acta phys. slov. 30. (1980), No. 3

APPROXIMATE CALCULATION OF THE BULK AND SHEAR MODULI AND DEBYE TEMPERATURES OF ORTHORHOMBIC CRYSTALS

J. K. D. VERMA*, (Miss) DEBASRI BASU*, Calcutta
M. D. AGGARWAL**, Kurukshetra

The Verma-Aggarwal approximation (VAA) for the shear modulus is employed in conjunction with a similar approximation for the bulk modulus to calculate elastic Debye temperatures of a number of orthorhombic crystals and the results are compared with those obtained by other approximations. It is found that the proposed approximation yields values of Debye temperatures much closer to the corresponding computationally exact values than other methods.

ПРИБЛИЖЕННОЕ ВЫЧИСЛЕНИЕ МОДУЛЯ ОБЪЕМНОГО СЖАТИЯ И МОДУЛЯ СДВИГА И ДЕБАЕВСКИХ ПАРАМЕТРОВ ОРТОРОМБИЧЕСКИХ КРИСТАЛЛОВ

В работе для расчета дебаевских параметров некоторых орторомбических кристаллов используется приближение Верма—Аггарваля для модуля сдвига совместно с аналогичным приближением для модуля объемного сдвига. Проводится сравнение этих результатов с результатами, полученными при помощи других приближений. Показано, что предлагаемое приближение дает значения дебаевских параметров более близкое к соответствующим точно вычисленным значениям, чем другие методы.

I. INTRODUCTION

The Debye characteristic temperature Θ is a parameter of considerable importance in the study of a large number of solid state problems involving lattice vibrations. The exact evaluation of Θ from single-crystal elastic coefficients, c_{ij}, is not easy, since it involves solving a cubic equation and then finding the average value of a function of the three roots. The basic relation defining Θ is given by the well-known relation [1]

$$\Theta = \frac{h}{k}\left(\frac{3qN\varrho}{4\pi M}\right)^{1/3} v\,, \tag{1}$$

---

* Saha Institute of Nuclear Physics, 92, Acharya P. C. Road, CALCUTTA — 700 009 India.
** Physics Department, Kurukshetra University, KURUKSHETRA — 132 119 India.

where the mean velocity v is given by

$$v=\left(\frac{1}{3}\int\sum_{i=1}^{3}v_i^{-3}\frac{d\Omega}{4\pi}\right)^{-1/3}. \tag{2}$$

Here q is the number of vibrating units in the molecule and all the other symbols have their usual meanings.

Although the solution of the integral in Eq. (2) by a numerical method is rigorous and exact, it is complicated enough even for such a highly symmetric crystal as the cubic one and the calculations must be carried out with a computer over a symmetry-irreducible solid angle using a large number of wave propagation vectors or by using, in case of cubic solids, parameterized tables based on extensive computer calculations by DeLaunay [2] and by Overton and Schuch [3]. Various approximational methods have, therefore, been devised for solving Eq. (2). The conventional method of evaluating the integral in Eq. (2) for non-cubic solids is to expand it in a series of harmonic polynomials. Using this method explicit expressions have been obtained for various crystal symmetries [4]. The method proposed by Fedorov [5] is also applicable to solids of all symmetries. However, both the polynomial and Fedorov's method are unwieldy, involving cumbersome calculations.

The purpose of the present paper is to demonstrate that the VRHG method [1] can yield quite accurate values of Debye temperatures without being prohibitive in time and effort provided that a suitable averaging of single crystal elastic coefficients is done to obtain effective bulk and shear moduli. The method which is briefly outlined in the next section is applicable to crystals of all classes and has been applied here to orthorhombic crystals.

II. NEW AVERAGING METHOD AND AGGREGATE DEBYE TEMPERATURE

The mean velocity [Eq. (2)] can also be determined from averaged c_{ij} obtained by replacing the single-crystal with an isotropic aggregate, and by assuming the aggregate to behave as a Debye continuum. This average mean velocity, denoted by $\bar{v}$ in this case, is given by

$$\frac{3}{\bar{v}^3}=\frac{1}{v_l^3}+\frac{2}{v_t^3}, \tag{3}$$

where

$$\varrho v_l^2=B+\frac{4}{3}G \tag{4}$$

and

$$\varrho v_t^2=G. \tag{5}$$

Here B and G are the bulk and shear moduli, respectively. The Debye temperature can be calculated with the help of Eqs. (1) and (3)—(5) and is generally referred to in this case as Θ_{agg}.

The isotropic constants B and G can be calculated from c_{ij}'s using the well-known relations of Voigt [6] and Reuss [7]. These relations represent the upper and lower bounds on these constants, respectively. Hence an arithmetic or geometric mean (AMA or GMA) of the two extreme limits has been suggested [8] to calculate the values of B and G. The arithmetic mean is widely used for computing Debye temperatures [1, 9]. It has been found that the values of Θ_{agg} calculated by using GMA are closer to exact values than those where AMA has been used [10, 11]. Shukla and Padial [12] have proposed the harmonic mean (HMA) between the extreme bounds. This approximation has been found to be even better than GMA. Recently, Verma and Aggarwal [11] have suggested another approximation, referred to hereafter as VAA, for the shear modulus, viz.,

$$G=\frac{1}{3}(G_V+2G_R), \tag{6}$$

where G_V and G_R are the values of G in the Voigt and Reuss relation, respectively. The values of Θ_{agg}, using Eq. (6), have been found to be in excellent agreement with the corresponding computationally exact Θ for a number of cubic elements, semiconducting compounds [11] and alkali halides [13].

For cubic crystals, B is uniquely determined. However, for non-cubic symmetry, no such unique relationship exists between the bulk modulus of single crystals and that of polycrystals. Thus, $B(C_{ij})$ must be specified as part of the averaging method. The values of B in AMA, GMA and HMA are given by the corresponding similar relations in G [11]. The value of B in VAA is given by

$$B=\frac{1}{3}(B_V+2B_R), \tag{7}$$

where B_V and B_R are the values of B in the Voigt and Reuss relations, respectively.

So far only AMA has been used to calculate $\bar{v}$ of orthorhombic crystals [1]. All the three approximations, viz., GMA, HMA and VAA have been used in this paper in order to compare their relative accuracies with respect to the exact value of v obtained by numerical integration of Eq. (2).

III. HARMONIC POLYNOMIAL SERIES EXPANSION METHOD

The value of Θ, using this method, is given by the relation

$$\Theta=\frac{h}{k}\left(\frac{3qN\varrho}{4\pi M}\right)^{1/3}v_J, \tag{8}$$

where

$$v_J = 3^{1/3} \varrho^{-1/2} J^{-1/3} . \tag{9}$$

The parameter J is a function of c_{ij}'s and Joshi [14] has given three different expressions corresponding to five, six and seven terms used in the expansion. The expressions containing 6- and 7-terms are supposed to be more accurate [14] than the expression having 5-terms and will be used in this paper for comparison with the values obtained by four averaging methods mentioned in the earlier section. The evaluation of J is, however cumbersome and time consuming.

It has been often found that information on the value of q, the number of vibrating units per molecule is lacking althoug c_{ij} data are available.

It has also been observed that different chemical formulae for the same crystal are quoted in literature, thus leading to different values of M and q. These parameters are needed to calculate the Debye temperatures [Eq. (1)]. A typical example is that of topaz. The formula used by Joshi [14] in his calculation is $Al_2(F \cdot OH)_2SiO_4$, while that quoted elsewhere [7, 15] is $2\,AlFO \cdot SiO_2$. Thus it may lead to different values of Debye temperatures even though v, $\bar{v}$ or v_J may be the same. In order to eliminate this ambiguity and to obtain information about the relative accuracy of different methods of calculating Debye temperatures, it will, therefore, suffice to compare only v, $\bar{v}$ and v_J and this has been done in the present paper. The Debye temperatures can then be simply obtained by multiplying v, $\bar{v}$ or v_J by $(h/k) \cdot (3Nq\varrho/4\pi M)^{1/3}$ if no ambiguity exists regarding the values of M and q.

IV. RESULTS AND DISCUSSION

Although c_{ij} values are available for a number of orthorhombic crystals, the choice of the particular crystals here has been confined to only those for which exact values of v are available in literature [16]. For the Baryte and Rochelle salt two sets of elastic constants have been reported, which differ appreciably from each other; calculations were carried out for both sets and these are represented as Baryte-1 and Baryte-2, Rochelle salt-1 and Rochelle salt-2 in Table 1. The references for experimental data, c_{ij} and ϱ, used in the calculations of mean velocities are listed in Table 1.

The elastic compliances, s_{ij}'s can be computed from elastic stiffnesses, c_{ij}'s or vice versa, by a subroutine which inverts any reasonably sized $n \times n$ matrix. However, for the sake of convenience explicit relations between c_{ij}'s and s_{ij}'s obtained by taking the inverse of the c_{ij} matrix are given in the Appendix.

The mean velocity $\bar{v}$ has been calculated using four averaging methods, viz., AMA, GMA, HMA and VAA. The mean velocity v_J has also been calculated, using both six term and seven term polynomial expansions. The results of these

Table 1

Mean velocity ($10^3\ \mathrm{ms^{-1}}$) and relative percentage error of some orthorhombic crystals according to different methods. The relative error for each crystal is given in the second row, ζ is the anisotropy parameter.

Material	ref.	ζ	$\bar{v}$				v_J		v_{exact}
			AMA	GMA	HMA	VAA	6-terms	7-terms	
Topaz	[14]	0.022	6.342	6.341	6.341	6.330	6.337	6.342	6.332
			0.158	0.142	0.142	−0.032	0.079	0.158	
Olivine	[16]	0.038	5.472	5.472	5.472	5.455	5.443	5.449	5.409
			1.165	1.165	1.165	0.850	0.629	0.740	
Iodic acid	[14]	0.072	2.139	2.139	2.138	2.127	2.122	2.134	2.126
				0.612	0.612	0.564	0.047	−0.188	0.376
α-Uranium	[16]	0.092	2.324	2.323	2.322	2.308	2.314	2.313	2.304
			0.868	0.825	0.781	0.174	0.434	0.391	
Aragonite	[14]	0.104	3.992	3.990	3.987	3.959	3.933	3.971	3.942
			1.268	1.218	1.142	0.431	−0.228	0.736	
Strontium formate dihydrate	[16]	0.129	2.881	2.879	2.876	2.853	2.849	2.862	2.840
			1.444	1.373	1.268	0.458	0.317	0.775	
Baryte-1	[16]	0.164	2.545	2.542	2.538	2.514	2.606	2.615	2.525
			0.792	0.673	0.515	−0.436	3.208	3.564	
Sulphur	[16]	0.170	2.020	2.016	2.014	1.993	2.015	2.018	1.978
			2.123	1.921	1.820	0.758	1.871	2.022	
Baryte-2	[16]	0.178	2.492	2.488	2.484	2.459	2.538	2.547	2.463
			1.177	1.015	0.853	−0.162	3.045	3.410	
Sodium ammonium tartrate	[17]	0.240	2.388	2.382	2.375	2.346	2.303	2.329	2.364
			1.015	0.761	0.465	−0.761	−2.580	−1.480	
Goslarite	[18]	0.288	2.794	2.783	2.773	2.737	2.953	3.006	2.758
			1.305	0.906	0.544	−0.761	7.070	8.992	
Rochelle salt-1	[16]	0.317	2.382	2.372	2.361	2.329	2.268	2.305	2.356
			1.104	0.679	0.212	−1.146	−3.735	−2.165	
Sodium tartrate	[16]	0.333	2.478	2.465	2.453	2.419	2.336	2.397	2.458
			0.814	0.285	−0.203	−1.587	−4.963	−2.482	
Rochelle salt-2	[16]	0.340	2.401	2.388	2.376	2.343	2.270	2.306	2.362
			1.651	1.100	0.593	−0.804	−3.895	−2.371	
Potassium pentaborate	[16]	0.468	2.360	2.340	2.319	2.286	2.362	2.394	2.264
			4.240	3.357	2.429	0.972	4.329	5.742	

calculations are presented in Table 1. Exact values of v, obtained by numerical integration of Eq. (2) and denoted as v_{exact}, are also included in Table 1. For the sake of ready comparison, the relative error velocity Δ, expressed in percent, for different methods is also shown in Table 1 in the second row against each crystal. The relative error velocity has been defined as

$$\Delta = \frac{v_x - v_{exact}}{v_{exact}}, \tag{15}$$

where v_x is either $\bar{v}$ or v_J..

It is seen from Table 1 that, in general, the proposed averaging method (VAA) for B and G yield values of $\bar{v}$ closer to v_{exact} than any other method. It is further seen that the trend is for various $\bar{v}$'s to be ordered according to

$$\bar{v}_{\mathrm{AMA}} \geqslant \bar{v}_{\mathrm{GMA}} \geqslant \bar{v}_{\mathrm{HMA}} \geqslant \bar{v}_{\mathrm{VAA}}. \tag{16}$$

Contrary to expectation, it has been observed that, in general, Δ, when the six-term expansion is used, is less than that for the seven-term expansion.

For a detailed discussion of the results it will be convenient to define the anisotropy parameter of non-cubic crystals. In case of cubic crystals, the anisotropy is evaluated through the relation $\eta = 2c_{44}/(c_{11} - c_{12})$. The degree of anisotropy is measured by the deviation of η from unity. This criterion is well adapted to the study of elastic anisotropy in cubic materials since it takes into account all elastic stiffnesses, but for materials of a lower symmetry η cannot be directly evaluated. An attempt to estimate the anisotropy of non-cubic solids has been made by Epelboin et al. [19] from the average elastic components of a macroscopically isotropic material composed of randomly oriented small anisotropic crystals. It can be shown that both the Voigt and the Reuss averages agree in the first order but differ in the second order. Hence their comparison through a parameter ζ given by,

$$\zeta = \frac{G_V - G_R}{G_R} \tag{17}$$

might be a good way to express the anisotropy of a non-cubic crystal. This anisotropy parameter is also listed in Table 1.

Fig. 1 shows the distribution of the crystals in the plot of relative error, Δ versus the anisotropy parameter ζ. (Here only the magnitude of the relative error has been plotted.) Only the relative errors for the six-term series expansion and VAA have been shown in Fig. 1, since the errors for other methods are, in general, relatively large, as seen from Table 1.

It is seen from Fig. 1 that the crystals fall into two distinct groups, with ζ less than 0.2 and ζ greater than 0.2. Topaz, olivine, iodic acid, α-uranium, aragonite, strontium formate dihydrate, baryte and sulphur form the first group, while sodium ammonium tartrate, goslarite, Rochelle salt, sodium tartrate and potassium pentaborate form the second group. It is seen from Fig. 1 (and Table 1) that when we use VAA for the first group of crystals the relative error is less than 0.5 % except for olivine and sulphur. The relative error for the six-term series expansion method is also nearly the same for $\zeta < 0.15$ but is considerably larger — between 2 to 3.5 % — for ζ lying between 0.15 and 0.2. It is also seen from Table 1 that for this first group of crystals, when VAA is used, Δ is much less than that for AMA, GMA, HMA or even the seven-term series expansion. In the case of olivine, aragonite and strontium formate dihydrate, the six-term series expansion seems to be slightly better than VAA. Since the Voigt [6] and the Reuss [7] relations define the upper and lower bounds on elastic moduli G and B, it is expected that v_{exact} should lie between v_{Voigt} and v_{Reuss}. However, it has been found for olivine that v_{Reuss}, calculated by using G_{Reuss} and B_{Reuss} values in Eqs. (4) and (5), is larger than v_{exact}. The reliability of c_{ij} data for this material is, therefore, to be viewed with caution.

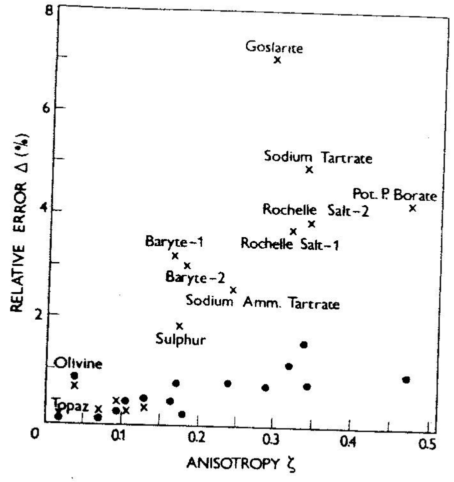

Fig. 1. Dependence of relative error Δ on the anisotropy parameter ζ. The crosses (×) indicate series expansion (6-term) values while the closed circles (●) show VAA values.

For the second group of crystals, the relative error if VAA is used is about 1 % except for sodium tartrate for which Δ is 1.6 %. The values of Δ for the six-term expansion for this group of crystals are 2 % and above; the error for the seven-term expansion is slightly higher. It is further seen from Table 1 that for this group of crystals, $\bar{v}_{\mathrm{HMA}}$ is always closer to v_{exact}. For sodium tartrate and Rochelle salt-2, even $\bar{v}_{\mathrm{AMA}}$ is closer to v_{exact} than $\bar{v}_{\mathrm{VAA}}$. It may be pointed out that c_{ij} data for the second group of crystals are rather old and need careful rechecking. No recent measurements have been reported for these crystals. In the opinion of the authors, the Δ value if VAA is used would be low if c_{ij}'s are determined accurately and carefully checked for internal consistency.

The dearth of reliable bulk and shear moduli data of truly polycrystalline material — free from errors like porosity, nonisotropy, etc. — precludes at the present state any further possibility of judging the relative merits of different averaging procedures for B and G merely by comparing the calculated and experimental values of these elastic constants. Under these circumstances one has to depend only upon the degree of relative agreement between $\bar{v}$ values calculated by using a given averaging method and v_{exact} values.

V. CONCLUSIONS

In summary, a new empirical method for averaging single-crystal elastic coefficients for computing an effective polycrystalline bulk modulus of non-cubic solids is proposed. Although this averaging method at present does not seem to have a physical basis, the empirical validity is demonstrated by a fairly good agreement between the computed mean velocity $\bar{v}$ and v_{exact} values. This suggests indirectly that the proposed approximations for the bulk and shear moduli of a polycrystalline mass are far superior than any other existing ones. Moreover, the proposed method is simple and does not involve lengthy computations. The application of this new averaging procedure to other non-cubic symmetries will be dealt with in a later publication.

REFERENCES

[1] Anderson, O. L.: J. Phys. Chem. Sol. *24* (1963), 909.
[2] DeLaunay, J.: *Sol. Stat. Phys. Vol. 2.* Academic Press, New York 1956.
[3] Overton Jr., W. C., Schuch, A. F.: *Los Alamos Scientific Laboratory Report* Nos. 3162 and 3615, unpublished.
[4] Alers, G. A.: *Phys. Acoustics Vol. 3B.* Academic Press, New York 1965.
[5] Fedorov, F. I.: *Theory of elastic waves in crystals.* Plenum Press, New York 1968.
[6] Voigt, W.: Ann. Phys. *38* (1899), 573.
[7] Reuss, A.: Z. angew. Math. Phys. *9* (1929), 49.
[8] Hill, R.: Proc. Phys. Soc. A *65* (1952), 349.
[9] Verma, J. K. D., Nag, B. D., Nair, P. S.: Z. Naturf. *19a* (1964), 1456.
[10] Aggarwal, M. D., Raju, V., Verma, J. K. D.: Indian J. Pure Appl. Phys. *11* (1973), 216.
[11] Verma, J. K. D., Aggarwal, M. D.: J. Appl. Phys. *46* (1975), 2841.
[12] Shukla, M. M., Padial, N. T.: Rev. Bras. Fis. *3* (1973), 39.
[13] Verma, J. K. D., Aggarwal, M. D.: J. Appl. Phys. *47* (1976), 2778.
[14] Joshi, S. K.: Phys. Rev. *121* (1961), 40.
[15] *Handbook of Chemistry and Physics.* Ed. Weast, R. C., Chemical Rubber Co., Ohio 1971–1972.
[16] Anderson, O. L.: *Phys. Acoust. Vol. 3B.* Academic Press, New York 1965.
[17] Hearmon, R. F. S.: Adv. Phys. *5* (1956), 323.
[18] Sundara Rao, R. V. G.: Proc. Indian Acad. Sci. *31 A* (1950), 365.
[19] Epelboin, Y., Gandais, M., Williams, C.: Phys. Stat. Sol. (a) *44* (1977), 651.

APPENDIX

Explicit relations for obtaining s_{ij}'s from stiffnesses c_{ij}'s for orthorhombic crystals are given below:

$$s_{11}=\frac{c_{22}c_{33}-c_{23}^2}{D} \quad \text{(A1)}$$

$$s_{22}=\frac{c_{11}c_{33}-c_{13}^2}{D} \quad \text{(A2)}$$

$$s_{33}=\frac{c_{11}c_{22}-c_{12}^2}{D} \quad \text{(A3)}$$

$$s_{44}=1/c_{44} \quad \text{(A4)}$$

$$s_{55}=1/c_{55} \quad \text{(A5)}$$

$$s_{66}=1/c_{66} \quad \text{(A6)}$$

$$s_{12}=\frac{c_{13}c_{23}-c_{12}c_{33}}{D} \quad \text{(A7)}$$

$$s_{13}=\frac{c_{12}c_{23}-c_{13}c_{22}}{D} \quad \text{(A8)}$$

$$s_{23}=\frac{c_{12}c_{13}-c_{11}c_{23}}{D} \quad \text{(A9)}$$

where

$$D=c_{11}c_{22}c_{33}+2c_{12}c_{13}c_{23}-c_{11}c_{23}^2-c_{12}^2c_{33}-c_{13}^2c_{22}. \quad \text{(A10)}$$

To obtain c_{ij}'s from s_{ij}'s, one has to replace c_{ij}'s by s_{ij}'s in the above set of relations.

Received December 11th, 1979.