THE THERMAL ENERGY OF CRYSTALLINE SOLIDS: LITHIUM, TUNGSTEN, GOLD, SILICON AND GREY TIN

By Bisheswar Dayal

(*From the Department of Physics, Indian Institute of Science, Bangalore*)

1. Introduction

THE success of Debye's formula in representing the variation with temperature of the specific heat of a large number of metals crystallizing in the cubic system has for many years been regarded as conclusive evidence for the correctness of the assumptions on which this theory is based. Gradually, however, various experimental facts have come to light which do not fit into the theory. According to Debye, the specific heat of an elementary solid is expressible as a function involving only one arbitrary constant known as the Debye characteristic temperature for the substance, this constant itself being expressible in terms of the elastic modulii of the solid. Several cases have however come to light in which it is impossible to fit the specific heat data into a formula of this kind. In order to preserve at least the framework of the theory, it has become the fashion to regard the " characteristic temperature " as being itself a function of the temperature and to exhibit its variation graphically. On a close examination of the matter, it is found that there are comparatively few cases in which the " Debye temperature " is even approximately constant over a wide range of temperature. Lead, calcium, molybdenum and vanadium are examples of cases in which a fairly satisfactory fit is obtained. On the other hand, there are equally numerous cases in which the " characteristic temperature " shows quite distinct variations, increasing with the temperature as is the case of gold, diminishing as in tungsten, and in other cases, again, showing more complicated types of variation. In the cases of lithium, grey tin and metallic silicon, the variations are so large that the Debye formula does not even roughly represent the specific heat curve.

An extensive literature has grown up in the attempt to interpret these failures of the Debye theory on the basis of special hypotheses. It is not proposed here to enter into that literature, as we shall consider the whole question from a more general point of view. Debye's identification of the possible atomic movements in a crystal with the elastic vibrations of a continuous solid seems justifiable only when the wave-length of such vibrations is

sufficiently large in comparison with the lattice spacings of the crystal. There appears, however, no reason for assuming that all the possible types of atomic movement can be described in this fashion. Indeed, wherever it has been possible to make a direct experimental study of the question, *e.g.*, by photographing the Raman spectra, it is found that such an assumption does not correctly represent the facts. The spectroscope, in fact, discloses that the atomic vibrations even in elementary solids, *viz.*, diamond, phosphorus and sulphur, exhibit numerous monochromatic frequencies, the position and number of which may be correlated with the crystal structure of the solid. Such methods of optical study are, unfortunately, not open to us in the case of metals. But we have no reason to suppose that a similar situation does not exist in their case as well. It may be recalled that in making the first attempt to develop a quantum theory of specific heats, Einstein (1907), assumed that the vibrations of the atoms in a solid are monochromatic. The difficulty felt by him later (1911) in sustaining this hypothesis, namely that the vibrations of an atom would be highly damped by its reactions with its neighbours, disappears when it is recalled that the characteristic vibrations of the lattice necessarily occur in the same way in all its cells and are therefore undamped. The highly monochromatic character of the frequencies usually exhibited by crystals in the Raman effect is, in fact, a complete vindication of Einstein's original hypothesis.

From the foregoing considerations, it is clear that for the evaluation of the specific heat, we have to find the frequencies of atomic vibration in the crystal and to assign to each such frequency an Einstein function with the appropriate weight factor. The principal Einstein terms relate to the frequencies of vibration in which the lattice cell is the repeating unit of the vibration pattern in space. Further terms would also have to be added to represent the superlattice frequencies for which the vibration pattern in space is a multiple of the size of the lattice cell, as explained more fully in papers by Sir C. V. Raman and Dr. C. S. Venkateswaran appearing in these *Proceedings*. The elastic vibrations of the solid properly so-called, however, make no sensible contribution to the thermal energy.

2. *Relation to Crystal Structure*

We may take the basis group in the cases now under consideration to be the unit cube. This contains two atoms in the case of body-centred lattices, four in the case of face-centred ones, and eight in diamond-like structures. The case of the body-centred lattice is the simplest of all. This may be considered as made up of two interpenetrating simple cubic lattices, one of which is formd by the corner atoms and the other by the central atom of the cube. The three translations of the cell as a whole involve three degrees of freedom.

The Einstein frequency would then correspond to the movement of one single cubic lattice against the other and because of the cubic symmetry, this must be triply degenerate. The case of a face-centred lattice is somewhat more complicated. There are four interpenetrating simple cubic lattices to be considered. Here as well, three degrees of freedom relate to the translation of the cell. The remaining nine degrees of freedom are associated with the possible modes of vibration of the four lattices against each other. Since each frequency must be triply degenerate, we are concerned with three Einstein frequencies. In the case of diamond-like lattices, the unit cell of eight atoms is made up of two groups of four each forming a face-centred cubic lattice. Assigning three degrees of freedom to the translations, twenty-one degrees of freedom are left over. There would then be, in general, seven triply degenerate Einstein frequencies.

The evaluation of the Einstein terms in the specific heat thus involves a knowledge of one characteristic frequency for body-centred lattices, three for face-centred ones, and seven for diamond-like structures. Provisionally and for the sake of simplicity, the three frequencies of a face-centred lattice may be replaced by a single representative frequency. In the case of diamond-like structures, the spectroscopic evidence afforded by diamond itself indicates that it is necessary to have at least two representative frequencies; one of these corresponds to an oscillation of the two face-centred cubic lattices against each other; the other frequency may be pictured as an oscillation of the component atoms in each such lattice amongst themselves. Of the total number of degrees of freedom, one half should evidently be assigned to the vibrations of the first type which would naturally have the higher frequency. Three degrees of freedom being assigned to the translations, the remainder are associated with the second and lower frequency.

The three degrees of translatory freedom of the unit cell appear in each case as superlattice frequencies. Taking a superlattice cell whose edge is double that of the unit cell, we assign three degrees of freedom to the translations of the enlarged cell and the remaining 21 degrees of freedom to seven triply degenerate superlattice frequencies. The three reserved degrees can then be passed on to superlattice frequencies of the second order, and so forth. For our present purpose, we may replace the seven superlattice frequencies of a particular order by a single representative frequency and also restrict ourselves to superlattice frequencies of the first two orders. The expressions for the specific heat accordingly reduce to

$$C_v = 3\,R \left[\frac{1}{2}\, E\left(\frac{h\nu_1}{kT}\right) + \frac{7}{16}\, E\left(\frac{h\nu_2}{kT}\right) + \frac{1}{16}\, E\left(\frac{h\nu_3}{kT}\right) \right]$$

for body-centred structures

A2

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$$C_v = 3\,R\left[\frac{3}{4}\,E\left(\frac{h\nu_1}{kT}\right) + \frac{7}{32}\,E\left(\frac{h\nu_2}{kT}\right) + \frac{1}{32}\,E\left(\frac{h\nu_3}{kT}\right)\right]$$

for face-centred structures

and $\quad C_v = 3\,R\left[\frac{1}{2}\,E\left(\frac{h\nu_1}{kT}\right) + \frac{3}{8}\,E\left(\frac{h\nu_2}{kT}\right) + \frac{7}{64}\,E\left(\frac{h\nu_3}{kT}\right) + \frac{1}{64}\,E\left(\frac{h\nu_4}{kT}\right)\right]$

for diamond-like structures,

where E stands for Einstein function. The last two terms in each case refer to the superlattice frequencies of the first and second orders respectively.

Failing spectroscopic data, the frequencies can be evaluated from the specific heat data themselves. The superlattice frequency of the lowest order is obtained from the specific heat data at the lowest temperature where the contribution of other frequencies becomes negligible. Superlattice frequencies of other orders can similarly be found from the specific heat data at intermediate temperatures. The high-temperature specific heats where the contribution of superlattice vibrations is constant give the lattice frequencies. Towards the end of the paper we shall compare the lattice frequencies empirically found with those given by the melting point formula of Lindemann.

In the present paper the author has used the above method for calculating specific heats of several elements crystallizing in the cubic system which do not fit into the Debye theory. In other cases where the Debye theory gives an approximate fit with the experimental values, calculations show that it is always possible to express the specific heats slightly better by the new method. Such calculations have however, not been given here to save space.

3. Specific Heats of Body-Centred Structures

(a) *Lithium.*—Of all the metals having this structure, lithium is the most interesting since no single Debye function will fit the experimental results, the value of θ Debye changing from 328 at low temperatures to 430 at room temperatures. Various hypotheses have been suggested to explain this so-called anamoly, that given by Simon and Swain (1935) being the most discussed. They believe that Li ions are of two different kinds and some heat is taken up in changing one kind into another. The soundness of this assumption has been questioned and their value of θ Debye (510) is not supported by experimental evidence (Pankow, 1936). Fuch (1936) has tried to explain the specific heats on the assumption of anisotropy, but the values of θ Debye calculated by him on that basis show an even larger deviation than is experimentally the case. The values of the specific heat calculated by us (given below), however, are very close to the experimental values at all temperatures. It is noteworthy also that our Einstein frequency comes very close to that given by Lindemann's melting point formula.

The values of C_v have been taken from the paper by Simon and Swain (*loc. cit*). Beutler and Levis' (1934) results have not been used because the accuracy claimed by them is not very high, only the first place of decimals being shown.

TABLE I

Specific Heats of Li in Cals./deg. gm. atom

$$\nu_1 = 8 \cdot 4 \times 10^{12}, \quad \nu_2 = 4 \cdot 64 \times 10^{12}, \quad \nu_3 = 1 \cdot 84 \times 10^{12}$$

Experimental Data of Simon and Swain (1935)

Absolute tempe- rature	Einstein contri- bution ν_1	Einstein contri- bution ν_2 and ν_3	Calculated C_v	Observed C_v	Difference observed −calculated	Debye function $\theta = 350$	Difference observed C_v −Debye C_v
15	..	·0364	·0364	·045	+·009	·037	+·008
20	..	·095	·095	·095	±·000	·087	+·008
25	..	·173	·173	·169	−·004	·169	±·000
30	·001	·278	·279	·273	−·006	·289	−·016
35	·0046	·4112	·416	·413	−·003	·452	−·039
40	·0133	·567	·580	·573	−·007	·652	−·079
45	·0327	·7376	·770	·770	±·000	·884	−·114
50	·064	·910	·974	·995	+·021	1·137	−·142
60	·169	1·239	1·41	1·42	+·01	1·67	−·45
70	·324	1·525	1·85	1·87	+·02	2·197	−·327
80	·509	1·757	2·27	2·31	+·04	2·67	−·36
90	·71	1·948	2·66	2·67	+·01	3·09	−·42
100	·906	2·104	3·01	3·02	+·01	3·46	−·44
110	1·093	2·228	3·32	3·32	±·000	3·77	−·45
120	1·269	2·330	3·60	3·59	−·01	4·02	−·43
140	1·569	2·479	4·05	4·01	−·04	4·45	−·44
160	1·813	2·586	4·40	4·34	−·06	4·75	−·41
180	2·006	2·656	4·66	4·57	−·09	4·98	−·42
200	2·156	2·724	4·88	4·78	−·10	5·14	−·36
240	2·372	2·793	5·17	5·28	+·11	5·36	−·08
280	2·518	2·844	5·36	5·31	−·05	5·52	−·21
300	2·575	2·860	5·44	5·39	−·05	5·63	−·24

(*b*) *Tungsten.*—This is the only metal for which the frequency spectrum has been worked out on the Born-Karman model (Fine, 1939). An approximate method which involved a solution of 140 cubic equations and in which the interaction of an atom and its fourteen neighbours only was considered, was used. The values calculated on that basis do not however show any distinct improvement on those calculated by Debye's formula for $\theta = 310$.

The agreement of the calculated values with Lange's data is excellent. The small deviations with respect to Zwikker's data are well within the experimental errors. This is shown by the considerable differences between the two series of measurements made by him in the region of temperatures given below.

TABLE II

Specific Heats of W in Cals./deg. gm. atom

$$\nu_1 = 5 \cdot 4 \times 10^{12}, \quad \nu_2 = 4 \cdot 48 \times 10^{12}, \quad \nu_3 = 1 \cdot 67 \times 10^{12}$$

Experimental Data of Lange (1924) *from 26–91° A and Zwikker* (1929) *from 100–300° A*

Absolute temperature	Einstein contribution ν_1	Einstein contribution ν_2 and ν_3	Calculated C_v	Observed C_v	Difference observed $-$calculated	Debye function $\theta = 310$	Difference observed C_v $-$Debye C_v
26·01	·013	·224	·237	·213	$-$·024	·272	$-$·059
32·3	·0617	·387	·449	·434	$-$·015	·506	$-$·072
38·8	·165	·587	·752	·750	$-$·002	·826	$-$·076
46·7	·355	·866	1·22	1·21	$-$·01	1·28	$-$·07
54·7	·592	1·144	1·74	1·80	$+$·06	1·77	$+$·03
74·4	1·176	1·701	2·88	2·87	$-$·01	2·85	$-$·02
78·3	1·272	1·797	3·07	3·07	$\pm$·00	3·03	$+$·04
84·2	1·42	1·908	3·33	3·33	$\pm$·00	3·29	$+$·04
91·1	1·576	2·026	3·60	3·60	$\pm$·00	3·55	$+$·05
100	1·745	2·156	3·90	3·77	$-$·13	3·85	$+$·08
200	2·592	2·741	5·33	5·30	$-$·03	5·30	$\pm$·00
300	2·796	2·869	5·67	5·87	$+$·20	5·65	$+$·22

4. Specific Heats of a Face-Centred Structure

Gold.—The specific heats of this metal have been measured by Clusius and Harteck (1928) and unlike most other metals of this structure are not expressed by one Debye function. The values of θ Debye vary between 160 and 186.

TABLE III

Specific Heats of Gold in Cals./deg. gm. atom

$$\nu_1 = 3 \cdot 14 \times 10^{12}, \quad \nu_2 = 1 \cdot 80 \times 10^{12}, \quad \nu_3 = 1 \cdot 15 \times 10^{12}$$

$$C_p - C_v = 2 \cdot 09 \times 10^{-5} \, C_p \, T$$

Experimental Data of Clusius and Harteck (1928)

Absolute temperature	Einstein contribution ν_2 and ν_3	Einstein contribution ν_1	Calculated C_v	Observed C_v	Difference observed $-$calculated	Debye function $\theta = 163$	Difference observed C_v $-$Debye C_v
14·96	·351	·0195	·371	·357	$-$·014	·354	$+$·003
15·73	·389	·029	·418	·431	$+$·013	·408	$+$·023
20·33	·618	·158	·776	·782	$+$·006	·816	$-$·024
24·9	·8057	·3945	1·200	1·252	$+$·052	1·32	$-$·068
32·5	1·0461	·9575	2·004	1·998	$-$·006	2·184	$-$·186
44	1·207	1·840	3·047	3·034	$-$·013	3·27	$-$·236
63·6	1·3243	2·8642	4·189	4·144	$-$·045	4·39	$-$·246
82·5	1·400	3·414	4·814	4·706	$-$·108	4·938	$-$·232
105	1·434	3·759	5·193	5·128	$-$·065	5·158	$-$·030
147·5	1·460	4·101	5·561	5·578	$+$·017	5·604	$-$·026
176·5	1·468	4·206	5·674	5·706	$+$·032	5·71	$-$·004
212·5	1·476	4·283	5·759	5·762	$+$·003	5·782	$-$·02

The deviations of the calculated values from the observed data are smaller than those of the Debye function and are not, as is the case with the latter in the same direction throughout. They are however larger than those observed with the body-centred structures. This is possibly due to the fact that we have taken a single Einstein frequency as a representative of a group of three, which may be different from one another.

5. Specific Heats of Diamond-like Structures

(*a*) *Metallic Silicon.*—Specific heats of this substance have been measured at six temperatures by Nernst and Schwers (1930) (20-90)° K, by Anderson (1930) (61–296)° K, and by Magnus (1923) (138–1000)° K. The Debye characteristic temperatures necessary to explain these results vary between 440 and 715. Nernst and Schwers' values are considerably (2–30)% lower than those extrapolated by Anderson from his own data. We have used the latter's extrapolated values in Table IV. C_p–C_v has been calculated by the usual formula from the compressibility ($\cdot325 \times 10^{-12}$), linear coefficient of expansion ($7\cdot15 \times 10^{-6}$) and C_p at 296 ($4\cdot652$), the former two being taken from the *International Critical Tables*.

With reference to the distinctly noticeable deviation at $296\cdot3°$K, it must be pointed out that Anderson does not claim a very high degree of accuracy for his work. The observed values of specific heats deviate considerably from those given by his curve in this region of temperature. Similar deviations take place at very low temperatures. The order of error can be judged from the fact that the specific heat given by him by interpolation at $65\cdot6°$ K is $\cdot920$, while his own determination at a slightly lower temperature ($65\cdot1$) is $\cdot974$. The small deviations from Magnus' data are not unexpected, since his values differ by about 4% from Anderson's at the temperatures 297 and $296\cdot3°$ nearly common to both sets of observations.

(*b*) *Grey Tin.*—The calculation of $C_p - C_v$ requires the exact knowledge of the specific heat, compressibility, coefficient of expansion and density at one and the same temperature. For grey tin only the density and the mean coefficient of expansion between –163 and 18° C. are known. We have therefore calculated the values of $C_p - C_v$ by an approximate formula of Grüneisen $\frac{C_p}{C_v} = 1 + 2\gamma T$, where γ is the coefficient of expansion, on the supposition that the coefficient of expansion is the same at all temperatures. γ is taken as $1\cdot59 \times 10^{-6}$.

The specific heats were expressed by Lange (1924) by two Debye functions $\frac{3}{4}$ Debye 280 + $\frac{1}{4}$ Debye 76. In terms of one Debye function the θ Debye ranges from (140– 225)° K.

TABLE IV

Specific Heats of Metallic Silicon in Cals./deg. gm. atom

$$\nu_1 = 14\cdot7 \times 10^{12}, \quad \nu_2 = 6\cdot59 \times 10^{12}, \quad \nu_3 = 3\cdot66 \times 10^{12}, \quad \nu_4 = 1\cdot30 \times 10^{12}$$

$$C_p - C_v = 1\cdot84 \times 10^{-5} \, C_p{}^2 \, T.$$

Experimental Data Extrapolated from Anderson (20·1 – 89·8) Anderson) 89·8 – 296·3), Magnus (350–1000)

Absolute temperature	Einstein contribution ν_3 and ν_4	Einstein contribution $\frac{9}{8} RE\left(\frac{315}{T}\right)$	Einstein contribution $\frac{12}{8} RE\left(\frac{705}{T}\right)$	Calculated C_v	Observed C_v	Difference observed –calculated	Debye function $\theta = 440$	Difference observed C_v –Debye C_v
20·1	·0527			·0527	·042	–·0107	·044	–·002
28·2	·1174			·121	·123	+·002	·122	+·001
39·7	·2351	·0038	·0009	·286	·336	+·050	·336	±·000
53·1	·3650	·0506	·0076	·576	·630	+·054	·752	–·122
65·6	·4575	·210	·073	·896	·920	+·024	1·255	–·335
89·8	·5682	·4305	·1205	1·515	1·495	–·02	2·27	–·775
98·8	·5932	·8741	·2605	1·731	1·695	–·036	2·61	–·915
116·7	·6327	1·0178	·5845	2·151	2·152	+·001	3·207	–1·055
145·5	·6690	1·2573	·7095	2·804	2·740	–·064	3·97	–1·23
158·8	·6826	1·5506	·7875	3·019	2·993	–·016	4·18	–1·187
165·8	·6864	1·6271	1·0225	3·141	3·156·	+·015	4·29	–1·134
186·9	·6976	1·667	1·1485	3·490	3·496	+·006	4·58	–1·1084
199·2	·7032	1·7696	1·289	3·673	3·684	+·011	4·73	–1·046
213·6	·7085	1·821	1·497	3·868	3·841	–·027	4·866	–1·025
237·5	·7150	1·8709	1·6225	4·143	4·076	–·067	5·05	–·974
253·3	·7187	1·9313	1·820	4·307	4·335	+·028	5·144	–·809
283·3	·7236	1·9654	1·896	4·565	4·566	+·001	5·30	–·734
296·3	·7258	2·0209	2·1445	4·660	4·534	–·126	5·347	–·813
350	·7308	2·0378	2·5295	4·963	4·972	+·009	5·525	–·553
500	·7380	2·088	2·738	5·428	5·298	–·130	5·73	–·432
700	·7408	2·1603	2·8556	5·550	5·558	+·008	5·835	–·277
1000	·7423	2·071		5·808	5·622	+·186	5·898	–·276

TABLE V

Specific Heats of Grey Tin in Cals./deg. gm. atom

$\nu_1 = 5.44 \times 10^{12}$, $\nu_2 = 2.20 \times 10^{12}$, $\nu_3 = \nu_4 = 0.77 \times 10^{12}$

Experimental Data of Lange (1924)

Absolute temperature	Einstein contribution ν_3 and ν_4	Einstein contribution $\frac{9}{8} RE\left(\frac{105}{T}\right)$	Einstein contribution $\frac{12}{8} E\left(\frac{260}{T}\right)$	Calculated C_v	Observed C_v	Difference observed −calculated C	Debye function $\theta=140$	Difference observed C_v −Debye C_v
15·5	·471	·1168	··	·588	·599	+ ·011	·599	± ·000
18·2	·534	·2335		·768	·755	− ·013	·909	− ·154
22·35	·5899	·4568	·004	1·051	1·056	+ ·005	1·45	− ·394
26·8	·637	·7088	·017	1·363	1·375	+ ·009	2·04	− ·665
31·5	·6645	·9488	·053	1·666	1·675	+ ·009	2·63	− ·955
37·3	·6864	1·1966	·136	2·019	2·00	− ·019	3·23	−1·23
44·9	·704	1·443	·307	2·45	2·36	− ·09	3·83	−1·47
52·3	·714	1·612	·518	2·84	2·80	− ·04	4·27	−1·37
59·3	·721	1·731	·734	3·19	3·14	− ·05	4·58	−1·44
69·5	·727	1·850	1·039	3·62	3·67	+ ·05	4·91	−1·24
92·5	·735	2·007	1·602	4·34	4·42	+ ·08	5·33	− ·91
102·6	·737	2·05	1·799	4·59	4·73	+ ·14	5·44	− ·71
283·6	·743	2·208	2·776	5·72	6·08	+ ·36	5·88	+ ·20

6. Remarks on the Frequencies Assumed

In Table VI the values of the lattice frequencies obtained from the specific heat data are compared with those deduced from the Lindemann melting point formula. The following form given by Grüneisen in his article in the " Handbuch der Physik " has been used

$$\nu = 2 \cdot 5 \times 10^{12} \sqrt{\frac{T_s}{AV_0^{2/3}}}$$

where T_s = melting point in absolute degrees, A = atomic weight and V_o = atomic volume.

TABLE VI

Comparison of Frequencies

Substance	ν from Lindemann formula		Einstein ν from specific heat data	
	ν	$\theta = \frac{h\nu}{K}$	ν	$\theta = \frac{h\nu}{K}$
		deg. K		deg. K
Lithium	$8 \cdot 7 \times 10^{12}$	417	$8 \cdot 4 \times 10^{12}$	400
Tungsten	$5 \cdot 23 \times 10^{12}$	253	$5 \cdot 4 \times 10^{12}$	260
Gold	$3 \cdot 34 \times 10^{12}$	160	$3 \cdot 14 \times 10^{12}$	350
Silicon	$8 \cdot 51 \times 10^{12}$	407	$6 \cdot 59 \times 10^{12}$	315
			$14 \cdot 7 \times 10^{12}$	705
Grey tin	$1 \cdot 86 \times 10^{12}*$	89*	$2 \cdot 20 \times 10^{12}$	105
			$5 \cdot 44 \times 10^{12}$	260

* From data for ordinary tin.

For the first three metals the frequencies obtained from Lindemann formula are very near to those used by us. In the latter two cases such agreement is not to be expected because two frequencies are involved. The lower of the two frequencies, however, comes near the Lindemann frequency. It is noteworthy that, as in the case of diamond, one frequency is about double the other.

An independent estimate of the higher frequency of silicon can be made by the use of Nagendra Nath's theory of the vibrations of the diamond lattice (1934). His formula for the higher frequency 1332 cm.$^{-1}$ of diamond is

$$\nu = \frac{1}{2\pi c} \sqrt{\left[\frac{8}{3M} \left(K + 8 \frac{K' - K'''}{p^2} \right) \right]}$$

which must also hold good for silicon because of the similarity of structure. K, K' and K''' in the formula stand for the force constants for primary valence, directed valence and intravalence, respectively, while M is the mass of the atom and p the distance between any two connected atoms. The second term in the above formula is unknown for silicon but is comparatively small (about 30% of the first) for the force constants used by Nagendra Nath for carbon. The value of K for silicon has been found to be $1 \cdot 7 \times 10^5$ dynes/cm.

by Still and Yost (1937) from the Raman spectrum of disilane. The corresponding value of K for carbon from a compound of similar structure is $4 \cdot 64 \times 10^5$ dynes/cm. If the latter value is put in the above formula for diamond, the first term by itself (neglecting the other) gives the frequency as 1308 cm.$^{-1}$ which is near the observed value. We shall therefore not be far wrong in calculating the frequency for silicon in the same way from the value K and neglecting $\left(\dfrac{K' - K'''}{p^2}\right)$. The frequency thus obtained is 516 cm.$^{-1}$ which is not so different from the 491 cm.$^{-1}$ adopted for the specific heat calculations. An alternative method of calculation is to assume that

$$\frac{\nu \text{ silicon}}{\nu \text{ carbon}} = \sqrt{\frac{M_{carbon} \times K_{si}}{M_{si} \times K_{carbon}}} = \frac{\nu_{si}}{1332}$$

which gives us 525 cm.$^{-1}$ for ν_{si} on using the values of K quoted above.

In conclusion the author wishes to thank Professor Sir C. V. Raman, KT., F.R.S., N.L., for his guidance and encouragement.

7. Summary

It is shown in the paper that the specific heat formula for all metals must necessarily include two types of Einstein terms, one corresponding to the lattice frequencies and the other to the superlattice frequencies. The number of lattice frequencies is shown to be one in the case of body-centred cubic lattices, three in the case of face-centred cubic types and seven in diamond-like structures. In the latter two cases the groups of frequencies have been replaced for simplicity by one and two representative frequencies respectively. The specific heats of the so-called anomalous cases, Li, W, Au, Si and grey tin have been calculated on the above basis and a satisfactory agreement with experimental results has been obtained. In the first two types of structures the monochromatic lattice frequencies obtained are shown to be of the same order as those given by Lindemann's melting point formula.

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