Vol. A58 (1980) *ACTA PHYSICA POLONICA* No 5

THE WEIGHTING COEFFICIENTS IN HBT METHOD AND DEBYE TEMPERATURES OF TETRAHEDRALLY BONDED SEMICONDUCTORS

BY DEBASRI BASU AND J. K. D. VERMA

Saha Institute of Nuclear Physics, Calcutta*

(Received April 1, 1980)

The Debye characteristic temperature θ has been calculated from elastic constant data for a number of binary tetrahedrally bonded semiconductors. The weighting coefficients for the three principal cubic directions for these crystals, as determined by a least square best-fit procedure based on computationally exact values of θ, have been found to differ from those for metals and alkali halides.

PACS numbers: 63.20.-e, 62.20.Dc

1. *Introduction*

The Debye characteristic temperature θ is an important parameter in the study of a large number of solid state problems involving lattice vibrations. One of the methods of calculating θ is from elastic constant data using the relation

$$\theta = \frac{h}{k}\left(\tfrac{4}{3}\pi V_a\right)^{-1/3} v_m, \tag{1}$$

where h is Planck's constant, k is Boltzmann's constant, and V_a is the atomic volume. The velocity v_m is defined by

$$\frac{3}{v_m^3} = \int\limits_{\text{all directions}} \left(\sum_{i=1}^{3} \frac{1}{v_i^3}\right) \frac{d\Omega}{4\pi}, \tag{2}$$

where $d\Omega$ denotes an element of solid angle and v_i is the velocity which depends on the direction and is obtained from Christoffel's equations of elasticity theory.

---

* Address: Saha Institute of Nuclear Physics, 92, Acharya P. C. Road, Calcutta — 700009, India.

Equation (2) is not integrable analytically and numerical methods must be used for its approximation, that is,

$$\frac{3}{v_m^3} \simeq \frac{1}{n} \sum_{j=1}^{n} \Bigl(\sum_{i=1}^{3} \frac{1}{v_i^3} \Bigr)_{d(j)}, \tag{3}$$

where n is an integer. The solution to equation (3) for a "large" n is considered to give an "exact" value of θ when substituted in (1). However, the computational labour also increases with large values of n. In case of cubic crystals, parametrized tables [1, 2], which are based on numerical solution of (2), can be used to obtain accurate values of θ. The values computed by using latter tables [2] will be considered here as "exact" and are designated as θ_{exact}.

In order to reduce the computational labour of solving equation (3) and the corresponding elastic secular equation, a number of approximate methods [3, 4] have been proposed. One of the most often used methods is due to Houston [5] and Bhatia and Tauber [6]. In this method which is commonly referred as HBT, equation (3) is solved only for $n = 3$, specifically $d^{(1)} = [100]$, $d^{(2)} = [110]$ and $d^{(3)} = [111]$, the three vectors whose solid angle contains the irreducible highest cubic symmetry. Thus the computational labour of solving the elastic secular equation for a large number of irrational directions is avoided. Equation (3) then becomes

$$\frac{3}{v_m^3} \simeq w_1 \Bigl(\sum_{i=1}^{3} 1/v_i^3 \Bigr)_{[100]} + w_2 \Bigl(\sum_{i=1}^{3} 1/v_i^3 \Bigr)_{[110]} + w_3 \Bigl(\sum_{i=1}^{3} 1/v_i^3 \Bigr)_{[111]}, \tag{4}$$

where w_α ($\alpha = 1, 2, 3$) corresponding to $d^{(1)}$, $d^{(2)}$, $d^{(3)}$ are the weighting coefficients. The w_α of [6] are exactly the same as of [5]. The HBT method has been extended by various workers to include 5 [7], 6 [8] and 9 and 15 [9] terms. It has, however, been found [10] that 9-term expression yields θ values closer in agreement to θ_{exact} than 15-term form. Hence no special advantage is gained in choosing additional d; on the other hand the lower symmetry of the less rational vectors increases significantly the computational labour in solving the elastic secular equation.

Nutkins [11] has also derived a set of w_α values which should apply generally to all cubic crystals. However, her values are quite different from those of HBT. While the two methods weight the [100] vector exactly the same, the [110] and [111] vectors are weighted quite differently. Nutkins' w_α minimize the [110] contribution to θ. Ledbetter [12] has proposed a variant of Nutkins' method to obtain a set of w_α values for cubic metals. This set agrees reasonably well with that of Nutkins. The method, though semi-empirical, has the advantage that it gives more accurate values of θ than the HBT three direction approximation. This method has been used to calculate the Debye temperatures of alkali halides [13]. It was found that there were considerable differences between w_α for metals and those for alkali halides. The weighting coefficients obtained by different workers are shown in Table I.

It would be reasonable to assume that w_α will be the same only for such substances whose $\sum_{i=1}^{3} 1/v_i^3$ surfaces are very nearly of the same shape. Binary semiconductors having zinc-blende structure, particularly $A^{III}B^{V}$ and $A^{II}B^{VI}$ type of compounds, have similar chemical binding. However, the reduced elastic constants [14] though same for a group are different for the two groups. It would be reasonable to infer that for a particular group the velocity surfaces are similar. The applicability of Ledbetter's procedure to these two groups of compounds is examined in this paper. While the main interest is in tetrahedrally bonded zinc-blende structure semiconductors $A^{III}B^{V}$ and $A^{II}B^{VI}$, the results for some other binary semiconductors viz., MgO, PbS, PbTe, Mg_2Si, Mg_2Ge and Mg_2Sn are also included for sake of interest. While the first three compounds have NaCl structure, the latter three have fluorite structure.

TABLE I

Weighting coefficients w_α

Author	Type of substance	w_1	w_2	w_3
Houston [5] and Bhatia–Tauber [6]	general	0.286	0.457	0.257
Nutkins [11]	sodium	0.286	0.143	0.571
Ledbetter [12]	metals	0.246	0.135	0.620
Varshni–Konti [13]	NaCl type alkali halides	0.394	−0.089	0.695
	CsCl, CsBr, CsI	0.408	−0.006	0.598
This paper (Table II, group h)	ZnS type binary semiconductors	0.355	0.210	0.435

2. *Calculations and results*

Except for AlSb, GaP and GaSb, the input data (single crystal elastic coefficients c_{ij} and density ϱ) employed in the calculations were taken from [15]. The data for AlSb are from [16] and those for GaP and GaSb are from [17]. The "exact" values of θ were calculated [15] by using parametrized tables [2]. The θ_{exact} values were used to determine the weighting coefficients [12]. The results of the calculations for w_α for various combinations of 19 cubic binary semiconductors are given in Table II. The standard deviations s_{w_α} of the approximate with respect to the "exact" were also evaluated and the arithmetic mean of s_{w_1} and s_{w_2} is given in the column labelled s_w in Table II.

These weighting coefficients were then used to calculate the Debye temperatures. The results are presented in Table III. The Debye temperatures θ_a, θ_d and θ_h refer to the values of θ calculated by using w_α derived from the groupings (a), (d) and (h) respectively as referred in Table II. The entries in the columns labelled θ_{HBT} and θ_N were obtained using w_α of Houston–Bhatia–Tauber and Nutkins, respectively. The "exact" values of θ are also listed in Table III for the sake of comparison. The Debye temperatures have been calculated to a greater number of significant figures than is warranted by the accuracy of the experimental input data. This has been done to bring out small differences, if any, between the different values.

TABLE II

Best-fit weighting coefficients w_α for cubic binary semiconductors

Group	Compounds	m	w_1	w_2	w_3	s_w, pct
(a)	AlSb, GaP, GaAs, GaSb, InP, InAs, InSb	7	0.341	0.087	0.572	0
(b)	GaP, GaAs, GaSb	3	0.338	0.034	0.628	0
(c)	InP, InAs, InSb	3	0.349	0.156	0.495	0
(d)	β-ZnS, ZnSe, ZnTe, CdTe, HgTe, HgSe	6	0.358	0.222	0.420	5.10
(e)	MgO, PbS, PbTe	3	0.621	−0.571	0.949	11.74
(f)	Mg_2Si, Mg_2Ge, Mg_2Sn	3	0.467	−0.442	0.975	0
(g)	(d) + MgO	7	0.358	0.222	0.420	4.56
(h)	(a) + (d)	13	0.355	0.210	0.435	2.51
(i)	AlSb, GaSb, InSb	3	0.342	0.108	0.550	0
(j)	ZnS, ZnSe, ZnTe	3	0.294	−0.036	0.742	0
(k)	ZnTe, CdTe, HgTe	3	0.374	0.318	0.307	10.27
(l)	(k) + PbTe	4	0.323	0.081	0.596	2.22

TABLE III

Comparison of exact and approximate values of θ_{elastic} for binary semiconductors

Compound	θ_{exact}	θ_a	θ_d	θ_h	θ_{HBT}	θ_N
AlSb	292.8	292.79	293.22	293.11	289.82	290.46
GaP	443.8	443.87	444.55	444.39	439.67	440.49
GaAs	345.6	345.57	346.07	345.95	342.16	342.88
GaSb	269.2	269.21	269.66	269.56	266.80	267.20
InP	301.1	301.10	301.06	300.98	296.16	298.12
InAs	249.6	249.45	249.58	249.50	245.92	247.13
InSb	206.0	206.06	206.13	206.07	203.05	204.12
β-ZnS	343.6	344.70	343.53	343.52	335.44	340.34
ZnSe	275.3	276.10	275.45	275.42	269.60	272.86
ZnTe	222.3	223.44	223.45	223.39	219.89	221.25
CdTe	161.7	161.48	161.42	161.37	158.50	159.73
HgTe	140.3	141.20	140.63	140.63	137.04	139.30
HgSe	150.9	151.43	150.63	150.64	146.39	149.24
MgO	951.0	949.39	951.81	951.45	947.16	945.07
PbS	229.1	230.27	226.66	227.05	225.64	232.01
PbTe	177.2	175.24	169.00	169.63	166.46	177.76
Mg_2Si	550.1	550.10	549.84	549.87	549.90	550.29
Mg_2Ge	440.8	440.69	440.40	440.43	440.45	440.91
Mg_2Sn	367.0	366.45	367.12	367.04	366.61	365.72

3. *Discussion*

It is seen from Table III that generally no single set of w_α exists which can give good agreement between approximate θ and θ_{exact} for all the tetrahedrally bonded semiconductors considered here. Different sets of w_α — groups (a) and (d) — are required for the two groups of semiconductors. However θ_h values, calculated by using the set (h) of w_α (Table II), are significantly in better agreement with θ_{exact} than by any other set. The maximum difference between θ_h and θ_{exact} is about 0.5% while that between θ_{HBT} and θ_{exact} or θ_N and θ_{exact} is 1% and above. The θ_{HBT} values are, in general, poor agreement with θ_{exact} as compared to θ_N with θ_{exact}.

As mentioned earlier, the Debye temperatures of other binary semiconductors not belonging to either $A^{III}B^{V}$ or $A^{II}B^{VI}$ were also calculated using different sets of w_α only for the sake of interest. It will be noticed from Table III that though θ_a values for these semiconductors are in closer agreement with θ_{exact} than θ_h, the values of θ_a and θ_h themselves differ very little. Thus the set (h) of w_α can be used to obtain fairly accurate values of Debye temperatures of cubic binary semiconductors.

As seen from Table I, the proposed set (h) of w_α does not agree with any of the other proposed sets. The weighting coefficients of HBT differ considerably with those of Nutkins [11] and Ledbetter [12]. However, w_α of [11] agree reasonably well with those of [12]. Also, as seen from Table I, there are considerable differences between w_α for metals and those for alkali halides. These differences may be due to different shapes of the $\sum_{i=1}^{3} 1/v_i^3$ surfaces in the two cases. Although differences between w_α for metals and the semiconductors considered here also exist, these are smaller but the relative pattern $w_3 > w_1 > w_2$ is same. In other words, the [111] contribution to θ is weighted most heavily. In terms of simple ratio ($w_1 : w_2 : w_3$) for the w_α, 1.7: 1: 2 appears to be the most appropriate for tetrahedrally bonded semiconductors. It is interesting to note that the ratio proposed (1.8:1:4.6) in [12] for cubic metals is nearly identical with the present except for the heavier w_3 contribution.

REFERENCES

[1] J. DeLaunay, *Solid State Physics*, 2, Eds. Seitz and Turnbull, Academic Press, New York 1956, p. 220.
[2] W. C. Overton, A. F. Schuch, Los Alamos Scientific Laboratory Report, LA-3615, 1966.
[3] M. Blackman, *Handbuch der Physik*, Vol. VII-1, Ed. Fluggs, Springer-Verlag, Berlin 1955, p. 325.
[4] G. A. Alers, *Physical Acoustics*, IIIB, Ed. Mason, Academic Press, New York 1965, p. 1.
[5] W. V. Houston, *Rev. Mod. Phys.* **20**, 161 (1948).
[6] A. B. Bhatia, G. F. Tauber, *Philos. Mag.* **45**, 1211 (1954); (errata **46**, 108 (1955)).
[7] E. Tenerz, *Ark. Fys.* **11**, 247 (1956).
[8] D. D. Betts, A. B. Bhatia, M. Wyman, *Phys. Rev.* **104**, 37 (1956).
[9] D. D. Betts, *Can. J. Phys.* **39**, 233 (1961).
[10] R. Wanner, *Can. J. Phys.* **48**, 1270 (1970).
[11] M. A. E. Nutkins, *Proc. Phys. Soc.* **72**, 810 (1958).
[12] H. M. Ledbetter, *J. Phys. F* **2**, 262 (1972).

[13] Y. P. Varshni, A. Konti, *J. Phys. C* **5**, 2562 (1972).
[14] R. W. Keyes, *J. Appl. Phys.* **33**, 3371 (1962).
[15] J. K. D. Verma, M. D. Aggarwal, *J. Appl. Phys.* **46**, 2841 (1975).
[16] D. J. Bolef, M. Menes, *J. Appl. Phys.* **43**, 4271 (1972).
[17] W. F. Boyle, R. J. Sladek, *Phys. Rev.* **B11**, 2933 (1975).