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ON THE DEBYE TEMPERATURES OF HEXAGONAL AND TETRAGONAL CRYSTALS

(Miss) DEBASRI BASU[1], J. K. D. VERMA[1], Calcutta

The elastic Debye temperatures of a number of hexagonal and tetragonal crystals have been calculated by different approximate methods and the results compared with computationally exact values. It is found that the Verma-Aggarwal approximation (VAA) is simpler, less time-consuming and yields fairly accurate values of the Debye temperatures.

К ВОПРОСУ О ДЕБАЕВСКИХ ТЕМПЕРАТУРАХ ГЕКСАГОНАЛЬНЫХ И ТЕТРАГОНАЛЬНЫХ КРИСТАЛЛОВ

В работе приведены результаты различных приближенных вычислений упругих дебаевских температур ряда гексагональных и тетрагональных кристаллов, а также их сравнение с точно рассчитанными значениями. Обнаружено, что приближение Верма-Аггарвала является наиболее простым, требует меньше машинного времени и дает довольно точные значения дебаевских температур.

I. INTRODUCTION

In a previous paper [1], the authors proposed a new method of averaging isotropic bulk and shear moduli obtained from single crystal elastic coefficients and calculated the aggregate Debye temperature, Θ_{agg}, of a number of orthorhombic crystals. It was found that the values of the Debye temperatures thus calculated were much closer to computationally exact values than those calculated by other methods. The purpose of this paper is to further demonstrate the validity of the proposed averaging method for other non-cubic crystals, viz., hexagonal and tetragonal ones.

The Debye characteristic temperature Θ is related to the average sound velocity v_m by the well-known relation [2]:

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[1] Saha Institute of Nuclear Physics, 92, Acharya P. C. Road, CALCUTTA — 700 009, India.

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

where the symbols used have their usual meanings.

The velocity v_m is given by

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

The calculation of v_m for a material whose elastic properties are anisotropic is quite laborious and practically impossible without the use of a computer. Hence, several approximate methods have been devised to evaluate equation (2).

There exist at present three different methods of evaluating elastic Debye temperatures of tetragonal crystals and four for hexagonal ones. These methods are briefly outlined in the next section for the sake of completeness as they have been used to calculate the Debye temperatures.

II. METHODS OF EVALUATING DEBYE TEMPERATURES

IIa. Numerical integration

To obtain the exact value of v, the integrand in equation (2) has to be evaluated. For a tetragonal crystal, a computer programme was set up to cover the 1/16th of a sphere bounded by the (100), (110) and (001) directions. The integral was evaluated using a 5° interval of variable angles ϕ and δ. The limits of integration for ϕ and δ were from 0 to 90° and 0 to 45°, respectively. Reducing the size of the interval from 5° to 1° did not affect the value of v up to the sixth decimal place. Hence it is concluded that integration with a 5° interval of variable angles ϕ and δ with its consequent saving in computer time is sufficiently accurate. The values of v thus obtained will be designated as v_{exact} and the corresponding Θ values as Θ_{exact}.

For crystals having hexagonal symmetry integration turns out to be the simplest case. Relation (1) can be written, in this case, as [2]:

$$\Theta = \frac{h}{k}\left(\frac{4}{3}\pi V_a\right)^{-1/3}\left[\frac{1}{3}\int_0^{\pi/2}\left(\frac{1}{v_1^3}+\frac{1}{v_2^3}+\frac{1}{v_3^3}\right)\sin\phi\, d\phi\right]^{-1/3}, \tag{3}$$

where v_1, v_2 and v_3 are the three roots of the third-order secular equation for the sound velocities in a hexagonal crystal and ϕ is the angle between the hexagonal axis and the propagation direction. The integral can be evaluated by replacing it with a summation which sums the integral according to Simpson's rule. The integral was evaluated using a 1° interval of the variable angle ϕ. A further reduction of the size of this interval did not affect the value of Θ up to the sixth decimal place.

IIb. Wolcott's tables

This method is applicable only for hexagonal crystals. Wolcott [3] used a computer to calculate the values of the integral in relation (2) in terms of certain ratios of elastic stiffness coefficients, c_{ij}'s. Using these tables, it is possible to calculate Θ of hexagonal crystals. The values of Θ thus calculated will be referred to as Θ_w.

IIc. Harmonic series expansion method

In this method, the integrand in relation (2) is expanded in a series of harmonic polynomials. The value of Θ in this case is given by [4].

$$\Theta = \frac{h}{k}\left(\frac{4}{9}\pi V_a\right)^{-1/3} \varrho^{-1/2} J^{-1/3}, \tag{4}$$

where ϱ is the density of the crystal and J is a function of c_{ij}'s.

Betts et al. [4] have derived three different expressions for J for both crystal systems. These correspond to four, five and six terms in the expansion for tetragonal crystals and to three, four and five terms in case of hexagonal crystals. Calculation have been carried out by using all the three expansions and the values of Θ thus obtained are referred to as Θ_{series}.

IId. Fedorov's method

Fedorov [5] has presented a general theory for the propagation of plane elastic waves in homogeneous crystalline solids. The expression for the Debye temperature is given by

$$\Theta = \frac{h}{k}\left(\frac{4}{9}\pi V_a\right)^{-1/3} I^{-1/3}, \tag{5}$$

where I is a function of c_{ij}'s. Two approximations have been proposed for I for hexagonal crystals but only one for tetragonal ones. The Debye temperatures corresponding to these two approximations have been referred to as Θ_{1F} and Θ_{2F}.

IIe. Anderson's method and VA approximation

This method is based on an artificial conversion of an anisotropic state of a crystal to an isotropic case [1]. The mean velocity $\bar{v}$ (relation (2)) is given by

$$\frac{3}{\bar{v}^3} = \frac{1}{v_l^3} + \frac{2}{v_t^3}, \tag{6}$$

where

$$\varrho v_l^2 = B + \frac{4}{3}G; \quad \varrho v_t^2 = G. \tag{7}$$

Here B and G are bulk and shear moduli, respectively. The evaluation of this Debye temperature, designated as Θ_{agg}, has been dealt with in detail in the earlier paper [1]. The abbreviation AMA, GMA, HMA and VAA stand for the different averaging schemes for bulk and shear moduli, viz., the arithmetic mean, the geometric mean, the harmonic mean and the Verma-Aggarwal approximations, respectively.

III. RESULTS AND DISCUSSION

The Debye temperatures of a large number of hexagonal and tetragonal crystals have been calculated by the above mentioned methods and the results are presented in Tables 1 and 2, respectively. The calculations have been carried out 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 values calculated by different methods.

The comparison of mean velocities instead of Debye temperatures, in case of tetragonal crystals (Table 2), has been necesitated by the lack of information about the values of q and M. This type of comparison has also been adapted in case of orthorhombic crystals [1] for the same reason.

In both tables, 1 and 2, the crystals have been arranged in the order of an increasing anisotropy $\zeta(=(G_V - G_R)/G_R)$ [1]. The references for experimental input data — c_{ij} and ϱ, used in these calculations are given in the second column of Table 1 and Table 2, respectively. The elastic compliances, s_{ij}'s can be computed from c_{ij}'s or vice versa, either by a subroutine which inverts any reasonably sized (nxn) matrix or by using the relations between c_{ij}'s and s_{ij}'s [31].

IIIa. Hexagonal crystals

The Debye temperatures of thirty hexagonal crystals have been calculated by different methods and the results compared. The Debye temperatures of Ru, Tl, Er, Pr, CaMg₂, Cd₃Mg, Cd₃Mg and TiB₂ are reported here for the first time.

It is seen from Table 1 that the values of Θ_W are in most cases in poor agreement with Θ_{exact} as compared to Θ_{series}, Θ_{VAA} and $\Theta_{Fedorov}$. Moreover, the evaluation of Θ_W, using the Wolcott tables, involves twelve 7-digit Wolcott table entries if one uses simple linear interpolation and this number rises to twenty-seven 7-digit entries for the more accurate De Launay [32] interpolation. Thus, handling the data as input is unwieldy even for a computer.

The trend in Θ_{series} values is $\Theta_{exact} \geqslant \Theta_{5\text{-}term} \geqslant \Theta_{4\text{-}term} \geqslant \Theta_{3\text{-}term}$. The relative error, defined as $(\Theta - \Theta_{exact})/\Theta_{exact}$, will, therefore, be the smallest for the 5-term approximation. Although calculations were made for all the three approximations, only 4-term and 5-term values are shown in Table 1 for this reason. While 5-term values are, in general, in good agreement with Θ_{exact} and also with Θ_{VAA} and

Table 1

Debye temperatures (K) of some hexagonal crystals by different methods

Material	Ref.	Θ_W	Θ_{series}		Θ_{VAA}	$\Theta_{Fedorov}$		Θ_{exact}
			4-terms	*5-terms*		1F	2F	
Y	6	245.21	245.24	245.32	245.31	245.32	245.32	245.32
Tb	7	170.20	170.37	170.39	170.40	170.39	170.39	170.30
Dy	8	177.21	177.32	177.35	177.36	177.35	177.35	177.35
Er	9	186.09	186.18	186.21	186.20	186.21	186.21	186.21
Ho	10	181.45	181.27	181.30	181.30	181.30	181.30	181.30
Hf	6	242.84	243.04	243.08	243.10	243.07	243.07	243.08
Gd	9	171.06	171.04	171.11	171.12	171.11	171.10	171.11
Ru	6	543.11	543.45	543.65	543.76	543.63	543.60	543.66
Mg	6	366.93	366.85	367.02	367.04	367.03	367.01	367.02
CaMg₂	6	363.30	363.55	363.75	363.79	363.74	363.70	363.76
Be	6	*	1445.13	1445.21	1445.68	1445.28	1445.27	1445.21
ZnO	6	415.32	414.97	415.29	415.30	415.32	415.30	415.31
Cd₃Mg	11	154.06	154.19	154.29	154.33	154.26	154.25	154.30
BeO	12	1277.25	1277.00	1278.20	1278.66	1278.31	1277.98	1278.27
Re	6	394.84	394.21	394.73	394.94	394.76	394.60	394.77
Zr	6	274.48	274.11	274.57	274.69	274.57	274.42	274.61
Cd₂Mg	11	180.21	180.43	180.53	180.70	180.39	180.30	180.53
Nd	13	155.77	155.42	155.62	155.74	155.64	155.57	155.64
Ag₂Al	6	265.19	265.20	265.31	265.53	265.26	265.24	265.32
CdS	6	212.89	212.54	213.04	213.12	213.10	213.00	213.08
Ti	6	396.34	396.05	396.11	396.16	396.09	396.09	396.11
ZnS	12	349.03	348.27	349.13	349.45	349.24	348.88	349.22
Pr	14	149.82	149.50	149.74	149.95	149.75	149.62	149.77
CdSe	12	179.94	179.40	179.93	180.10	180.00	179.84	180.00
MgZn₂	15	308.93	308.15	309.07	309.68	309.22	308.50	309.19
Co	6	452.99	452.12	453.13	454.11	453.22	452.65	453.24
TiB₂	6	970.61	965.02	973.90	972.22	981.98	969.34	972.73
Cd	6	192.80	193.78	193.76	195.74	194.69	193.84	193.76
Zn	6	302.78	306.39	306.54	306.86	312.87	310.26	306.46
Tl	6	71.73	71.60	71.78	72.64	71.78	71.76	71.80

* Θ_W could not be calculated as the existing Wolcott tables do not encompass the range of elastic constants encountered in this case

$\Theta_{Fedorov}$, this method has been seldom used to evaluate the Debye temperatures of hexagonal crystals.

In case of Anderson's method, it is found that the trend for various Θ_{agg} is $\Theta_{AMA} \geqslant \Theta_{GMA} \geqslant \Theta_{HMA} \geqslant \Theta_{VAA} \geqslant \Theta_{exact}$. Hence, only Θ_{VAA} values are listed in Table 1; the relative error will be larger for all other averaging schemes. It is seen from Table 1 that Θ_{VAA} values are in good agreement with Θ_{exact} and also with Θ_{1F}.

As seen from Table 1, Θ_{2F} is less than $\Theta_{1F'}$. The agreement between Θ_{1F} and Θ_{exact} is good. The second approximation is, however, not satisfactory especially when the anisotropy is large. This was also observed in case of cubic elements [33]. The second approximation is, therefore, not worth using, considering the additional computational labour involved.

An inter-comparison between Θ_{VAA}, $\Theta_{5\text{-}term}$ and Θ_{1F} values indicate that for low anisotropy crystals (say, up to Cd_3Mg in Table 1) there is not any appreciable difference among these values. The difference becomes greater as the anisotropy increases. In general, $\Theta_{5\text{-}term}$ values are closer to Θ_{exact} than Θ_{1F}. Although the agreement between Θ_{VAA} and Θ_{exact} is not as good as that compared between $\Theta_{5\text{-}term}$ or Θ_{1F} and Θ_{exact}, the computational labour involved in evaluating Θ_{VAA} is very much less. To illustrate, in case of zinc — a highly anisotropic crystal — the relative errors for Θ_{VAA}, $\Theta_{5\text{-}term}$ and Θ_{1F} are 0.13%, 0.03% and 2.09%, respectively. The calculation of Θ_{VAA} can be carried out with a slide rule while the evaluation of $\Theta_{5\text{-}term}$ or Θ_{1F} needs a programmable electronic calculator. The VAA is simpler, less timeconsuming and yields fairly accurate values of the Debye temperature.

IIIb. Tetragonal crystals

The Debye temperatures of twenty seven tetragonal crystals have been calculated by different methods described in section II and the results compared. The Debye temperatures of MgF_2, RbH_2PO_4, TeO_2, RbH_2AsO_4, KH_2AsO_4, KD_2PO_4, CoF_2, ZnF_2, $Ba_2Si_2TiO_8$, Hg_2Br_2, Hg_2Cl_2 and Hg_2I_2 are reported here for the first time.

It is seen from Table 2 that there is no definite trend in the series expansion values viz., v_4, v_5 and v_6. In general, the agreement with v_{exact} is rather poor. On the other hand, in most cases $v_{Fedorov}$ values are, in general, in good agreement with v_{exact}. However, the relative error becomes larger as the anisotropy increases. It has been observed that in general $v_{AMA} \geqslant v_{GMA} \geqslant v_{HMA} \geqslant v_{VAA}$. Therefore only v_{GMA}, v_{HMA} and v_{VAA} values are shown in Table 2. It is also seen that there exist no appreciable differences between $v_{Fedorov}$ and v_{VAA} values for most crystals. Hence, no definite conclusion can be drawn regarding the superiority of one method over the other. However, VAA in most cases yields more accurate values of Debye temperatures.

Table 2

Mean velocity (in 10^3 m/sec) of some tetragonal crystals by different methods

Material	Ref.	v_{series}			v_{agg}			$v_{Fedorov}$	v_{exact}
		4-*terms*	5-*terms*	6-*terms*	GMA	HMA	VAA		
$Ba_2Si_2TiO_8$	16	3.383	3.379	3.340	3.423	3.422	3.403	3.374	3.374
Al_2Cu	17	3.302	3.311	3.277	3.361	3.360	3.341	3.346	3.339
$BaTiO_3$-I	6	3.585	3.617	3.616	3.762	3.756	3.718	3.741	3.716
MgF_2	6	4.337	4.334	4.352	4.522	4.513	4.464	4.503	4.510
$ZrSiO_4$	18	5.209	5.235	5.143	5.375	5.362	5.302	5.410	5.280
TiO_2	6	5.406	5.401	5.479	5.713	5.694	5.624	5.765	5.717
$BaTiO_3$-II	6	3.183	3.209	3.202	3.359	3.348	3.305	3.292	3.280
Zr_2Ni	19	1.816	1.825	1.800	1.861	1.855	1.832	1.827	1.832
ZnF_2	20	2.978	2.976	2.997	3.152	3.140	3.100	3.144	3.145
$NiSO_4 . 6\,H_2O$	6	2.449	2.449	2.456	2.557	2.547	2.514	2.593	2.585
Sn	6	1.651	1.651	1.695	1.757	1.749	1.725	1.808	1.791
KH_2AsO_4	21	2.252	2.257	2.252	2.423	2.412	2.380	2.356	2.338
NiF_2	22	3.205	3.203	3.244	3.442	3.421	3.374	3.457	3.446
$NH_4H_2PO_4$	6	2.569	2.568	2.554	2.767	2.750	2.712	2.597	2.633
MnF_2	23	2.922	2.919	2.966	3.167	3.144	3.100	3.180	3.164
CoF_2	24	3.000	2.997	3.026	3.241	3.218	3.173	3.209	3.206
KD_2PO_4	25	2.579	2.590	2.567	2.790	2.770	2.732	2.741	2.681
KH_2PO_4	21	2.599	2.609	2.589	2.823	2.802	2.763	2.752	2.704
InBi	26	1.125	1.155	1.169	1.261	1.251	1.233	1.289	1.240
In	27	0.799	0.815	0.832	0.919	0.909	0.897	0.922	0.908
RbH_2AsO_4	28	1.934	1.946	1.918	2.127	2.101	2.075	2.075	2.007
$NH_4H_2AsO_4$	6	2.151	2.152	2.134	2.401	2.369	2.341	2.153	2.210
RbH_2PO_4	6	2.078	2.109	2.044	2.293	2.256	2.233	2.338	2.202
Hg_2Cl_2	29	0.735	0.735	0.875	1.017	0.940	1.001	1.176	1.052
TeO_2	6	1.314	1.314	1.614	1.882	1.717	1.867	2.273	2.053
Hg_2Br_2	30	0.606	0.606	0.755	0.912	0.812	0.916	1.100	0.947
Hg_2I_2	30	0.544	0.544	0.671	0.848	0.737	0.862	1.016	0.841

IV. CONCLUSIONS

The Debye temperatures of a number of hexagonal and tetragonal crystals have been calculated by different approximate methods and their relative superiority compared. It has been found for both systems of crystals that the Verma-Aggarwal approximation (VVA) is far superior to the arithmetic mean approximation (AMA), which is being used extensively at present for computing Debye temperatures. In case of hexagonal crystals it has been observed that Wolcott's tables are not only unwidely to use but also do not yield as accurate values as the 5-term series expansion method (which is comparatively less time-consuming) or Fedorov's first approximation. For tetragonal crystals, no appreciable difference has been found between v_{VAA} and $v_{Fedorov}$ but VAA is simpler and less time-consuming. It is, therefore, concluded that for a quick and fairly accurate evaluation of Debye temperatures of hexagonal and tetragonal crystals, VAA can be used with advantage. It may be mentioned here that VAA has already been found superior to other methods in case of orthorhombic crystals [1].

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