

Debye Temperature of Orthorhombic Crystals at 0°K

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(Received July 26, 1960; revised manuscript received September 20, 1960)

Explicit formulas are obtained for the Debye characteristic temperature of orthorhombic crystals by an extension of Houston's method of expanding the integrand involved in terms of appropriate harmonic polynomials. Θ (elastic) values have been computed for twelve crystals and the results are discussed.

I. INTRODUCTION

AT sufficiently low temperatures, approaching 0°K, only the extreme low-frequency end of the lattice vibration spectrum which corresponds to waves of very long wavelength, will be excited. The propagation of these waves, whose wavelength is long as compared to interatomic distances, should not be affected by the details of the atomic arrangement. The lattice specific heat then becomes that of an elastic continuum, and Θ_D , the characteristic temperature determined calorimetrically, should agree with Θ (elastic) calculated from elastic constants.

Many methods of evaluating Θ (elastic) for cubic crystals are available.^{1,2} For hexagonal crystals Wolcott³ has provided tables for evaluating Θ (elastic) over a range of elastic parameters. For substances of lower symmetry than hexagonal, such as tetragonal and trigonal, the method of Betts, Bhatia, and Horton⁴ needs to be used. Here an analogous method for orthorhombic crystals is proposed, which makes possible the computation of their characteristic temperatures, without being prohibitive in time and effort.

II. THEORY

In the Debye continuum model Θ (elastic) is given by

$$\Theta_0(\text{elastic}) = (h/k)(9N/4\pi VI)^{\frac{1}{3}}, \quad (1)$$

where N is the number of vibrating units in the volume V , h and k have their usual meanings, I is defined by

$$I = \sum_{i=1}^3 \int_0^{4\pi} \frac{d\Omega}{v_i^3}, \quad (2)$$

and the v_i are the velocities of propagation of elastic waves in the continuum at 0°K. These velocities are given by the three roots of the third order Christoffel equation⁵ and hence, in general, involve the solution of a cubic equation. These roots will be functions of elastic constants and direction of propagation of the wave.

¹ M. Blackman, *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII, Part I, p. 325.

² G. A. Alers and J. R. Neighbours, *Revs. Modern Phys.* **31**, 675 (1959).

³ N. W. Wolcott, *J. Chem. Phys.* **31**, 536 (1959).

⁴ D. D. Betts, A. B. Bhatia, and G. K. Horton, *Phys. Rev.* **104**, 43 (1956).

⁵ A. E. H. Love, *Mathematical Theory of Elasticity* (Dover Publications, New York, 1944), p. 299.

The problem of estimation of Θ (elastic) is thus really reduced to the evaluation of the integral I , which we write as

$$I = \rho^{\frac{1}{3}} \int_0^{4\pi} f(\theta, \phi) d\Omega. \quad (3)$$

In (3), $f(\theta, \phi) = \sum_i [v_i]^{-3} \rho^{-\frac{1}{3}}$, which can be expanded in terms of harmonics, $F_{lm}(\theta, \phi)$, having the same symmetry as the corresponding Christoffel equation⁴:

$$f(\theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^l a_{lm} F_{lm}(\theta, \phi). \quad (4)$$

From the properties of spherical harmonics we have the exact relation

$$\frac{1}{4\pi} \int_0^{4\pi} f(\theta, \phi) d\Omega = a_{00} = a_0. \quad (5)$$

Our approximation consists in stopping the summation in (4) at a particular l and m . The coefficient a_0 is found by solving the linear equations (4), obtained by giving various values to (θ, ϕ) .

For orthorhombic crystals we take a twofold rotation axis as the polar axis, $\theta=0$. The Christoffel equation is invariant under the transformations

$$\theta = \pi - \theta, \quad \phi = -\phi \quad \text{or} \quad \phi = \phi + \pi.$$

The appropriate "orthorhombic harmonics" are

$$O_{2l, 2m}(\theta, \phi) = \cos 2m\phi P_{2l}^{2m}(\cos \theta), \quad (6)$$

with $2m \leq 2l$, $l, m=0, 1, 2, \dots$. Solving the corresponding equations (4), we find

$$a_0 = [7f_B - 36f_C + 16f_D + 48f_E + 25f_F]/15, \quad (7.1)$$

$$a_0 = [20f_A + 21f_B - 48f_C + 48f_D + 64f_E + 75f_F]/180, \quad (7.2)$$

$$a_0 = [519f_A + 45f_B - 1008f_C + 480f_D + 1344f_E + 1575f_F + 825f_G]/3780, \quad (7.3)$$

in which the subscripts on f signify its value in the corresponding directions. The directions chosen are, $A(100)$, $B(001)$, $C(010)$, $D(101)$, $E(1\sqrt{3}0)$, $F(021)$, and $G(102)$. In deriving (7.1), (7.2), and (7.3) all orthorhombic harmonics (6) up to O_{42} , O_{44} , and O_{60} , respectively, are utilized. We stop at O_{60} because Eqs.

TABLE I. Debye characteristic temperatures and elastic constants for certain orthorhombic crystals.

Formula	Substance	ρ g cm ⁻³	Molecular weight	Elastic constants in units of 10 ¹¹ dynes/cm ²									Ref.	Characteristic temp. in °K		
				c_{11}	c_{22}	c_{33}	c_{44}	c_{55}	c_{66}	c_{12}	c_{13}	c_{23}		Θ_0^1	Θ_0^2	Θ_0^3
CaCO ₃	Aragonite	2.93	100.09	16.0	8.7	8.5	4.12	2.56	4.27	3.73	0.17	1.57	6	383	382	387
BaSO ₄	Baryte	4.50	233.43	8.62	9.17	10.8	1.20	2.87	2.74	5.23	3.41	3.56	6	224	221	222
SrSO ₄	Celestite	3.96	183.70	10.44	10.61	12.86	1.35	2.79	2.66	7.73	6.05	6.19	6	226	233	226
MgSO ₄ ·7H ₂ O	Epsom salt	1.636	246.50	6.98	5.29	8.22	1.07	2.33	2.22	3.90	2.82	2.83	7	345	331	332
HIO ₃	Iodic acid	4.629	175.93	3.03	5.45	4.36	1.84	2.19	1.74	1.19	1.17	0.55	7	157	159	160
NaK(C ₄ H ₄ O ₆)·4H ₂ O	Rochelle salt	1.77	282.23	3.62	4.72	5.47	1.27	0.308	0.975	2.31	2.73	2.69	8	213	207	204
Na ₂ (C ₄ H ₄ O ₆)·2H ₂ O	Sodium tartarate	1.818	230.10	4.61	5.47	6.65	1.24	0.31	0.98	2.86	3.20	3.52	7	215	203	206
Sr(CHO ₂) ₂	Strontium formate	2.69	177.67	4.39	3.48	3.74	1.54	1.07	1.72	1.04	-1.49	-0.14	7	232	234	235
S ₈	Sulfur	2.07	256.53	2.40	2.05	4.83	0.43	0.87	0.76	1.33	1.71	1.59	6	102	104	103
Al ₂ (F,OH) ₂ ·SiO ₄	Topaz	3.5	218.07	28.2	34.9	29.5	10.8	13.3	13.1	12.6	8.5	8.8	6	743	772	765
U	uranium	18.9	238.09	21.47	19.86	26.71	12.444	7.342	7.433	4.65	2.18	10.76	9	230	238	240
ZnSO ₄ ·7H ₂ O	Zinc sulfate	1.97	287.56	4.00	3.22	5.45	0.50	1.70	1.81	1.32	1.08	1.19	7	312	292	298

(7) are found to be sufficiently convergent and also because the subsequent formulas tend to become unwieldy.

The Christoffel equation for the sound velocities for the general direction (l, m, n) , in case of orthorhombic crystals, takes the form,

$$\begin{vmatrix} c_{11}l^2 + c_{66}m^2 + c_{55}n^2 - \rho v^2 & (c_{12} + c_{66})lm & (c_{13} + c_{55})ln \\ (c_{12} + c_{66})lm & c_{66}l^2 + c_{22}m^2 + c_{44}n^2 - \rho v^2 & (c_{23} + c_{44})mn \\ (c_{13} + c_{55})ln & (c_{23} + c_{44})mn & c_{55}l^2 + c_{44}m^2 + c_{33}n^2 - \rho v^2 \end{vmatrix} = 0. \quad (8)$$

On solving this equation along the directions $A, B, \dots G$, defined above, one finds the following expressions for f_A, f_B , etc.

$$\begin{aligned} f_A &= [c_{11}]^{-\frac{1}{2}} + [c_{55}]^{-\frac{1}{2}} + [c_{66}]^{-\frac{1}{2}}, \\ f_B &= [c_{33}]^{-\frac{1}{2}} + [c_{44}]^{-\frac{1}{2}} + [c_{55}]^{-\frac{1}{2}}, \\ f_C &= [c_{22}]^{-\frac{1}{2}} + [c_{44}]^{-\frac{1}{2}} + [c_{66}]^{-\frac{1}{2}}, \\ f_D &= \left[\frac{1}{2}(c_{44} + c_{66}) \right]^{-\frac{1}{2}} + \left[\frac{1}{4}(c_{11} + c_{33} + 2c_{55}) + \frac{1}{4}\{(c_{11} - c_{33})^2 + 4(c_{13} + c_{55})^2\}^{\frac{1}{2}} \right]^{-\frac{1}{2}} \\ &\quad + \left[\frac{1}{4}(c_{11} + c_{33} + 2c_{55}) - \frac{1}{4}\{(c_{11} - c_{33})^2 + 4(c_{13} + c_{55})^2\}^{\frac{1}{2}} \right]^{-\frac{1}{2}}, \\ f_E &= \left[\frac{1}{4}(3c_{44} + c_{55}) \right]^{-\frac{1}{2}} + \left[\frac{1}{8}(c_{11} + 3c_{22} + 4c_{66}) + \frac{1}{8}\{(c_{11} - 3c_{22} + 2c_{66})^2 + 12(c_{12} + c_{66})^2\}^{\frac{1}{2}} \right]^{-\frac{1}{2}} \\ &\quad + \left[\frac{1}{8}(c_{11} + 3c_{22} + 4c_{66}) - \frac{1}{8}\{(c_{11} - 3c_{22} + 2c_{66})^2 + 12(c_{12} + c_{66})^2\}^{\frac{1}{2}} \right]^{-\frac{1}{2}}, \\ f_F &= \left[\frac{1}{5}(c_{55} + 4c_{66}) \right]^{-\frac{1}{2}} + \left[\frac{1}{10}(4c_{22} + c_{33} + 5c_{44}) + \frac{1}{10}\{(c_{33} + 3c_{44} - 4c_{22})^2 + 16(c_{23} + c_{44})^2\}^{\frac{1}{2}} \right]^{-\frac{1}{2}} \\ &\quad + \left[\frac{1}{10}(4c_{22} + c_{33} + 5c_{44}) - \frac{1}{10}\{(c_{33} + 3c_{44} - 4c_{22})^2 + 16(c_{23} + c_{44})^2\}^{\frac{1}{2}} \right]^{-\frac{1}{2}}, \\ f_G &= \left[\frac{1}{5}(4c_{44} + c_{66}) \right]^{-\frac{1}{2}} + \left[\frac{1}{10}(c_{11} + 4c_{33} + 5c_{55}) + \frac{1}{10}\{(c_{11} + 3c_{55} - 4c_{33})^2 + 16(c_{13} + c_{55})^2\}^{\frac{1}{2}} \right]^{-\frac{1}{2}} \\ &\quad + \left[\frac{1}{10}(c_{11} + 4c_{33} + 5c_{55}) - \frac{1}{10}\{(c_{11} + 3c_{55} - 4c_{33})^2 + 16(c_{13} + c_{55})^2\}^{\frac{1}{2}} \right]^{-\frac{1}{2}}. \end{aligned} \quad (9)$$

III. CALCULATION OF Θ (ELASTIC) AND DISCUSSION

The characteristic temperatures for almost all the orthorhombic crystals for which elastic constants are available, are calculated. The elastic constants and the calculated Θ (elastic) values are presented in Table I.⁶⁻⁹ Θ_0^1 , and Θ_0^2 , and Θ_0^3 in the table refer to the characteristic temperatures calculated from (1) using (7.1), (7.2), and (7.3), respectively. Θ_0^2 and Θ_0^3 differ only little from each other in most of the cases. However, for SrSO₄ and ZnSO₄·7H₂O this difference is about 2.6% and 2.7%, respectively. To improve the situation,

one will have to use higher term approximations than those used here.

For an accurate evaluation of Θ (elastic), the values of elastic constants measured near 0°K should have been used. In the absence of such data we are forced to use elastic constants measured at or near room temperature. Hence, the absolute values of the characteristic temperatures are unreliable to some extent, but the variation in Θ (elastic) values in consequence of the variation of elastic constants with temperature is not very large.¹ No calorimetric data are available for these listed substances in the true T^3 region, to make a comparison possible.

ACKNOWLEDGMENTS

The author is deeply indebted to Professor K. Banerjee for his interest in the investigation and to Dr. A. B. Bhatia of the University of Alberta, Canada, for helpful correspondence.

⁶ H. B. Huntington, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 284.

⁷ R. F. S. Hearmon, *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1956), Vol. 5, p. 323.

⁸ R. F. S. Hearmon, *Brit. J. Appl. Phys.* **3**, 120 (1952).

⁹ E. S. Fisher and H. J. McSkimin, *J. Appl. Phys.* **29**, 1473 (1958).