THE THEORY OF THE SPECIFIC HEAT OF SOLIDS

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§ 1. INTRODUCTION

THE specific heat of a substance under given external conditions (denoted by x) is defined by $c_x = (dQ/dT)_x$, i.e. the ratio of the heat, added to a gram of the substance, to the temperature rise. In most cases the specific heat is measured at constant pressure (c_p) and at constant volume (c_v). When experiments yield c_p, as is the case in solids, this can be converted to c_v by means of the general thermodynamical relation

$$c_p - c_v = 9\alpha^2 VT/\kappa,$$

where α is the coefficient of linear expansion, V the specific volume, κ the compressibility, and T the absolute temperature.

This conversion is necessary because the theory gives specific heats, or rather heat capacities, per gram molecule at constant volume. It is usual, in theoretical considerations, to ignore the expansion of the solid and the consequent changes in elastic properties; this neglect involves only small errors (probably of a few per cent (Kellermann, 1941)), and can be remedied if the accuracy of the theory should warrant it.

Historically, the theory of heat capacities falls into two distinct parts: (*a*) classical theory, which yielded a constant heat capacity per gram molecule of $3\boldsymbol{R}$(where $\boldsymbol{R}$ is the gas constant per gram molecule), and (*b*) quantum theory, due in the first instance to Einstein (1907), and given a more complete form by Debye (1912), Born and v. Kármán (1912), and Born (1923). The full implications of the crystal theory of Born have, however, been worked out only recently (Blackman, 1935-7; Kellermann, 1941), and this has thrown some light on the more detailed properties of the heat capacity shown by experiments at low temperatures.

From the point of view of classical theory the rather complex problem of dealing with a large number of particles bound together to form a solid presented little difficulty. Since the solid is stable, the heat energy is simply the energy of a set of vibrating particles, the average value being $3N\boldsymbol{k}T$, (N is number of particles, $\boldsymbol{k}$ Boltzmann's constant and T the absolute temperature). Hence $C_v = 3N\boldsymbol{k}$, which is independent of temperature. This sufficed to explain the well-known law of Dulong and Petit—the atomic heat capacity at constant pressure is equal to 6·2 for a large number of substances. It did not explain the exceptions to the Dulong and Petit law, the low values for some substances, e.g. diamond at normal temperatures, or the low values obtained at liquid-air temperatures for substances obeying the Dulong and Petit law at high temperatures (Behn, 1898).

The solution to this difficulty was given in a fundamental paper by Einstein (1907), who applied the (then) new quantum theory of Planck to the motion of the particles of a solid, i.e. he replaced the classical mean energy for a linear oscillator $\bar{\epsilon} = \boldsymbol{k}$ by the expression $\bar{\epsilon} = \boldsymbol{h}\nu/\{\exp.(\boldsymbol{h}\nu/\boldsymbol{k}T) - 1\}$, where ν is the frequency of oscillation and $\boldsymbol{h}$ is Planck's constant. The general problem was idealized by assuming every particle in the solid to vibrate with a single frequency, and the heat capacity for N particles then assumes the form

$$C_v = 3N \frac{d}{dT}\left(\frac{\boldsymbol{h}\nu}{e^{\frac{\boldsymbol{h}\nu}{\boldsymbol{k}T}} - 1}\right) = 3N\boldsymbol{k}\left(\frac{\boldsymbol{h}\nu}{\boldsymbol{k}T}\right)^2 \frac{e^{\frac{\boldsymbol{h}\nu}{\boldsymbol{k}T}}}{\left(e^{\frac{\boldsymbol{h}\nu}{\boldsymbol{k}T}} - 1\right)^2} = 3NE\left(\frac{\boldsymbol{h}\nu}{\boldsymbol{k}T}\right).$$

This formula fitted the experimental data for diamond very well (as far as these were known, i.e. down to liquid-air temperatures). Though the fundamental difficulties were now solved, the details of the motion of the particles were not solved, and no very accurate agreement with experiment could be expected.

As the Einstein theory indicates, it is essential to know more about the frequencies of vibrations of the solid. The general theory of the motion of a dynamically stable system of coupled particles shows that one can resolve the motion into a superposition of number of independent oscillations of the system (" normal vibrations "), there being $3N$ of these (more strictly, $3N-6$), if N is the number of particles in the system. Each of these normal vibrations will have a definite frequency. If these frequencies are known, the total heat capacity can immediately be determined, since it is simply the sum of the contributions due to the individual vibrations,

$$C_v = \sum_{\nu} E(\boldsymbol{h}\nu/\boldsymbol{k}T).$$

A strict proof of this relation can be given, using quantum statistics (*vide*, for instance, R. H. Fowler, *Statistical Mechanics*). Quantum theory adds the zero-point energy, $\frac{1}{2}\boldsymbol{h}\nu$, to the expression used by Einstein for the mean energy of a linear oscillator, but the expression for the heat capacity remains unaltered.

The above summation can be turned into an integral if we introduce a function $\rho(\nu)\Delta\nu$ giving the number of frequencies between ν and $\nu+\Delta\nu$; $\rho(\nu)$ represents the vibrational spectrum. In terms of $\rho(\nu)$, the heat capacity becomes

$$C_v = \int_0^{\nu_m} \rho(\nu) E(\boldsymbol{h}\nu/\boldsymbol{k}T) d\nu.$$

As regards the general features of the spectrum, one knows, firstly, that there is a lower limit which depends on the properties and dimensions of the crystal, but which is sufficiently low to be put equal to zero for the purpose of calculating the specific heat; secondly, there is a definite upper limit (ν_m)—the highest frequency with which the solid can vibrate—which depends on the binding forces in the solid and on the masses of the particles taking part in the vibration.

It follows that the heat capacity must be a continuously increasing function of the temperature, since the function E has this property; also, since $E(\boldsymbol{h}\nu/\boldsymbol{k}T)=\boldsymbol{k}$ when $\boldsymbol{h}\nu \ll \boldsymbol{k}T$, it follows that we obtain the classical form for C_v when $\boldsymbol{h}\nu \ll \boldsymbol{k}T$. The accurate description of specific-heat phenomena depends on a knowledge of the spectrum. It is, for this reason, instructive to consider the various theoretical approximations to the spectrum implicit in the different theories of specific heat.

Einstein's theory replaces the whole of the spectrum by a single line at a definite frequency (chosen to fit the experimental data), which will usually be in the neighbourhood of the maximum frequency.

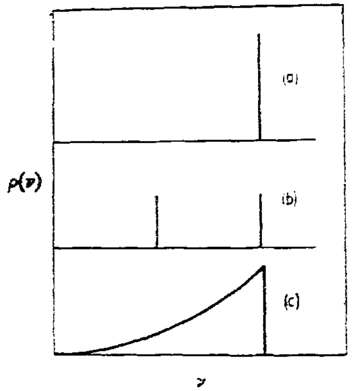

Figure 1. Vibrational spectra: (*a*) Einstein; (*b*) Nernst-Lindemann; (*c*) Debye. The same value has arbitrarily been chosen for the characteristic frequency in each of the cases (*a*), (*b*) and (*c*).

Einstein's specific-heat function proved rather unsatisfactory at low temperatures, and an empirical formula was put forward by Nernst and Lindemann (1911) in order to fit the results. This consisted in replacing the spectrum by two " lines " of equal weight, one at a frequency ν and one at $\nu/2$. This specific-heat function was very successful over a wide region of temperatures, though it failed at the lowest temperatures. It is rather a curious point that a theoretical justification for the Nernst-Lindemann spectrum is provided by recent work on the spectrum of cubic crystals (see figures 3, 4, 5).

The next step in the development of the theory was made almost at the same time by Debye (1912) and by Born and v. Kármán (1912). Debye showed that the function $\rho(\nu)$ was proportional to ν^2 in the region of low frequencies, where the theory of the solid could be replaced by that of an isotropic elastic continuum. An approximation to the spectrum was then obtained by continuing the ν^2 function up to a maximum frequency ν_D and cutting off the spectrum sharply at this point (figure 1). The cut-off ν_D is chosen so as to give the correct total number of vibrations ($3N$), i.e.,

$$\rho(\nu)=a\nu^2, \quad 0<\nu<\nu_D \quad \text{and} \quad \int_0^{\nu_D} a\nu^2 d\nu = 3N,$$

with

$$a=3V\frac{4\pi}{3}\left\{\left(\frac{(1+\sigma)\kappa\rho}{(1-\sigma)}\right)^{3/2}+2\left(\frac{2(1+\sigma)\kappa\rho}{3(1-2\sigma)}\right)^{3/2}\right\},$$

where V = volume of solid, ρ = density, κ = compressibility, σ = Poisson's ratio. From this it follows that

$$\begin{aligned} C_v &= a\int_0^{\nu_D} \nu^2 E(\boldsymbol{h}\nu/\boldsymbol{k}T)d\nu \\ &= 3N\boldsymbol{k}\left\{12\cdot\frac{T^3}{\theta^3}\int_0^{\theta/T}\frac{\zeta^3}{e^\zeta-1}d\zeta-\frac{3\,\theta/T}{e^{\theta/T}-1}\right\} \\ &= 3ND(\theta/T) \quad \text{with} \quad \theta=\boldsymbol{h}\nu_D/\boldsymbol{k}. \end{aligned}$$

The value of ν_D can be calculated from the elastic constants of the elastic continuum, since the value of the constant a is determined by these elastic constants.

The Debye formula has the following properties:

(*a*) the specific heat is determined by one parameter (θ/T);

(*b*) at low temperatures ($T<\theta/12$) the specific heat is proportional to T^3;

(*c*) at high temperatures the classical value of $3N\boldsymbol{k}$ is approached in the form

$$C_v=3N\boldsymbol{k}\left(1-\frac{1}{20}\frac{\theta^2}{T^2}\right).$$

As to the spectrum, it was reasonable to believe that a satisfactory approximation had been obtained, since the detailed solution for a linear chain showed a great similarity to the corresponding " continuum " spectrum—the main difference being the heaping up of vibrations in the neighbourhood of the maximum frequency. It was thought that this effect would be less prominent in the three-dimensional case.

Born and v. Kármán discussed, in their first paper, the calculation of the frequencies of the vibrations of a simple cubic lattice. The detailed spectrum was, however, not worked out at that time and an approximate spectrum was constructed in close analogy with the spectrum of the linear chain. The distribution function $\rho(\nu)$ has the form (ν_0 being the maximum frequency)

$$\rho(\nu)=\frac{72N}{\pi^3\nu_0}\frac{(\sin^{-1}(\nu/\nu_0))^2}{(1-\nu^2/\nu_0^2)^{\frac{1}{2}}},$$

which for small values of ν/ν_0 reduces to the ν^2 form. Both the spectrum and the resultant specific-heat function are rather more complicated than the corresponding Debye functions, without being superior in representing the results of experiments. The Born-v. Kármán function has accordingly receded into the background, but the general theory on which the approximate function was built up has become a part of the lattice theory of vibrations, which forms the basis of much of the recent work on the specific heat of crystals.

§ 2. EARLY WORK ON THE LATTICE THEORY OF SPECIFIC HEAT

The work of Born and v. Kármán was followed by a very interesting calculation by Thirring (1913, 14) on the specific heat of the cubic lattices dealt with by the former authors. Thirring showed that it was possible to work out the specific heat of these lattices at moderately high temperatures without working out the spectrum explicitly, and without any further approximations. The method is based on the following idea. If one writes the mean energy of a linear oscillator in the usual form,

$$\bar{\epsilon} = \tfrac{1}{2}\boldsymbol{h}\nu + \boldsymbol{k}T \frac{\boldsymbol{h}\nu/\boldsymbol{k}T}{\exp.(\boldsymbol{h}\nu/\boldsymbol{k}T) - 1},$$

and expands in powers of $\boldsymbol{h}\nu/\boldsymbol{k}T$, one obtains

$$\bar{\epsilon} = \boldsymbol{k}T\left(1 - \sum_{n=1}^{\infty} (-1)^n \frac{B_n}{(2n)!}\left(\frac{\boldsymbol{h}\nu}{\boldsymbol{k}T}\right)^{2n}\right),$$

where B_n are the Bernoulli numbers; the first four have the following values:

$$B_1 = \frac{1}{6}, \quad B_2 = \frac{1}{20}, \quad B_3 = \frac{1}{42}, \quad B_4 = \frac{1}{30}.$$

The heat capacity of the linear oscillator then becomes

$$C_v = \frac{d\bar{\epsilon}}{dT} = \boldsymbol{k}\left(1 - \frac{B_1}{2}\left(\frac{\boldsymbol{h}\nu}{\boldsymbol{k}T}\right)^2 + \ldots\right)$$

$$= \boldsymbol{k}\left(1 + \sum_{n=1}^{\infty} (-1)^n \frac{B_n(2n-1)}{(2n)!}\left(\frac{\boldsymbol{h}\nu}{\boldsymbol{k}T}\right)^{2n}\right).$$

If $\boldsymbol{h}\nu/\boldsymbol{k}T < 2\pi$, this is a convergent series containing terms depending on ν^2, ν^4, ν^6, etc.

In order to obtain the specific heat for a lattice, it is necessary to sum the expression for all the $3N$ frequencies of vibration of the lattice, i.e.,

$$C_v = \boldsymbol{k}\left(3N + \sum_{n=1}^{\infty} (-)^n \frac{B_n(2n-1)}{(2n)!}\left(\frac{\boldsymbol{h}}{\boldsymbol{k}T}\right)^n \sum_{\nu} \nu^{2n}\right).$$

Now the Born-v. Kármán treatment of the vibrations of a crystal lattice gave an expression for the frequencies in the form of a determinant involving ν^2. It is a relatively easy matter to work out $\sum_{\nu} \nu^{2n}$ from this determinant for small values of n, as was shown by Thirring, and so it was possible to work out fully the implications of the theory of the Born-v. Kármán model. Results were obtained for NaCl, KCl, FeS_2 and CaF_2 (Thirring, 1914) as exemplified in table 1.

Table 1

C_p (NaCl)			C_p (KCl)		
T° K.	Observed	Calculated	T° K.	Observed	Calculated
83·4	3·75	3·71	86	4·26	4·29
81·4	3·54	3·67	76·6	4·11	3·95
69·0	3·13	3·09	70·0	3·79	3·66
67·0	3·06	3·02	62·9	3·36	3·30

Thirring's method is completely general and can be applied to any crystal; it has hardly received the prominence it deserves, especially as it was, for about twenty years, the only calculation of specific heats which did not involve the usual approximations which obscure the whole of the effect of a crystal, i.e. a crystal as distinct from a continuum (in the Debye sense).

The development of the theory of specific heats from this point onwards was concerned with the mathematical rather than with the physical side. The general theory of the vibrations of a crystal was worked out by Born (see Born, 1923) following the earlier work of Born and v. Kármán (1913). It was shown that the vibrations of a crystal could be divided into $3s$ groups, where s is the number of particles in the unit cell of the crystal. Of these, three represent low-frequency (long wave-length) vibrations which in the limit become identical with the vibrations of an elastic continuum. These are termed *acoustical* vibrations and the remaining $3s-3$ *optical* vibrations, the frequencies of these latter vibrations being, as a rule, of the order of optical frequencies ($\sim 10^{13}$).

The general equations determining these frequencies were worked out for the case of central forces, but the determination of the spectrum was (and in most cases still remains) far too complex and laborious to be attempted; the specific heat was therefore given only in an approximate form. In the simplest formulation, each of the three acoustical groups of vibrations was represented by a Debye spectrum and the optical vibrations by single-line (Einstein) spectra; the specific heat then becomes

$$C_v = \sum_{j=1,2,3} D(\theta_j/T) + \sum_{j=4}^{3s} E(\theta_j/T).$$

The functions D and E are suitably normalized Debye and Einstein functions. In the case of monatomic crystals, in which the unit cell contains one particle, the above expression reduces to the terms with D only.

The values of θ_1, θ_2, θ_3 can be calculated from the elastic constants; in some cases the values of the optical frequencies can be obtained from absorption bands in the solid, though these are not necessarily accurate representations of the positions of the maxima in the spectra. The calculations can therefore be carried out in only a few cases, mainly for crystals of the alkali-halide type. These were made by Försterling (1920 b), who found good agreement with experiment in the cases of KCl, NaCl and CaF_2.

It should, however, be noted that in none of these is the agreement with experiment very much better than with a Debye formula, and that the initial approximations made to the spectrum are probably no closer in these cases than in the assumption of a Debye spectrum. The approximations involved can be seen in figure 2, in which the spectrum of a simple cubic lattice (Blackman, 1937) is given together with the representation as the sum of the three Debye spectra.

The main use of the general formula of Born lies in its indication of the way in which an approximate formula can be built up in the case of complicated crystals; this serves a very useful purpose in calculating the entropy of such crystals. An outstanding example of a representation on these lines is the specific-heat curve of benzene (Andrews, D. H.; *cf.* Eucken, 1929).

Some calculations on simple crystals at high temperatures were also made by Försterling (1920 a, c) using the method of Thirring. The equations for the frequency of the vibrations were, however, those of the continuum and not those of the crystal lattice, so that there is no real advantage as compared with the Debye theory.

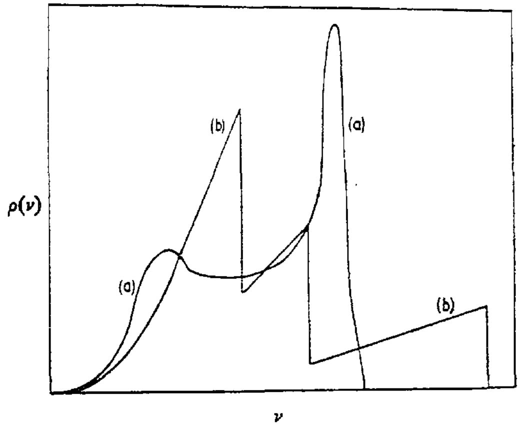

Figure 2. Vibrational spectrum of a cubic lattice, curve (*a*), together with the representation of the spectrum as a sum of three Debye spectra, curve (*b*), obtained from the low-frequency end of the spectrum.

A rather different approach to the representation of the specific heat of complicated crystals (which show a deviation from Debye theory) was made by Lewis and Gibson (1917). The specific-heat curve was fitted with a function $D(\theta^n/T^n)$, where n is an empirical constant. Some success was obtained, as is to be expected with two parameters instead of one, but there does not seem to be any theoretical justification for the form of the function.

§ 3. LATTICE THEORY AND SPECIFIC HEATS AT LOW TEMPERATURES

Although the general theory of crystals did not at first provide a detailed description of the vibration spectrum, Born (1923) showed that when the wavelength of the vibration was long (compared with the crystal spacing) the crystal behaved like a continuum, and further (from the general theory of normal vibrations), that the spectrum followed the ν^2 law. On this point the theory agrees with and extends the Debye theory, and in particular it follows that the specific heat must follow a T^3 law at " sufficiently " low temperatures. One of the points left open in the general theory is a mathematical description of the important adverb " sufficiently ". If the equations for the frequencies are known, the temperature below which the T^3 law holds can be worked out from case to case, but it will depend very much on the forces between the particles in the crystal.

Debye (1912) showed that, in the case of an elastically isotropic medium, the heat capacity had the form (if $T<\theta/12$),

$$C_v = \frac{12\pi^4}{5} N\boldsymbol{k} \frac{T^3}{\theta^3},$$

where $\theta = \frac{\boldsymbol{h}}{\boldsymbol{k}} c_m \left(\frac{3}{4\pi} \cdot \frac{N}{V}\right)^{\frac{1}{3}}$; c_m is a mean velocity of elastic waves given by the relation $3/c_m{}^3 = 1/c_l{}^3 + 2/c_t{}^3$ where c_l and c_t are the velocities of the longitudinal and transverse waves which can be determined from the elastic constants of the medium. In the general case (where the medium is not isotropic) the velocities of the three groups of waves, which are in general of a mixed character, depend on the direction of propagation. The same expression holds, however, with an appropriate definition of c_m. This is (Born, 1923)

$$\frac{1}{c_m{}^3} = \frac{1}{3} \sum_{j=1,2,3} \iiint \frac{1}{c_j{}^3} \frac{d\Omega}{4\pi},$$

where $d\Omega$ is the element of solid angle in the direction associated with c_j. This quantity can be worked out from the elastic constants, and the value of θ found in this way should agree with that obtained from specific-heat data at low temperatures. It is of course necessary that the elastic data used should also be low-temperature values, but in general the extrapolation to low temperatures can be made without serious error.

A number of investigations have been concerned with the calculation of the value of c_m, as the direct evaluation is rather laborious. In the case of cubic crystals which are nearly isotropic, a simple formula has been given by Born and v. Kármán (1914), namely,

$$\frac{3}{c_m{}^3} = \rho^{3/2} \left\{\frac{2}{c_{44}{}^{3/2}} + \frac{1}{c_{11}{}^{3/2}} + \frac{3}{5}\left(c_{12} - c_{11} + 2c_{44}\right)\left(\frac{1}{c_{44}{}^{5/2}} - \frac{1}{c_{11}{}^{3/2}}\right)\right\},$$

where c_{11}, c_{44}, c_{12} are the three elastic constants of the cubic crystal (in Voigt's notation), ρ the density, and it is assumed that $(c_{12} - c_{11} + 2c_{44})/(c_{11} - c_{44})$ is small compared with unity. (The original formula of Born and v. Kármán includes a factor of 4π, which seems to be an oversight.) A very useful numerical method is due to Hopf and Lechner (1914); the method is applicable, in principle, to all cubic crystals, and can be extended to other types of crystals. The general applicability of the numerical method has, however, tended to obscure the usefulness of the Born-v. Kármán formula. For example, the case of tungsten has been treated (Honnefelder, 1923) by the, by no means quick, numerical method, whereas the value of c_m could have been worked out immediately as the elastic constants for tungsten satisfy the condition for isotropy, i.e. $c_{12} - c_{11} + 2c_{44} = 0$. In the case where $(c_{12} + c_{44}) \ll c_{11}$ an explicit formula can be given for the θ value (Blackman, 1935 d).

The first comparison of the theoretical values of c_m (or θ) with those deduced from experiments at low temperatures provided quite interesting results (Hopf and Lechner, 1914; Eucken, 1929) which are shown in table 2.

Table 2

Crystal	θ (elastic data)	θ (thermal data)
KCl	230	224
NaCl	296	286
CaF_2	499	470
FeS_2	682	645

The agreement appears quite fair, but the " elastic " values are all slightly higher than the " thermal " values. This difference would be further accentuated if the elastic data at low temperatures (instead of at room temperature) were used, as the general rule is that the θ (elastic) values increase as the temperature goes down. At the time the above comparison was made, only a rough estimate of the change was available. In the case of KCl and of NaCl, measurements of the elastic constants as functions of temperature have been made by Durand (1936) and are quoted below. The elastic constants are in units of 10^{11} dyne/cm·; the values at 0° K. being, of course, obtained by extrapolation.

Table 3

KCl				NaCl			
$T°$ K.	c_{11}	c_{44}	c_{12}	$T°$ K.	c_{11}	c_{44}	c_{12}
280	4·09	0·634	0·60	400	4·40	1·234	1·17
180	4·45	0·655	0·60	300	4·82	1·264	1·17
0	4·91	0·669	0·60	0	5·85	1·339	1·17

The increase in the value of c_m can be obtained fairly accurately from the above elastic constants, and is $\sim$5 % for KCl and $\sim$6 % for NaCl. One would expect that the θ values for CaF_2 and FeS_2 would have to be increased by similar amounts. If this is the case, the discrepancy for CaF_2 becomes 11 %; these two values should, according to crystal theory, be identical. The case of CaF_2 is of particular interest as the specific heat at low temperatures follows the T^3 law so well as to make it one of the standard examples of the validity of this law.

Discrepancies of about 10% fade, however, into the background when the comparison is made for some other single crystals (table 4: cf. Eucken, 1929).

Table 4

Substance	θ (elastic data)	θ (thermal data)
Zinc	309	205
Cadmium	180	128
Zincblende	350	270

Here again the elastic data are for room temperature, the thermal data for ~20° K. These discrepancies were particularly puzzling, because in the case of zinc the specific heat at low temperatures shows very good agreement with the T^3 law (Clusius and Harteck, 1929).

Two suggestions were made at the time to account for the difference. Eucken (1929) suggested the possibility of large systematic errors in the experimental measurement of the elastic constants. Grüneisen and Goens (1926), who carried out the experiments, derived a "theoretical" correction to the θ (elastic) value of the right order of magnitude. Unfortunately, this correction does not appear to be sound (Eucken, 1929; Blackman, 1935 a), as the two values must agree at sufficiently low temperatures. A certain amount of light was thrown on this point by investigations into the specific heats of lattices, which showed that a T^3 region at low temperatures is no proof that the "continuum" region has been reached, i.e. it is possible for spurious T^3 regions to be found (Blackman, 1935 b). Furthermore, it was found that the criterion of Debye, $T<\theta/12$, was by no means a good criterion of "sufficiently low temperatures". The conclusion is, therefore, that measurements of the specific heat at still lower temperature in the above cases would show a decided change, and that eventually the true T^3 region would be reached; for this region the θ value should fit with that determined from elastic data at low temperatures.

There are measurements of a few substances at helium temperatures, which allow the above conclusions to be tested (table 5). Zinc has been investigated by Keesom and van den Ende (1932), silver by Keesom and Kok (1932) (table 8). In both these cases there is a complication in that the specific heat due to the free electrons becomes important. This is a term proportional to T (cf. Sommerfeld and Bethe, 1933), and the θ value at 4° K. was found by fitting a curve $C_v = aT + bT^3$, to the measurements, it being assumed that b was constant below 4° K. In the case of rocksalt and sylvine there are direct measurements by Clusius and Perlick (*vide* Keesom, 1934) and by Keesom and Clark (1935). The θ (elastic) values for the two last-named substances are due to Durand (1936).

Table 5

Substance	θ (thermal)	T° K.	θ (elastic)	T° K.
Silver	237	4	216	~290
Zinc	308	4	305	~290
Rocksalt	308	10	320	0
Sylvine	230	3	246	0

The most striking fact is that the very puzzling discrepancy in the case of zinc has practically disappeared. It should also be noted that there is good reason for believing (§ 4) that for KCl and NaCl the θ (thermal) values at the absolute zero are rather higher. The value for silver does, however, seem a little high if the correction to the elastic value, to allow for the difference in temperature, is not more than 5 %. The subtraction of the electronic term does, however, make the value somewhat uncertain, and it may be as low as 220 at 2° K.

What does seem evident from the above is, that the specific-heat curve should be followed to much lower temperatures than one would have thought likely on the Debye theory. A critical review of the Debye theory does, therefore, appear necessary.

§ 4. COMPARISON OF DEBYE THEORY WITH EXPERIMENT

The Debye theory had remarkable success in representing the variation with temperature of the specific heat of a large and varied assortment of substances.

Table 6

Substance	θ			Reference
	$T \sim \theta$	$T \sim \theta/6$	$T \sim \theta/12$	
Gold	180	172	162	Clusius and Harteck (1928)
Silver	220	210	209	Eucken, Clusius, and Woiteneck (1931)
Copper	315	317	319	Dockerty (1937)
Platinum	230	224	220	Simon and Zeidler (1926)
Lead	88	87	85	Keesom and v. d. Ende (1931); Eucken and Schwers (1923)
Lithium	430	379	356	Simon and Swain (1935)
Sodium	150	159	—	Simon and Zeidler (1926)
Potassium	99	98	—	Simon and Zeidler (1926)
Tungsten	310	305	337	Lange (1924) ; Zwikker (1928)
Molybdenum	378	378	378	Simon and Zeidler (1926)
Magnesium	—	318	329	Clusius and Vaughan (1930)
Cadmium	170	147	129	Lange and Simon (1928)
Zinc	240	211	205	Clusius and Harteck (1928)
Sylvine	230	225	218	Southard and Nelson (1933)
Silver bromide	156	137	118	Eucken, Clusius, and Woiteneck (1931)
Silver chloride	211	170	133	Clusius and Harteck (1928)

It is hardly surprising that it was taken for granted that the underlying assumption (i.e. the general form of the vibrational spectrum) was sound, so long as the agreement was good. This tendency took a rather exaggerated form when it was thought necessary to assume " extra " effects whenever deviations from the Debye theory were observed—an interesting example of what Spengler terms the " canonization " of a physical theory.

The Debye theory was originally derived for monatomic and (elastically) isotropic substances. It has been applied unhesitatingly to all types of crystals. Seeing that the ν^2 law for the spectrum is perfectly general, there does indeed seem no valid reason for discrimination. It should be noted that the lower end of the spectrum—in the isotropic case—is made up of separate contributions from (*a*) longitudinal, (*b*) transverse waves, and that the relative weights of these can be varied over a considerable range if the two elastic constants of an isotropic medium are allowed to vary. There is, indeed, only one cubic crystal for which the condition for isotropy is perfectly fulfilled—tungsten—and this is one of the cases where an appreciable deviation from the Debye curve is found.

In table 6 the experimental results are shown for a variety of substances. The Debye function gives a unique correlation between the heat capacity per gram atom and the value of θ/T. Hence any specific-heat curve can be represented (as a function of T) by a set of values of θ as a function of T. A perfect fit with the Debye curve would mean a constant value for θ. In the table the values of θ are given in three temperature regions—at relatively high temperatures, at relatively low temperatures (where the T^3 region should start on Debye theory) and at an intermediate temperature.

The conclusion from the table would certainly be that in general the agreement is good, particularly for face-centred cubic crystals. There are deviations for gold and for tungsten of about 10 % in the θ value in the extreme cases, and rather larger deviations for lithium, zinc and cadmium (30 % to 50 %). These three substances are strongly anisotropic elastically, and it might seem that there is a correlation between this " anisotropy " and the deviation from the Debye theory (Fuchs, 1939). Against this may be set the case of potassium, which has much the same elastic properties as lithium; the θ value for potassium (99) shows no variation as far as the measurements go (Simon and Zeidler, 1926). Further, the θ value from elastic data at low temperatures (Bender, 1937) is 96·5. It seems certain, therefore, that even if a variation in the θ value should occur at lower temperature than those measured, the behaviour will be quite different from that of lithium.

The agreement between Debye theory and experiment becomes surprisingly different, however, if one considers lower temperatures, $T<\theta/12$, i.e. the region where the T^3 law " ought " to hold (*vide* table 7).

Table 7

NaCl			KCl			Li		
T° K.	θ	$\frac{C_v}{T^3} \cdot 10^4$	T° K.	θ	$\frac{C_v}{T^3} \cdot 10^4$	T° K.	θ	$\frac{C_v}{T^3} \cdot 10^4$
20	288	0·388	14	213	0·960	30	356	0·101
15	297	0·356	8	222	0·832	20	340	0·118
10	308	0·334	4	236	0·708	15	328	0·131
			3	227	0·798			

In the above table C_v is, in the case of NaCl and KCl, the molar heat capacity and, in the case of Li, the atomic heat capacity.

It will be seen that the T^3 law is rather elusive. In both lithium and NaCl it seems that the ratio C_v/T^3 is tending to become constant, but there is no sign of a constant region having been reached at the lowest temperature.

The variation for KCl (Keesom and Clark, 1935) is rather peculiar, especially below 4° K., and this may be spurious; Clark (1935) suggests that this " dip " in the value of θ may be due to the desorption of helium adsorbed on to the sylvine —a small quantity of helium had to be admitted to the calorimeter in order to ensure good heat contact. This view is supported by the difference in the θ value at 3° K. and that derived from elastic data ($\theta = 246$). What is clear in any event is, that for such a " standard " crystal as KCl the T^3 region does not start above 4° K., i.e. even at $T = \theta/50$.

Similar results are obtained when one considers silver and zinc (table 8).

Table 8

Silver				Zinc			
T° K.	C_v	$\frac{C_v}{T^3} \cdot 10^4$	θ	T° K.	C_v	$\frac{C_v}{T^3} \cdot 10^4$	θ
1·671	0·0004149	—	173·5	2·0	0·000386	—	212·6
2·037	0·0006537	—	181·8	3·2	0·000935	—	253·8
3·079	0·001664	—	200·9	4·0	0·00155	—	268·5
3·534	0·002253	—	208·6	6·0	0·00476	—	265·0
5·4	0·00634	0·401	226	10·0	0·0387	0·387	229·2
7·0	0·0151	0·439	219	14·0	0·137	0·499	210·2
10·0	0·0475	0·475	214	16·0	0·219	0·534	205·6
14·0	0·1336	0·486	212	12·95*	0·1140	0·511	207
16·0	0·2020	0·493	211	14·45*	0·1645	0·542	204
18·0	0·2898	0·497	210	16·40*	0·233	0·528	206
20·0	0·3995	0·500	209	18·58*	0·344	0·535	205

The above data are due mainly to Keesom and van den Ende (1932) and Keesom and Kok (1932) ; the starred values are taken from a paper by Clusius and Harteck (1928).

It will be seen that there is a small region where C_v/T^3 is nearly constant, followed, however, by a drop as the temperature is decreased, i.e. a rise in the θ value. This rise would be further accentuated if allowance were made for the heat capacity of the free electrons, which becomes important below 10° K. and which is responsible for the final drop in the θ value. One can attempt to separate the two effects, as the electronic specific heat will be proportional to T, but this is not necessary for our purpose. The main points are that the agreement with the Debye theory is by no means good in this region of very low temperature, that there is no clear sign of the true T^3 region, and that there is a spurious T^3 region over a short range of temperatures near 20° K.

There are, however, two cases in which very good agreement is obtained. These are the standard example, CaF_2, and FeS_2; the constancy of C_v/T^3 is practically perfect over a range of θ/T from 12 to 25 in each case. The only point which arises here is that both the θ values, 470 and 645, are lower than the values obtained from elastic constants at room temperature (namely, 499 and 682 respectively), and the discrepancy would be increased if low-temperature values were taken.

The experimental evidence for the existence of a T^3 region in the specific heat is, on the whole, weak (cf., in this connection, Eucken and Werth, 1930); in no case has it been clearly demonstrated that the true T^3 region has been reached; this would involve correspondence between " thermal " and " elastic " values of θ, and there is no case where there is exact agreement. What evidence there is on this point seems to be that the true T^3 region, if it exists at all, will be in the region below 4° K. for most substances.

It is also evident that the good agreement of the Debye theory with experiment does not in general extend to the region of very low temperatures. It is on this point that the lattice theory of specific heats has been able to throw some light.

§ 5. LATTICE THEORY OF SPECIFIC HEATS

The general explanation of the effects discussed in § 4 seems to be that the Debye theory deals with a crystal as if it were an elastic continuum, and that the specific crystal properties are of much greater significance than had been realised. In particular, the vibrational spectrum of a crystal can be very different from a Debye spectrum. This was first demonstrated in an investigation on the

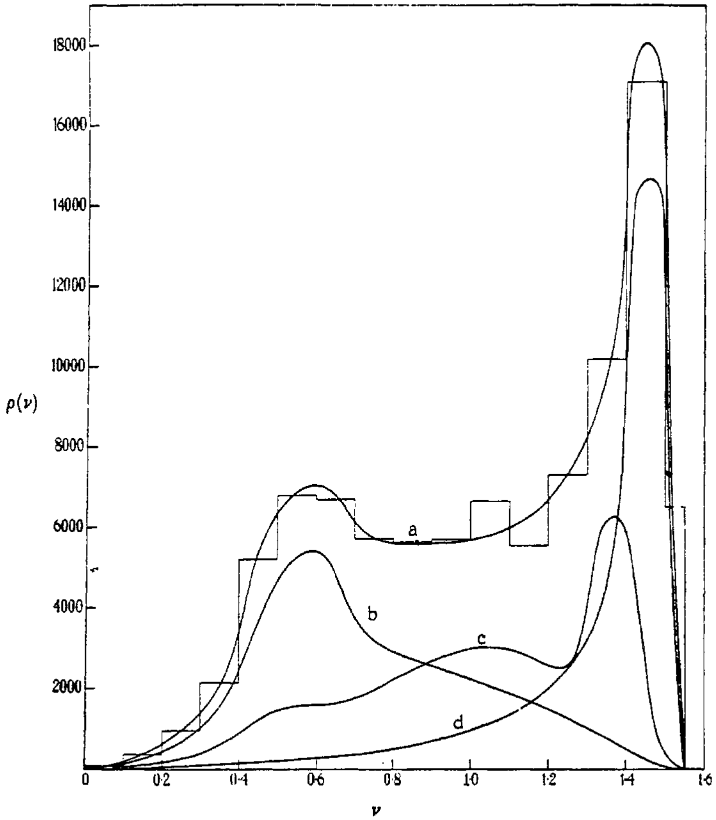

Figure 3 (*a*). Vibrational spectrum of a simple cubic lattice, curve *a*, together with the three branches *b*, *c*, *d* which make up the spectrum (Blackman, 1937 a).
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vibrational spectrum of a two-dimensional lattice (Blackman, 1935 b), and confirmation of this was obtained in a calculation of the spectrum of a simple cubic lattice (Blackman, 1937) of the type discussed by Born and v. Kármán (1912) in their first paper on the specific heats of solids. They worked out the equations for the frequencies of a lattice of the NaCl type, with forces between neighbours and " next neighbours ", and showed that the model represented a fair approximation (cf. also the work of Thirring, above).

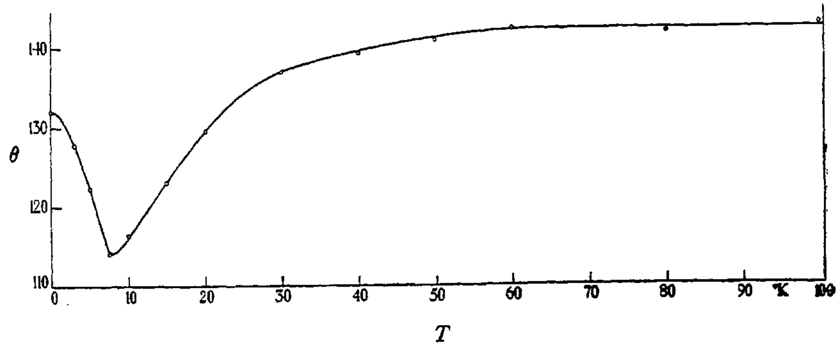

Figure 3 (*b*). θ,T curve for the vibrational spectrum of figure 3 (*a*) (Blackman, 1937 a). (*Reproduced by permission of the Council of the Royal Society.*)

The spectrum obtained with a particular model is shown in figure 3 (*a*). The variation of the θ value with temperature (when the specific heat is calculated from this spectrum) is shown in figure 3 (*b*). The constants involved in the calculation were chosen, for convenience, in a manner which made the lattice rather anisotropic elastically, more so than is the case for KCl—which is otherwise the nearest approach to the model.

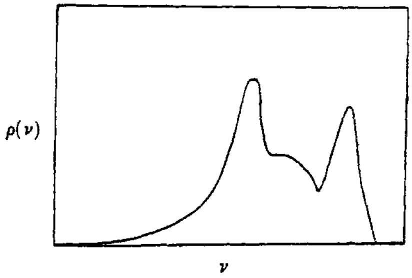

Figure 4. Vibrational spectrum of a body-centred cubic lattice (Fine, 1939). (*Reproduced from the 'Physical Review' by permission of the American Physical Society.*)

Calculations on the lines of a Born-v. Kármán model have been made by Fine (1939) for a body-centred lattice with the force constants chosen so as to fit the case of tungsten. The spectrum is shown in figure 4. Though one would have thought such a model a rather poor substitute for a metal, the calculation does show the main features of the specific-heat curve (the increase in θ as the temperature is lowered (cf. table 6)), without, however, giving complete agreement.

A careful investigation of NaCl has recently been made by Kellermann (1940, 41) using ionic and repulsive forces between the particles. The resultant spectrum (figure 5 (*a*)) shows the same general features as that obtained with the Born-v. Kármán model, and the specific heat shows remarkable agreement with experiment (figure 5 (*b*)). The work of Kellermann confirms the view that the deviation of the specific heat of NaCl from a Debye curve below 20° K. is due to the inadequacy of that theory and represents no new phenomenon. It also shows that the true T^3 region is to be found at very low temperatures—as has already been suggested by the calculations on lattice models.

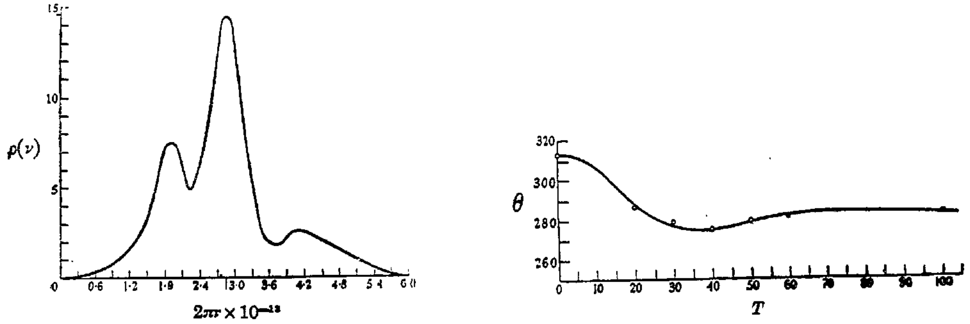

Figure 5 (*a*). Figure 5 (*b*).

Figure 5 (*a*). Vibrational spectrum of sodium chloride (Kellermann, 1941).
Figure 5 (*b*). θ, T curve for sodium chloride. The smooth curve is constructed from experiment. The points shown are calculated (Kellermann, 1941).
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A calculation of the vibrational spectrum of lithium due to Fuchs (1936 b), is based on the assumption that one can obtain the spectrum from the " continuum " end alone, with an appropriate cut-off, at any rate for such an extremely anisotropic case. Though it is likely that a very anisotropic substance will have an anomalous spectrum, it is not easy to see how one can obtain more than a vague indication of the whole spectrum from the behaviour at very low frequencies. The assumption could be tested only if one knew the whole spectrum; a case which fulfils this requirement is the cubic lattice discussed above (Blackman, 1937), which shows a great deal of elastic anisotropy. The comparison with three Debye spectra (figure 2) shows no particular agreement; though the method used by Fuchs is somewhat different, and smooths out the sharp peaks, the general principle of the method is the same as that which gives the three Debye spectra, and the agreement with the true spectrum cannot be expected to be good.

§ 6. LATTICE THEORY AND DEBYE THEORY

In order to understand the details of the variation of the specific heat with temperature, it would seem to be necessary to calculate the spectrum in each case. Beside being in general extremely tedious, if not impossible, such calculations are hardly likely to throw much light on general questions. For instance, the relation of the Debye theory to the lattice theory is of some interest, especially as the lattice theory has no alternative " formula " to offer to experimental physicists.

One of the main features of the Debye function is its dependence on one parameter only. Lattice theory suggests that a one-parametric representation cannot be valid in general. To show this one can consider the specific heat in two limiting cases—high temperatures and low temperatures (T^3 region). At high temperatures the specific heat is controlled by the sum of the squares of the frequencies of the normal vibrations of the crystals, i.e. by $\int \rho(\nu)\nu^2 d\nu$ (*cf.* the discussion on the work of Thirring in § 2); it follows from this that the low-frequency end of the spectrum plays no part in determining the value of the integral (and hence the θ value at high temperatures). The θ value at very low temperatures, on the other hand, is controlled by the low-frequency end of the spectrum; this can, in particular cases, be varied a great deal (by varying the forces between particles) without altering the high frequencies appreciably, e.g. in the case of a Born-v. Kármán model of a simple cubic lattice with weak shear forces, the density of the vibrations at low frequencies can be made very large without changing the high-frequency end (Blackman, 1935 b). It can further be seen that in the general case the θ values at low and at high temperatures depend on quite different combinations of the forces between particles, so that complete agreement cannot be expected.

So far only the θ values at the two ends of the specific-heat curve have been considered. The specific heat in the intermediate region is controlled by the spectrum as a whole. The resemblance of the calculated spectra to the Nernst-Lindemann spectrum is rather striking, and, as pointed out by Debye (1912), the two functions give practically the same specific-heat function over a large range of temperatures, though deviating at low temperatures. In particular cases this might account for an almost perfect Debye curve at moderately high temperatures.

A rather interesting property of the spectrum, which has some bearing on the variation of specific heats, is found in all the lattices for which the spectrum has been analysed; the density of normal vibrations, which starts off as a ν^2 law, seems to rise faster than ν^2 as soon as the " continuum " region is passed. This was shown to be a consequence of lattice theory for the Born-v. Kármán models of the simple cubic lattice (Blackman, 1937 b), and it can also be seen to be a general property of lattices in which short-range forces are employed. No general proof has so far been obtained, and it is by no means certain that the law is a general one; the same effect does, however, occur in ionic crystals as well, as can be seen by examining the work of Kellermann (1940). The linear (ionic) chain also shows this property (Broch, 1937).

This property of the spectrum means that the value of C_v/T^3, which should be constant at " sufficiently " low temperatures, will show an increase as the temperature is raised; in terms of Debye theory the θ value will drop, the magnitude of the " drop " depending, however, very much on particular properties of the spectrum. It is this effect which moves the true T^3 region to such low temperatures—in the case of the lattices investigated to a temperature $T<\theta/50$, possibly even to $T<\theta/100$ (Blackman, 1937, p. 430). This means, for all practical purposes, no T^3 region at all, as measurements at helium temperatures are a rarity.

In view of all the complications which occur in the lattice theory of specific heats, the Debye theory is remarkable, not in that it fails in some cases rather badly, but for the fact that it succeeds so well for most crystals. One is less surprised at deviations of, say, 30 % in the θ value (e.g. lithium) than at a deviation of less than 10 % (e.g. NaCl, KCl and Ag).

§ 7. MISCELLANEOUS APPLICATIONS OF LATTICE THEORY

The deviation of the specific heat from a Debye curve for some substances, e.g. lithium, led to the hypothesis that there is an extra term in the specific heat due to an " electronic excitation " (Simon, 1926). The case of lithium has aroused particular interest as the variation of the expansion coefficient with temperature —which in most crystals follows the same course as the specific heat—showed a different behaviour ($\theta=525$, instead of 330–430). As long as there is no actual maximum in the specific-heat curve, there is no reason to suppose that the lattice theory alone will not account for the variation of specific heat; in the case of lithium the recently calculated (Fuchs, 1936) and measured (Bender, 1937) elastic constants give values of θ—namely, 354 and 333 respectively—which agree quite well with that obtained from the specific heats at low temperatures (328). This forms conclusive evidence that, in the case of lithium, a value of 525 is incorrect, and hence the assumption of an extra specific-heat term is unnecessary. The evidence for sodium and potassium also indicates that the vibrational specific heat alone will be sufficient to account for the observed specific heats.

It has been the practice in early accounts of the theory of specific heats to compare the high-frequency end of the spectrum (or the θ value) with that obtained from other data, e.g. from *Reststrahlen* in the case of ionic crystals, from the variation of the expansion coefficient and from the variation of resistance with temperature. All these methods yield frequencies (or θ values) which agree more or less with that obtained from a Debye curve, but it is difficult to see what the comparison actually means. The spectrum of NaCl, for example, extends well above the frequency at which the main absorption of infra-red radiation takes place, and also well above the Debye frequency ($\nu_D=k\theta/h$). The danger of comparing values from different phenomena is well illustrated by the case of lithium, discussed above. Until the theories of the variation of the expansion coefficient and of the variation of resistance with temperature have been more carefully analysed, it is as well not to draw conclusions from apparent discrepancies.

§ 8. GENERAL CONCLUSIONS

The main feature in the recent developments of the theory of the specific heat of solids has been the emergence of the vibrational spectrum, which shows a different character from that assumed by Debye; this represents a vindication of the method adopted originally by Born and v. Kármán, which method, however, was not carried out completely at the time. The properties of the vibrational spectrum explain the deviations from Debye theory observed at low temperature for the (vibrational) specific heat, and enable one to clear up points such as the existence of T^3 regions which are not true T^3 regions. These latter regions occur in general at much lower temperatures than one would expect on Debye theory, in many cases at such low temperatures that they are not likely to be of practical interest.

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