume that the frequency distribution for each of the three classes of waves is the same as for an isotropic solid in which the velocity of propagation is the mean velocity obtained by averaging over all possible directions within the crystal.

3. EVALUATION OF THE SPECIFIC HEAT

The limiting frequency ν_i ($i = 1, 2, 3$) for the longitudinal and the two transverse waves is given by $\nu_i = \left(\frac{3N}{64\pi V}\right)^{\frac{1}{3}} W_i$, where W_i is the average velocity of the particular type of wave. Therefore the specific heat is given by

$$C_v = 3R \sum_1^8 \sigma_s E\left(\frac{h\nu_s}{kT}\right) + \frac{3R}{48} \sum_{i=1,2,3} D\left(\frac{h\nu_i}{kT}\right),$$

where E and D are respectively the Einstein and Debye functions, σ_s the weight factor for frequency ν_s , which can be obtained from the degeneracy.

The velocities in the 26 directions given by the six cubic, eight octahedral and twelve dodecahedral directions are taken and the average for each type of the waves is found. The velocities in these directions can be obtained from the well-known cubic equation in terms of the elastic constants which have been evaluated by the present author (1951), and the following values are found for ν_1 , ν_2 and ν_3 .

$$\nu_1 = 824 \text{ cm.}^{-1}; \quad \nu_2 = 497 \text{ cm.}^{-1}; \quad \nu_3 = 455 \text{ cm.}^{-1}$$

4. THE SPECIFIC HEAT AT LOW TEMPERATURES

Table II shows the specific heat calculated by the present method and compared with the experimental results of Pitzer. Pitzer himself states that his experimental values may be in error by as much as 5% at the lowest of temperatures and that the possible errors are quite small at about 150° K, but might again be larger towards the upper end of the temperature range. It is noticed also that in the latter part of the range, several of Pitzer's observational points fall out of the smooth graph reproduced in his paper by 1% or more. Examined in the light of these remarks, the differences

TABLE II

| Temp. ° K | Optical frequencies | Elastic spectrum | Total C_v | Observed C_v | Percentage Difference |
|-----------|---------------------|------------------|-------------|----------------|-----------------------|
| 70.16 | 0.0005 | 0.0224 | 0.0229 | 0.0224 | +2.2 |
| 75.37 | 0.0010 | 0.0273 | 0.0283 | 0.0296 | -4.4 |
| 81.59 | 0.0024 | 0.0338 | 0.0362 | 0.0362 | 0 |
| 88.65 | 0.0048 | 0.0418 | 0.0466 | 0.0452 | +3.1 |
| 96.68 | 0.0096 | 0.0517 | 0.0613 | 0.0592 | +3.5 |
| 105.1 | 0.0165 | 0.0625 | 0.0790 | 0.0785 | +0.6 |
| 113.04 | 0.0282 | 0.0732 | 0.1014 | 0.0991 | +2.3 |
| 125.28 | 0.052 | 0.090 | 0.142 | 0.138 | +2.9 |
| 134.29 | 0.076 | 0.102 | 0.178 | 0.174 | +2.3 |
| 144.1 | 0.107 | 0.115 | 0.222 | 0.218 | +1.8 |
| 153.71 | 0.144 | 0.128 | 0.272 | 0.267 | +1.9 |
| 162.76 | 0.185 | 0.139 | 0.324 | 0.318 | +1.9 |
| 173.33 | 0.237 | 0.152 | 0.389 | 0.386 | +0.8 |
| 181.96 | 0.286 | 0.161 | 0.447 | 0.444 | +0.7 |
| 191.44 | 0.330 | 0.172 | 0.502 | 0.518 | -3.1 |
| 200.94 | 0.405 | 0.182 | 0.587 | 0.595 | -1.3 |
| 211.84 | 0.481 | 0.193 | 0.674 | 0.685 | -1.6 |
| 231.06 | 0.628 | 0.210 | 0.838 | 0.858 | -2.3 |
| 241.09 | 0.709 | 0.218 | 0.927 | 0.918 | -1.0 |
| 252.37 | 0.804 | 0.227 | 1.031 | 1.033 | -0.2 |
| 264.31 | 0.907 | 0.236 | 1.143 | 1.137 | +0.5 |
| 276.61 | 1.016 | 0.244 | 1.260 | 1.257 | +0.2 |
| 287.96 | 1.105 | 0.251 | 1.356 | 1.355 | +0.1 |

between the observed and calculated values, which are shown as a percentage in the last column of Table II are not larger than might reasonably be expected. It may therefore be claimed that the theory gives a satisfactory account of the facts. This agreement is all the more significant when it is remembered that the theoretical calculations are completely independent and do not make use of the specific heat data themselves.

Table III shows the calculation of the specific heat on the lines indicated by Dayal (1944), in which the acoustic spectrum is represented by one single

TABLE III

| Temp. ° K | Optical Frequencies | Elastic Spectrum | Total C_v | Observed C_v | Percentage Difference |
|-----------|---------------------|------------------|-------------|----------------|-----------------------|
| 70.16 | 0.0005 | 0.0230 | 0.0235 | 0.0224 | +4.9 |
| 81.59 | 0.0024 | 0.0349 | 0.0373 | 0.0362 | +3.0 |
| 105.1 | 0.0165 | 0.0668 | 0.0833 | 0.0785 | +6.1 |
| 125.28 | 0.0519 | 0.0975 | 0.1494 | 0.1380 | +8.3 |
| 162.8 | 0.1845 | 0.1540 | 0.3385 | 0.3180 | +6.5 |

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cut-off frequency at 525 cm.^{-1} which was calculated after finding the mean velocity according to the interpolation method due to Hopf and Lechner (1914). The agreement with the experimentally observed values is seen to be much less satisfactory than in Table II.

5. THE SPECIFIC HEAT AT HIGH TEMPERATURES

Table IV gives the calculated values compared with the experimental values of Magnus and Hodler. Here again, the theory gives results in excellent agreement with the observations over the whole range of temperature

TABLE IV

| Temp. ° K | Optical Frequencies | Elastic Spectrum | Total C_v | Observed C_v | Percentage Difference |
|-----------|------------------------|---------------------|-------------|----------------|--------------------------|
| 273 | 0.984 | 0.241 | 1.225 | 1.252 | -2.2 |
| 300 | 1.217 | 0.258 | 1.475 | 1.520 | -3.0 |
| 350 | 1.688 | 0.281 | 1.969 | 1.985 | -0.8 |
| 400 | 2.128 | 0.298 | 2.426 | 2.411 | +0.6 |
| 450 | 2.526 | 0.312 | 2.838 | 2.798 | +1.4 |
| 500 | 2.883 | 0.322 | 3.205 | 3.149 | +1.8 |
| 550 | 3.191 | 0.330 | 3.521 | 3.465 | +1.6 |
| 600 | 3.460 | 0.336 | 3.796 | 3.749 | +1.3 |
| 650 | 3.686 | 0.341 | 4.027 | 3.999 | +0.7 |
| 700 | 3.890 | 0.345 | 4.235 | 4.222 | +0.3 |
| 750 | 4.065 | 0.348 | 4.413 | 4.414 | -0.02 |
| 800 | 4.216 | 0.351 | 4.567 | 4.580 | -0.3 |
| 850 | 4.342 | 0.353 | 4.695 | 4.717 | -0.5 |
| 900 | 4.452 | 0.355 | 4.807 | 4.833 | -0.5 |
| 950 | 4.557 | 0.357 | 4.914 | 4.923 | -0.2 |
| 1000 | 4.646 | 0.358 | 5.004 | 4.992 | +0.2 |
| 1050 | 4.724 | 0.359 | 5.083 | 5.030 | +1.05 |
| 1100 | 4.794 | 0.361 | 5.155 | 5.060 | +1.9 |

from 350° K to 1100° K . At the two lowest temperatures (273° and 300° K) there is a sensible discrepancy, but on a comparison of the data of Magnus and Hodler with those of Pitzer in the region where they overlap, it becomes clear that such discrepancy arises from errors in the experimental data.

Though the eight fundamental vibration frequencies show a sensible variation with temperature, such variation does not noticeably influence the calculated values of the specific heat, especially at the lower temperatures. A calculation made for the temperature 900° K taking such variations into account gives C_v as 4.831, while the values obtained without taking it into account is 4.807.

In conclusion, the author expresses his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for suggesting this problem and the inspiring guidance that he gave during the course of this investigation.

6. SUMMARY

The specific heat of diamond is evaluated from the knowledge of its vibration spectrum obtained principally from Raman effect studies. The vibration spectrum is known to consist of eight discrete monochromatic frequencies followed by a continuous spectrum of elastic vibrations. Accordingly, the specific heat is expressed as the sum of eight Einstein functions, supplemented by three Debye functions representing respectively the three types of elastic vibration possible in the crystal. A close agreement is found between the calculated and the experimental values over the entire range of temperatures between 70° K and 1100° K, which is all the more significant in view of the calculations being completely independent of the specific heat data themselves.

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