

Debye temperatures for hexagonal crystals

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The Debye temperatures of hexagonal crystals of 42 elements and compounds have been calculated from the elastic constants, by numerical integration and by Pynn's method. It is found that Pynn's method is inapplicable in certain cases; the cause of this is analyzed, and a modification of Pynn's method is suggested for these cases. The calculated Debye temperatures are compared with the calorimetric Debye temperatures, wherever data are available. Large discrepancies are pointed out for Pr, Dy, Ho, and Er, and small ones for Be, Mg, Y, Ti, Zr, Hf, and Tb.

I. INTRODUCTION

The Debye temperature is an important parameter of a solid.^{1,2} From calorimetric measurements it is well known that it varies with the temperature. The Debye temperature at 0 K is of special theoretical significance. It can be calculated from the elastic constants (Θ_0^{el}). From theory one expects that the Debye temperature thus calculated should be equal to the calorimetric Debye temperature (Θ_0^{c}) at 0 K:

$$\Theta_0^{\text{c}} = \Theta_0^{\text{el}}. \quad (1)$$

A comparison of the theoretical and experimental values is helpful in detecting inaccuracies in the elastic-constant and/or calorimetric data.

For cubic crystals, calculations of Θ_0^{el} have been made by a number of workers³⁻⁷ and Θ_0^{el} and Θ_0^{c} values have been compared.^{3,4} For hexagonal crystals, methods to calculate Θ_0^{el} have been developed⁸⁻¹¹ but no extensive comparison between Θ_0^{el} and Θ_0^{c} appears to have been made. Such a comparison is of special interest for hexagonal crystals because rare earths belong to this class. Most of the rare earths with the exception of thulium and lutetium are ferromagnetic or antiferromagnetic at low temperatures, displaying unusual types of magnetic orderings. Thus, their heat capacity C_p usually has four different components: (i) the lattice specific heat C_L , (ii) the electronic specific heat C_E , (iii) the magnetic specific heat C_M , and (iv) the nuclear specific heat C_N . Because of the large number of parameters involved, it becomes difficult

to extract an accurate value of Θ_0^{c} from the experimental data. Indeed, in actual practice a suitable value for Θ_0^{c} is assumed so that the parameters involved in other contributions may be determined. In the present paper we have calculated Θ_0^{el} using numerical integration (NI), and also Pynn's method¹¹ for such simple hexagonal crystals for which reasonably accurate data for elastic constants are available and whose crystal structures are reasonably well determined.¹² In the course of this investigation it was discovered that Pynn's method is not applicable in all cases; we have analyzed why it happens and when. The calculated Θ_0^{el} values are compared with Θ_0^{c} values wherever possible.

II. THEORY

A. Numerical-integration method

The Debye temperature at 0 K is related to the average sound velocity v_m by

$$\Theta_0^{\text{el}} = \frac{h}{k} \left[\frac{3N}{4\pi V} \right]^{1/3} v_m, \quad (2)$$

where h is the Planck constant, k is the Boltzmann constant, N/V is the number density of atoms, and

$$v_m^3 = 3 \left[\int \sum_{i=1}^3 \frac{1}{v_i^3} \frac{d\Omega}{4\pi} \right]^{-1}, \quad (3)$$

where v_i is the wave velocity which can be ob-

tained¹³ from the solution of

$$\begin{vmatrix} n_1^2 A + \frac{1}{2} n_2^2 C - \Lambda & n_1 n_2 G & n_1 n_3 D \\ n_1 n_2 G & \frac{1}{2} n_1^2 C + n_2^2 A - \Lambda & n_2 n_3 D \\ n_1 n_3 D & n_2 n_3 D & n_3^2 H - \Lambda \end{vmatrix} = 0, \quad (4)$$

where

$$A = c_{11} - c_{44},$$

$$C = c_{11} - c_{12} - 2c_{44},$$

$$D = c_{13} + c_{44},$$

$$G = \frac{1}{2}(c_{11} + c_{12}),$$

$$H = c_{33} - c_{44},$$

$$\Lambda = \rho v^2 - c_{44},$$

ρ is the density and (n_1, n_2, n_3) is a unit vector specifying θ and ϕ .

Thus,

$$v_i^3 = [(\Lambda_i + c_{44})/\rho]^{3/2}. \quad (5)$$

Writing $n = n_3 = \cos \theta$ and $m = (1 - n^2)^{1/2}$, we have

$$\Lambda_1 = \frac{1}{2} m^2 C,$$

$$\Lambda_2 = \frac{1}{2} (m^2 A + n^2 H)$$

$$+ [\frac{1}{4} (m^2 A + n^2 H)^2 + n^2 m^2 (D^2 - AH)]^{1/2}, \quad (6)$$

$$\Lambda_3 = \frac{1}{2} (m^2 A + n^2 H)$$

$$- [\frac{1}{4} (m^2 A + n^2 H)^2 + n^2 m^2 (D^2 - AH)]^{1/2}.$$

Noting that the only angular dependence is on $\cos^2 \theta$ and $\sin^2 \theta$, it is not required to average on ϕ , and moreover, the averaging on θ need only be done between 0 and $\pi/2$. Thus,

$$v_m^3 = 3 \left[\int_0^{\pi/2} \sin \theta \sum_{i=1}^3 \frac{1}{v_i^3} d\theta \right]^{-1}. \quad (7)$$

B. Pynn's method

For hcp crystals the constant-frequency surfaces for low-frequency acoustic waves are cylindrically symmetric about the hexad direction. Using the formulas for the low-frequency wave velocities, Pynn¹¹ obtained the following expressions for the

three constant-frequency surfaces:

$$r_1^2 = (\rho \omega^2 - z^2 c_{44})/c_{66}, \quad (8)$$

$$r_2^2 = -a \omega^2 - bz^2 + (cz^4 + dz^2 \omega^2 + e \omega^4)^{1/2}, \quad (9)$$

$$r_3^2 = -a \omega^2 - bz^2 - (cz^4 + dz^2 \omega^2 + e \omega^4)^{1/2}, \quad (10)$$

where ω is the frequency, r and z are the components of the wave vector which are perpendicular and parallel to the hexad direction, and the other parameters are defined by

$$a = -\rho(c_{11} + c_{44})/2c_{11}c_{44},$$

$$b = (c_{11}c_{33} - c_{13}^2 - 2c_{13}c_{44})/2c_{11}c_{44},$$

$$c = b^2 - c_{33}/c_{11},$$

$$d = \rho[c_{33} + c_{44} - b(c_{11} + c_{44})]/c_{11}c_{44},$$

and

$$e = [\rho(c_{11} - c_{44})/2c_{11}c_{44}]^2.$$

In terms of $y = z/\omega$ and $R_i = r_i/\omega$, Eqs. (8)–(10) can be written as

$$R_1^2 = (\rho - y^2 c_{44})/c_{66}, \quad (11)$$

$$R_2^2 = -a - by^2 + (cy^4 + dy^2 + e)^{1/2}, \quad (12)$$

$$R_3^2 = -a - by^2 - (cy^4 + dy^2 + e)^{1/2}. \quad (13)$$

Using this, the volume of wave-number space containing modes of frequency less than or equal to ω is given by

$$V(\omega) = 2\pi\omega^3 \sum_{i=1}^3 \int_0^{y_i} R_i^2 dy, \quad (14)$$

where y_i is the smallest positive root of R_i . Thus, y_1 is given by $(\rho/c_{44})^{1/2}$. To find y_2 and y_3 , R_2 and R_3 in Eqs. (12) and (13) are set equal to zero; both the equations yield the following:

$$(a + by^2)^2 = cy^4 + dy^2 + e. \quad (15)$$

This has roots at $y^2 = \rho/c_{44}$ and $y^2 = \rho/c_{33}$. If $c_{33} > c_{44}$, $y_2 = (\rho/c_{44})^{1/2}$ and $y_3 = (\rho/c_{33})^{1/2}$.

The density of vibrational states $g(\omega)d\omega$ is then given by

$$\begin{aligned} g(\omega) &= \frac{1}{8\pi^3} \frac{dV}{d\omega} = \frac{3\omega^2}{4\pi^2} \sum_{i=1}^3 \int_0^{y_i} R_i^2 dy, \\ &= A_P \omega^2, \end{aligned} \quad (16)$$

which leads to

$$\Theta_0^{\text{el}} = \frac{h}{k} \left[\frac{9N}{VA_P} \right]^{1/3}. \quad (17)$$

Pynn was able to show that the constant A_p , which appears in (16), can be expressed as a sum of simple algebraic functions and elliptic integrals of the first and second kinds.

III. DATA

The experimental data employed in the calculations are summarized in Table I. Usually the most recent measurement has been followed. For Tl and

BeO, two sets of elastic constants have been reported which differ from each other and appear to have the same sort of accuracy; calculations were carried out for both sets and these are represented by Tl-1 and Tl-2, and BeO-1 and BeO-2 in Tables I and II. When the density was given in the reference from which elastic constants were taken, it has been followed. For other cases, a number of sources¹⁴⁻¹⁸ were used and where necessary, correction was made for the thermal expansion.^{14,15,18,19}

TABLE I. Experimental data used in calculations. The sources for the elastic-constant data are given in the ninth column. All elastic constants are in the units of 10^{11} dyn/cm². The data are at the temperature indicated in the third column.

Group	Substance	Temp. (K)	c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	Ref.	Density ρ (g/cm ³)
0	He	1.4	0.00405	0.00554	0.00124	0.00212	0.00105	a	0.19087
2a	Be	0	29.94	34.22	16.62	2.76	1.1	b	1.851
	Mg	0	6.348	6.645	1.842	2.594	2.170	c	1.763
	Zn	4.2	17.909	6.88	4.595	3.75	5.54	d	7.277
	Cd	0	13.08	5.737	2.449	4.048	4.145	e	8.840
3a	Tl-1	4.2	4.44	6.02	0.88	3.76	3.0	f	12.134
	Tl-2	4.2	4.53	6.11	0.903	3.86	2.92	g	12.10
3b	Sc	300	9.93	10.7	2.77	3.97	2.94	h	2.989
	Y	0	8.34	8.01	2.69	2.91	1.9	i	4.498
4a	C	300	106	3.65	0.4	10.8	1.5	j	2.26
	(Graphite)								
4b	Ti	4	17.61	19.05	5.08	8.69	6.83	k	4.528
	Zr	4	15.54	17.25	3.63	6.72	6.46	k	6.524
	Hf	4	19.01	20.44	6.00	7.45	6.55	k	13.288
7b	Re	4.2	63.44	70.16	16.91	26.6	20.2	l	21.112
8	Co	298	30.71	35.81	7.55	16.50	10.27	m	8.836
	Ru	300	56.3	62.4	18.1	18.8	16.8	h	12.41
La	Pr	10	5.080	5.570	1.485	2.46	1.48	n	6.794
	Nd	6	5.878	6.513	1.620	2.458	1.62	o	7.007
	Gd	0	7.680	7.899	2.378	3.145	1.91	p	7.949
	Tb	0	7.836	8.243	2.518	2.777	2.005	p	8.232
	Dy	0	8.104	8.506	2.677	3.740	1.875	q	8.575
	Ho	0	7.99	8.223	2.847	2.66	1.845	q	8.840
	Er	10	8.675	8.205	2.648	2.851	2.418	r	9.158
	Lu	0	9.104	8.401	2.908	3.19	2.88	s	9.930
	H ₂	4.2	0.042	0.051	0.011	0.018	0.005	t	0.08745
	D ₂	4.2	0.082	0.102	0.023	0.029	0.009	t	0.1981
	AgI	10	3.74	4.39	4.10	2.88	2.38	u	5.994
	BeO-1	298	46.06	49.16	14.77	12.65	8.848	v	3.01
	BeO-2	298	47.0	49.4	15.3	16.8	11.9	w	3.01
	ZnO	300	20.70	20.95	4.48	11.77	10.61	x	5.676
	ZnS	298	12.42	14.00	2.864	6.015	4.54	v	4.089
	ZnTe	300	8.6	9.3	2.02	3.7	3.0	h	6.34
	CdS	4.2	8.75	9.57	1.48	5.455	4.825	y	4.822
	CdSe	298	7.490	8.451	1.315	4.609	3.926	v	5.684

TABLE I. (Continued.)

Group	Substance	Temp. (K)	c_{11}	c_{33}	c_{44}	c_{12}	c_{13}	Ref.	Density ρ (g/cm ³)
	MnAs	303	4.00	11.6	3.4	0.8	1.0	z	6.19
	SiC	300	50.2	56.5	16.9	9.5	5.6	aa	3.2145
	TbHo	300	6.97	7.593	2.371	2.229	1.588	bb	8.5
	CaMg ₂	100	6.124	6.552	1.927	1.76	1.50	cc	1.805
	Cd ₂ Mg	298	5.92	5.00	1.02	3.72	2.97	dd	6.35
	MgZn ₂	0	10.725	12.64	2.77	4.545	2.743	ee	5.09
	TiB ₂	300	69	44	25	41	32	ff	4.504
	CeF ₃	300	18.0	22.5	3.42	8.8	6.4	gg	6.160
	Cd ₃ Mg	298	6.66	4.51	1.33	3.9	2.3	dd	6.9
	SmCo ₅	300	19.68	23.98	4.84	10.32	10.49	hh	8.595
	CsCuCl ₃	300	2.896	4.649	5.490	1.128	1.030	ii	3.66

^aR. H. Crepeau, O. Heybey, D. M. Lee, and S. A. Strauss, Phys. Rev. A **3**, 1162 (1971).

^bJ. F. Smith and C. L. Arbogast, J. Appl. Phys. **31**, 99 (1960).

^cL. J. Slutsky and C. W. Garland, Phys. Rev. **107**, 972 (1957).

^dG. A. Alers and J. R. Neighbours, J. Phys. Chem. Solids **7**, 58 (1958).

^eC. W. Garland and J. Silverman, Phys. Rev. **119**, 1218 (1960).

^fJ. W. Flowers, K. C. O'Brien, and P. C. McEleney, J. Less Common Met. **7**, 393 (1964).

^gR. Weil and A. W. Lawson, Phys. Rev. **141**, 452 (1966).

^hR. F. S. Hearmon, in *Landolt-Bornstein: Numerical Data and Functional Relationships in Science and Technology* (Springer, New York, 1979), Group III, Vol. 11, p. 39.

ⁱJ. F. Smith and J. A. Gjevre, J. Appl. Phys. **31**, 645 (1960).

^jO. L. Blakslee, D. G. Proctor, E. J. Seldin, G. B. Spence, and T. Weng, J. Appl. Phys. **41**, 3373 (1970).

^kE. S. Fisher and C. J. Renken, Phys. Rev. **135**, A482 (1964).

^lM. L. Shepard and J. F. Smith, J. Appl. Phys. **36**, 1447 (1965).

^mH. J. McSkimin, J. Appl. Phys. **26**, 406 (1955).

ⁿJ. D. Greiner, R. J. Schlitz, J. J. Tonnies, F. H. Spedding, and J. F. Smith, J. Appl. Phys. **44**, 3862 (1973).

^oJ. D. Greiner, D. M. Schlader, O. D. McMasters, K. A. Gschneidner, and J. F. Smith, J. Appl. Phys. **47**, 3427 (1976).

^pS. B. Palmer, E. W. Lee, and M. N. Islam, Proc. R. Soc. London, Ser. A **338**, 341 (1974).

^qS. B. Palmer, J. Phys. Chem. Solids **31**, 143 (1970).

^rP. de V. du Plessis, J. Phys. F **6**, 873 (1976).

^sJ. J. Tonnies, K. A. Gschneidner, and F. H. Spedding, J. Appl. Phys. **42**, 3275 (1971).

^tR. Wanner and H. Meyer, J. Low Temp. Phys. **11**, 715 (1973).

^uT. A. Fjeldy and R. C. Hanson, Phys. Rev. B **10**, 3569 (1974).

^vC. F. Cline, H. L. Dunegan, and G. W. Henderson, J. Appl. Phys. **38**, 1944 (1967).

^wG. G. Bentle, J. Am. Ceram. Soc. **49**, 125 (1966).

^xE. F. Tokarev, I. B. Kobayakov, I. P. Kuzmina, A. N. Lobachev, and G. S. Pedo, Fiz. Tverd. Tela (Leningrad) **17**, 2487 (1975).

^yD. Gerlich, J. Phys. Chem. Solids **28**, 2575 (1967).

^zM. Dorfler and K. Barner, Phys. Status Solidi A **17**, 141 (1973).

^{aa}G. Arlt and G. R. Schodder, J. Acoust. Soc. Am. **37**, 384 (1965).

^{bb}C. Isci and S. B. Palmer, Philos. Mag. **35**, 1577 (1977).

^{cc}A. Sumer and J. F. Smith, J. Appl. Phys. **33**, 2283 (1962).

^{dd}Y. Kadota, Y. Ishibashi, and Y. Tokagi, J. Phys. Soc. Jpn. **40**, 1017 (1976).

^{ee}T. Seidenkranz and E. Hegenbarth, Phys. Status Solidi A **33**, 205 (1976).

^{ff}J. J. Gilman and B. W. Roberts, J. Appl. Phys. **32**, 1405 (1961).

^{gg}S. Hart, Phys. Status Solidi A **17**, K107 (1973).

^{hh}D. A. Doane, J. Appl. Phys. **48**, 2591 (1977).

ⁱⁱL. B. Soboleva, I. M. Silvestrova, Z. B. Perekalina, A. B. Gilvarg, and Y. N. Martyshev, Kristallografiya **21**, 1140 (1976).

TABLE II. Calculated and experimental values of Debye temperatures in K. The cases for which Pynn's method does not work are indicated by an asterisk after the calculated value in column 4.

Solid	T for elastic-constant data	$\Theta_0^{\text{dl}}(\text{calc.})$		$\Theta_0^{\text{c}}(\text{expt.})$
		NI	Pynn	
He	1.4	25.82	25.82	26.06 ^a
Be	0	1462.7	1462.7	1481±16 ^b
Mg	0	386.5	386.5	403±4, ^c 440 ⁺¹¹⁰ ₋₅₆ ^d
Zn	4.2	327.1	332.9*	326.8±1.8 ^e
Cd	0	213.8	213.8*	213.2±1.8 ^e
Tl-1	4.2	79.2	79.2	78.5±0.2 ^f
Tl-2	4.2	79.7	79.7	
Sc	300	362.0	362.0	359±4 ^g
Y	0	257.2	257.2	248±3 ^h
Graphite	300	393.9	393.9	413 ⁱ
Ti	4	425.4	425.4	420 ^j
Zr	4	296.1	296.1	291 ^j
Hf	4	251.4	251.4	248 ^j
Re	4.2	405.1	405.1	407±10 ^k
Co	298	453.3	453.3	443 ^l
Ru	300	499.0	499.0	530 ^m
Pr	10	152.0	152.0	85±1 ⁿ
Nd	6	163.4	163.4	
Gd	0	181.7	181.7	187±3 ^o
Tb	0	186.1	186.1	178±2 ^h
Dy	0	182.3	182.3	207±7, ⁿ 207 ^b
Ho	0	188.3	188.3	114±7 ⁿ
Er	10	186.0	186.0	134±10 ⁿ
Lu	0	184.3	184.3	185±1 ^q
H ₂	4.2	119.8	119.8	122 ^r
D ₂	4.2	120.4	120.4	114 ^r
AgI	10	142.2	149.8*	
BeO-1	298	1278.5	1278.5	
BeO-2	298	1260.0	1260.0	
ZnO	300	418.8	418.8	
ZnS	298	349.3	349.3	339 ^s
ZnTe	300	219.3	219.3	
CdS	4.2	215.3	215.3	
CdSe	298	178.3	178.3	
MnAs	303	248.1	248.1	
SiC	300	1172.4	1172.4	
TbHo	300	198.3	198.3	
CaMg ₂	100	376.4	376.4	
Cd ₂ Mg	298	158.3	158.3	
MgZn ₂	0	325.1	325.1	
TiB ₂	300	988.3	1010.3*	
CeF ₃	300	379.3	379.3	
Cd ₃ Mg	298	170.7	170.7	
SmCo ₅	300	330.9	330.9	
CsCuCl ₃	300	239.6	251.5*	

^aW. R. Gardner, J. K. Hoffer, and N. E. Phillips, Phys. Rev. A **7**, 1029 (1973). The quoted value corresponds to 20.97 cm³/mole.

^bG. Ahlers, Phys. Rev. **145**, 419 (1966).

- ^cJ. A. Rayne, *J. Phys. Chem. Solids* **7**, 268 (1958).
^dD. L. Martin, *Proc. Phys. Soc. London* **78**, 1482 (1961).
^eJ. C. Holste, *Phys. Rev. B* **6**, 2495 (1972).
^fB. J. C. van der Hoeven and P. H. Keesom, *Phys. Rev.* **135**, A631 (1964).
^gH. E. Flotow and D. W. Osborn, *Phys. Rev.* **160**, 146 (1967).
^hP. Wells, P. C. Lanchester, D. W. Jones, and R. G. Jordon, *J. Phys. F* **6**, 11 (1976).
ⁱB. J. C. van der Hoeven and P. H. Keesom, *Phys. Rev.* **130**, 1318 (1963).
^jE. W. Collings and J. C. Ho, *Phys. Rev. B* **4**, 349 (1971).
^kR. Blanpain, *Bull. Acad. R. Belg.* **47**, 750 (1961).
^lG. Deykaerts, *Physica (Utrecht)* **6**, 817 (1939).
^mJ. C. Ho and R. Viswanathan, *J. Phys. Chem. Solids* **30**, 169 (1969).
ⁿB. Dreyfus, B. B. Goodman, A. Lacaze, and G. Trolliet, *C. R. Acad. Sci.* **253**, 1764 (1961).
^oP. Wells, P. C. Lanchester, D. W. Jones, and R. G. Jordon, *J. Phys. F* **4**, 1729 (1974).
^pO. V. Lounasmaa and L. J. Sundstrom, *Phys. Rev.* **150**, 399 (1966).
^qW. A. Taylor, M. B. Levy, and F. H. Spedding, *J. Phys. F* **8**, 2293 (1978).
^rR. J. Roberts, *Phys. Abstr.* 72-43985, Stevens Institute Technology, Hoboken, N. J., thesis, 1971 (unpublished).
^sJ. A. Birch, *J. Phys. C* **8**, 2043 (1975).

Calculations of the Debye temperature were carried out using both the numerical-integration method and Pynn's method. The results are shown in Table II and where data are available, compared with experimental calorimetric Debye temperatures.

We have included in our list a number of substances for which elastic constants have been measured at room temperature but not in the vicinity of 0 K. The Debye temperature calculated from such data need not be equal to Θ_0^e . The Debye temperature is involved in a number of physical properties besides the heat capacity, e.g., thermal expansion, electrical resistivity, Debye-Waller factor, etc. While, strictly speaking, the Debye temperatures involved in the different physical properties are not identical, frequently they are close to each other. It was felt that even approximate values of the Debye temperature would be of use.

IV. DISCUSSION

A comparison of Θ_0^{el} values calculated by NI with those obtained from Pynn's method showed that in most cases the agreement between the two was excellent, as expected; however, there was a number of cases in which there were significant discrepancies. A careful analysis of these cases revealed that Pynn's method is not applicable under certain conditions. To explain the source of the trouble, we note that Pynn's method requires the integration of R_i^2 from zero to the first positive root of R_i [Eq. (16)]. Also one notes that in finding the roots of R_2^2 and R_3^2 one arrives at the same

equation, (15). At this point one must decide which solution of (15) refers to R_2^2 and which to R_3^2 . The term $(cy^4 + dy^2 + e)^{1/2}$ can be either positive or negative. We need consider only one case, say when it is positive, because when it is negative the roles of R_2^2 and R_3^2 are merely exchanged. For R_2^2 to have a root at a certain value of y , y_2 , the term $a + by^2$ must be positive, and conversely for R_3^2 to have a root at y_3 , $a + by^2$ must be negative. Also one notes that a is always negative. Thus, for $y^2 > (-a/b)$, $a + by^2 > 0$, and for $y^2 < (-a/b)$, $a + by^2 < 0$. Thus one must consider three cases. In the following it is assumed that $c_{33} > c_{44}$. If this is not the case, it is only necessary to interchange ρ/c_{33} and ρ/c_{44} in what follows.

Case 1: $(-a/b) < \rho/c_{33}$. Then $a + by^2$ is positive for both $y^2 = \rho/c_{33}$ and $y^2 = \rho/c_{44}$, so that R_3^2 has no roots. Both the solutions of (15) belong to R_2^2 .

Case 2: $\rho/c_{33} < (-a/b) < \rho/c_{44}$. In this case $a + by^2$ is negative for $y^2 = \rho/c_{33}$ and positive for $y^2 = \rho/c_{44}$, so that both R_2^2 and R_3^2 have a positive root.

Case 3: $\rho/c_{44} < (-a/b)$. Then $a + by^2$ is negative for both $y^2 = \rho/c_{33}$ and $y^2 = \rho/c_{44}$ so that R_2^2 has no roots. Both the solutions of (15) refer to R_3^2 . This situation is illustrated in Fig. 1 for TiB₂, which belongs to this class.

Thus, for cases 1 and 3 Pynn's method fails; the condition for the method to succeed is that $(-a/b)$ should lie between ρ/c_{33} and ρ/c_{44} . If this is the case, then

$$y_2 = \text{larger of } (\rho/c_{44})^{1/2} \text{ and } (\rho/c_{33})^{1/2}$$

and

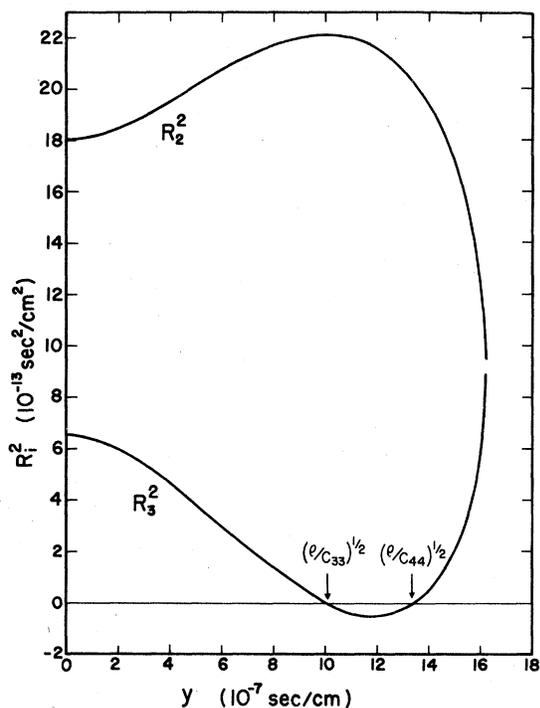


FIG. 1. The variation of R_2^2 and R_3^2 with y , for TiB_2 . R_2^2 does not become zero for any real value of y . For $y > 16.19 \times 10^{-7}$ sec/cm, $(cy^4 + dy^2 + e)$ becomes negative and both R_2^2 and R_3^2 become complex.

$$y_3 = \text{smaller of } (\rho/c_{44})^{1/2} \text{ and } (\rho/c_{33})^{1/2}.$$

There are five substances in our list which belong to case 1 or 3. Such substances are identified by an asterisk adjacent to the calculated value in column 4 of Table II. For Cd the discrepancy between the NI value and Pynn's value is negligible because it is a borderline case; the above condition is just violated for this crystal.

A way of modifying Pynn's method for "non-Pynn" substances is the following. It consists of adding to the areas included in the integrations of Pynn's method, the area between the curves R_3^2 and R_2^2 from the point $y = (\rho/c_{44})^{1/2}$ to the point y' , where the two curves intersect (see Fig. 1). y' is given by the positive real solution of $cy^4 + dy^2 + e = 0$. This reduces to replacing $[I(\rho/c_{44}) - I(\rho/c_{33})]$ in Pynn's¹¹ equation (9) by $[2I(y'^2) - I(\rho/c_{44}) - I(\rho/c_{33})]$. We have calculated the Debye temperatures for the five non-Pynn substances in our list by this modified Pynn's method and the results are shown in Table III. It will be noticed that the values thus obtained are in excel-

TABLE III. Calculated values of Debye temperatures (in K) from the modified Pynn's method for "non-Pynn" substances.

Solid	θ_0^{el} (calc.)	
	NI	Modified Pynn's method
Zn	327.1	327.1
Cd	213.8	213.8
AgI	142.2	142.2
TiB ₂	988.3	988.3
CsCuCl ₃	239.6	239.6

lent agreement with the NI values.

Next we consider the theoretical and experimental θ_0 's for individual substances. For Sc, graphite, Co, Ru, and ZnS the elastic constants used in the calculations are at a temperature of about 300 K, thus a meaningful comparison between θ_0^{el} and θ_0^{c} for these substances is not possible.

He. The agreement between the calculated and the experimental value is reasonable.

Be. There is a large uncertainty in the experimental value. The theoretical value lies just outside the lower limit of the experimental value. A fresh determination of θ_0^{c} would be worthwhile.

Mg. There is seen to be a large discrepancy between the calculated value and the first quoted experimental value. Wolcott²⁰ had drawn attention to this discrepancy. Subsequently, Martin²¹ measured the specific heat of magnesium in the temperature range 0.4–1.5 K, but found that the lattice specific heat in this range was so small that an accurate value of θ_0^{c} could not be obtained, as may be seen from the second θ_0^{c} listed in the table.

Zn, Cd, Tl. The agreement between the theoretical and experimental values is satisfactory.

Y. There is a 7° difference between θ_0^{el} and the upper limit of θ_0^{c} .

Ti, Zr, Hf. There are small differences between the calculated and experimental values, but the uncertainties in the experimental values are not known.

Re. Within the large uncertainty of the experimental value there is agreement with the calculated value.

Pr. There is a very large discrepancy between θ_0^{el} and θ_0^{c} . The experimental value almost certainly seems to be in error.

Tb. There is a discrepancy of 6° between θ_0^{el} and the upper limit of θ_0^{c} .

Dy. There is a discrepancy of 18° between θ_0^{el} and the lower limit of θ_0^{c} .

Ho. The calculated value is greater than the upper limit of the experimental value by 67° . The experimental value appears to be in error.

Er. Situation is similar to that of Ho. There is a large discrepancy of 42° .

H₂, D₂. The calculated values for the two are quite close. There appears to be a reasonable agreement between θ_0^{el} and θ_0^{c} for H₂, but for D₂ there seems to be a small discrepancy.

In summary, we find that there are large discrepancies between θ_0^{el} and θ_0^{c} for Pr, Dy, Ho,

and Er, and small ones for several other elements. Where there are large discrepancies, θ_0^{c} deserves to be reinvestigated. Small discrepancies could be due to inaccuracies in one or more of the three—elastic constants, density, and specific heat. For rare earths the calculated values of the Debye temperature presented here should prove to be useful for analyzing low-temperature specific-heat data.

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- ¹M. Blackman, *Encyclopedia of Physics*, edited by S. Flügge (Springer, Berlin, 1955), Vol. VII, p. 325.
- ²G. A. Alers, in *Physical Acoustics*, edited by W. P. Mason (Academic, New York, 1965), Vol. III B.
- ³A. Konti and Y. P. Varshni, *Can. J. Phys.* **47**, 2021 (1969).
- ⁴A. Konti and Y. P. Varshni, *Can. J. Phys.* **49**, 3115 (1971).
- ⁵Y. P. Varshni and A. Konti, *J. Phys. C* **5**, 2562 (1972).
- ⁶H. M. Ledbetter, *J. Phys. F* **2**, 262 (1972).
- ⁷H. M. Ledbetter, *J. Appl. Phys.* **44**, 1451 (1973).
- ⁸N. M. Wolcott, *J. Chem. Phys.* **31**, 536 (1959).
- ⁹D. D. Betts, A. B. Bhatia, and G. K. Horton, *Phys. Rev.* **104**, 43 (1956).
- ¹⁰T. G. Bystrova and F. I. Fedorov, *Kristallografiya* **12**, 11 (1967) [*Sov. Phys.—Crystallogr.* **12**, 9 (1967)].
- ¹¹R. Pynn, *Can. J. Phys.* **49**, 1690 (1971).
- ¹²R. W. G. Wyckoff, *Crystal Structures*, 2nd ed. (Interscience, New York, 1963), Vol. I, pp. 94–96.
- ¹³M. J. P. Musgrave, *Crystal Acoustics* (Holden-Day, San Francisco, 1970), p. 94ff.
- ¹⁴*American Institute of Physics Handbook*, edited by D. E. Gray (McGraw-Hill, New York, 1972).
- ¹⁵*Handbook of Chemistry and Physics*, edited by R. C. Weast (Chemical Rubber, Cleveland, 1978).
- ¹⁶W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, New York, 1958).
- ¹⁷A. Taylor and B. J. Kagle, *Crystallographic Data on Metal and Alloy Structures* (Dover, New York, 1963).
- ¹⁸K. A. Gschneidner, Jr., *Solid State Phys.* **16**, 275 (1964).
- ¹⁹*Thermophysical Properties of Matter*, edited by Y. S. Touloukian (IFI/Plenum, New York, 1975), Vol. 12; (IFI/Plenum, New York, 1977), Vol. 13.
- ²⁰N. M. Wolcott, *Proc. Phys. Soc. London* **77**, 218 (1961).
- ²¹D. L. Martin, *Proc. Phys. Soc. London* **78**, 1482 (1961).