

A Calculation of the Debye Characteristic Temperature of Cubic Crystals^{*}

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A new empirical expression is developed to calculate the Debye characteristic temperature of cubic crystals. The calculated Debye temperatures for 24 cubic crystals are shown to be in excellent agreement with other existing computations as well as with the experimental results.

Uma nova expressão empírica é desenvolvida para calcular a temperatura característica de Debye de cristais cúbicos. Mostra-se que as temperaturas de Debye, calculadas para 24 cristais cúbicos, estão em excelente acordo com outros cálculos bem como com os resultados experimentais.

1. Introduction

Near absolute zero, a solid can be very well represented by means of Debye's continuum model. The calculation of $\theta_0(D)$, the Debye characteristic temperature at absolute zero, is then given in terms of the elastic constants of the solid. In the past, several theoretical expressions have been developed by Blackman¹, de Launay², Hopf-Lechner³, Houston⁴, Bhatia and Tauber⁵ and by Fedorov⁶. All these methods utilize physical properties of the crystal which can be expressed in terms of averages involving its elastic constants. Recently, Konti and Varshni⁷ have reviewed and revised the different methods of calculating $\theta_0(D)$, for 24 cubic solids. We have developed a very simple expression to calculate $\theta_0(D)$ under the assumption that cubic solids show polycrystalline behavior as well as are well represented by Debye's model at absolute zero. The calculated values of $\theta_0(D)$, for 24 cubic crystals, have been compared

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with the experimental results as well as with the results of Konti and Varshni⁷.

2. Theory

In the Debye model, the expression of $\theta_0(D)$ is given by

$$\theta_0(D) = \frac{h}{k} \left(\frac{9N}{4\pi V^2} \right)^{1/3} \left[\frac{2}{u_t^3} + \frac{1}{u_l^3} \right]^{-1/3}, \quad (1)$$

where h = Planck's constant, k = Boltzmann's constant, N = Avogadro's number, V = atomic volume, u , = longitudinal sound velocity, u_t = transversal sound velocity. The sound velocities are given by the following relations:

$$u_l = (K + \frac{4}{3}G)^{1/2} \rho^{-1/2}, \quad (2)$$

$$u_t = G^{1/2} \rho^{-1/2}, \quad (3)$$

where ρ = density of solid, K = bulk modulus, C , = rigidity modulus. The bulk and rigidity moduli are functions of the elastic constants only.

If a solid exhibits monocrystalline behavior, then it possesses a single value for the quantities K and C . On the other hand, in the case of a solid showing polycrystalline behavior, there are two different approaches, one due to Reuss⁸ and the other to Voigt⁹, to calculate K and G in terms of the elastic constants of the solid. Let us denote these moduli by K_R and C , , when determined by Reuss' method, and K_V and G_V when determined by Voigt's method. These quantities are given by the following relations:

$$K_R = K_V = \frac{1}{3}(C_{11} + 2C_{12}), \quad (4)$$

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44})^{-1}, \quad (5)$$

$$G_R^{-1} = \frac{4}{5}(C_{11} - C_{12})^{-1} + \frac{3}{5}C_{44}^{-1}. \quad (6)$$

Hill¹⁰, in calculating some other properties of crystalline solids, has shown that, in practice, the actual values of K and C , lie in between the limits predicted by the two theories

$$K_V \leq K \leq K_R, \quad (7)$$

$$G_V \leq G \leq G_R. \quad (8)$$

The equality of K_R and K_V automatically makes $K = K_R = K_V$. Thus, we are left with the task of choosing a proper value for C ; lying in between G_R and G_V . Hill¹⁰ recommended that the appropriate value of C ; should be taken either as the arithmetic mean (A.M.) or the geometric mean (G.M.) of C_v and G_R . Zucker¹¹ has shown that both these means give identical results for isotropic solids but, for anisotropic solids, the G.M. was found a better choice than the A.M.. Brown¹² has utilized Zucker's formula to calculate $\theta_0(D)$ for palladium and also confirmed Zucker's hypothesis.

When we made a comparative study of $\theta_0(D)$ for several cubic solids, using Zucker's¹¹ expression, we found that the calculated $\theta_0(D)$ was always greater in the A.M. approximation than in the G.M. approximation. The results predicted by the G.M. approximation were also higher than the experimental results. We were thus convinced that to get the calculated values for $\theta_0(D)$ closer to the experimental results, we needed the value of C ; smaller than that predicted by the G.M. approximation. We thus thought of another mean averaging procedure, namely, the harmonic mean (H.M.), given by

$$G = \frac{2G_R G_v}{C_v + C_v} \quad (9)$$

With the help of equations (1), (4), (5), (6) and (9), we obtain the following empirical expression for $\theta_0(D)$

$$\theta_0(D) = \frac{h}{k} \left(\frac{9N}{4\pi V} \right)^{1/3} \left(\frac{C_{44}}{\rho} \right)^{1/2} \left[\frac{2}{A^{3/2}} + \frac{1}{(B + \frac{1}{3}A)^{3/2}} \right]^{-1/3}, \quad (10)$$

where

$$A = \frac{10}{3} \frac{(g^2 + g - 20)}{(g^2 + 30g - 300)}, \quad (11)$$

$$B = \frac{g + 5}{9} + t, \quad (12)$$

and

$$g = 4 - 3t + 3S + 3St, \quad (13)$$

$$S = (C_{11} - C_{44})/(C_{12} + C_{44}), \quad (14)$$

$$t = (C_{12} - C_{44})/C_{44}. \quad (15)$$

3. Numerical Computation

The calculation of $\theta_0(D)$ was carried out with the help of equation (10), for 24 cubic crystals. The input data with their appropriate sources are presented in Table 1 and the calculated $\theta_0(D)$ are given in Table 2 together with the experimental Debye temperature as well as the best calculated values for $\theta_0(D)$ as given by Konti and Varshni⁷. In order to compare our calculations with those of Ref. 7, we have used the same elastic constants as Konti and Varshni.

Element	T (°K)	a (10^{-8} cm)	C_{11} (10^{11} dyn/cm ²)	C_{12} (10^{11} dyn/cm ²)	C_{44} (10^{11} dyn/cm ²)	Source of the elastic constants
Ar	0	5.3110	0.3732	0.1262	0.1771	Moeller and Squire ¹³
Li ⁻	78	3.50	1.481	1.248	1.077	Nash and Smith ¹⁴
Na	78	4.2349	0.815	0.679	0.578	Diederich and Trivisonno ¹⁵
K	4.2	5.225	0.416	0.341	0.286	Marquardt and Trivisonno ¹⁶
Rb-1	0	5.585	0.316 ± 0.017	0.211 ± 0.020	0.211 ± 0.020	Robert and Meister ^{**}
Rb-2	0	5.585	0.358	0.221	0.221	Gutman and Trivisonno ¹⁸
Cu	0	3.6029	17.62	8.177	8.177	Overton and Gaffney ¹⁹
Ag	0	4.0691	13.149	5.109	5.109	Neighbours and Alers ²⁰
Au	0	4.0649	20.163	4.544	4.544	Neighbours and Alers ²⁰
Al	0	4.0328	11.430	3.162	3.162	Kamm and Alers ²¹
Diamond	300	3.5670	107.6	57.58	57.58	McSkimin and Bond ²²
Si	77	5.4294	16.772	8.035	8.035	McSkimin and Andreatch ²³
Ge	77	5.6524	13.11	6.816	6.816	McSkimin and Andreatch ²⁴
Pb	0	4.9146	5.554	1.942	1.942	Waldorf and Alers ²⁵
V	0	3.0352	23.24	4.595	4.595	Alers ²⁶
Nb	4.2	3.2961	25.27	3.097	3.097	Carroll ²⁷
Ta	0	3.2979	26.632	8.736	8.736	Featherston and Neighbours ²⁸
Mo	0	3.1470	45.002	12.503	12.503	Featherston and Neighbours ²⁸
W	0	3.1620	53.255	20.495	16.313	Featherston and Neighbours ²⁸
Fe	0	2.8607	23.7	13.5	11.95	Lord and Beshers ²⁹
Ni	0	3.5160	26.12	15.08	13.17	Alers <i>et al.</i> ³⁰
Pd	0	3.8808	23.41	17.61	7.12	Rayne ³¹
Ir	0	3.8336	59.6	25.2	27.0	MacFarlane <i>et al.</i> ³²
Pt	0	3.9160	35.8	25.36	7.74	MacFarlane <i>et al.</i> ³²
Th	0	5.0612	7.79	4.82	5.13	Armstrong <i>et al.</i> ³³

Table 1 - Summary of experimental data used in calculations. (The lattice constant³⁴⁻³⁵ and the elastic constants are at the temperature indicated in the 2nd column.

4. Discussion

a) Comparison with Experimental Results

Argon: A reasonable agreement between calculated and experimental Debye temperature.

Lithium: The agreement is poor. This is because elastic constants were not available at very low temperature and therefore we have used elastic constants at 78°K and at that temperature the solid is no more cubic.

Element	6 calculated	6 experimental	θ (Konti and Varshni)
Cu	345.9	345.6 \pm 1.0	344.0
Ag	227.1	226.6 \pm 1.0	226.2
Au	161.5	162.4 \pm 2	161.0
Pd	276.2	270	275.6
Ni	504.5	477.4 \pm 6.2	475.9
		489.9 \pm 2.0	
Th	165.4	170	163.7
Ar	91.22	93.3 \pm 0.6	91.2
		427.7 \pm 1.0	
Al	428.77	436.4 \pm 0.7	430.5
Ir	429.21	420	429.6
Pt	237.77	234.9 \pm 0.4	238.3
Pb	105.17	106.7 \pm 0.5	104.9
Li	314.81	344 \pm 2.5	317.8
Na	143.00	152.5 \pm 2	144.3
K	89.36	90.6 \pm 1.4	89.1
Diamond	2231.23	2219 \pm 20	2239.6
Si	648.34	645 \pm 5	648.9
Ge	373.5	374 \pm 2	373.4
V	397.58	399	399.1
Nb	277.05	277	275.7
Ta	263.37	258	263.7
Mo	472.38	460	474.5
W	382.58	390	384.4
		472.7 \pm 6.0	
Fe- α	474.72	485.6 \pm 1.3	472.4
Rb-2	53.67	—	54.4
Rb-1	54.47	55.6	54.5

Table 2 - Calculated values of Debye temperature in °K .

Sodium: The calculated result is about 8% lower than the experimental one. This is not very much surprising since we have used the value of elastic constants at 78°K, the only available experimental elastic constants at that temperature.

Potassium: Very good agreement.

Rubidium: Both sets of elastic constants give a good agreement with the experimental value.

Copper, Silver and Gold: Excellent agreement.

Diamond, Silicon, Germanium and Lead: Fair agreement. For diamond, the elastic constants are at 300°K; even so the result is good.

Transition Metals: For these metals the experimental errors in the determination of $\theta_0(D)$ are large and thus a critical comparison becomes meaningless. We can group all transition f.c.c. and b.c.c. crystals together and can say that, except for Molybdenum and Iridium, the calculated $\theta_0(D)$ are in fair agreement with the experimental results.

b) Comparison with Other Theoretical Calculations

Konti and Varshni⁷ have recently made an elaborate calculation using different theoretical models, and we have chosen the best values of $\theta_0(D)$ from their calculations (see Table 2). A survey of Table 2 shows that our calculated values of $\theta_0(D)$ for all the 24 cubic elements lie close to the ones obtained by Konti and Varshni⁷.

5. Conclusion

The calculated $\theta_0(D)$ for all 24 cubic crystals considered here have predicted results which are as good as those predicted by much more cumbersome models like that of Hopf-Lechner³, Houston-Bhatia-Tauber⁴⁻⁵ and of Federov⁶. This indicates that cubic solids can be very well represented by Debye's model and that they show, to a certain extent, polycrystalline behaviour at absolute zero.

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