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PHYSICAL PROPERTIES OF CRYSTALS

Debye Temperature for Materials with Arbitrary Anisotropy As a Function of the Series of Elastic Moduli

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Abstract—A compact approximation of an expression for an averaged sum of reciprocal cubed phase velocities of elastic waves, which determines the Debye temperature at 0 K in terms of the components of the tensor of the elastic moduli of solids with arbitrary anisotropy, has been obtained. The general relations are applied to a particular case of materials with cubic symmetry.

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INTRODUCTION

It is known that, according to the Debye theory, the molar specific heat of a solid is given by the following expression (see, e.g., [1–3]):

$$C_V = 9sR\left(\frac{T}{\Theta}\right)^3 \int\limits_0^{\Theta/T} \frac{z^4 e^z}{(e^z - 1)^2} dz, \tag{1}$$

where R is the universal gas constant, s is the number of atoms per unit cell, T is the body temperature, and Θ is the Debye temperature. Strictly speaking, the simplifying suggestions of the Debye model are not satisfied in practice and the parameter Θ is not constant and depends on temperature T. At low temperatures (much lower than Θ), the phonon contribution is critical for the specific heat and formula (1) is transformed as follows:

$$C_V = \frac{12\pi^4}{5} sR\left(\frac{T}{\Theta}\right)^3; \tag{2}$$

from here on, Θ is the Debye temperature at 0 K. This temperature can be calculated theoretically using the elastic-wave phase velocities [4]:

$$\Theta = \frac{\hbar}{k}\sqrt[3]{\frac{18\pi^2 s N_A \rho}{MI}}. \tag{3}$$

Here, $\hbar$ is Planck's constant, k is the Boltzmann constant, N_A is Avogadro's number, ρ is the solid density, M is its molar mass, and the value

$$I = \left\langle \frac{1}{v_0^3} + \frac{1}{v_1^3} + \frac{1}{v_2^3} \right\rangle \tag{4}$$

is the sum of reciprocal cubed elastic-wave phase velocities (quasi-longitudinal and two quasi-transverse ones), averaged over all directions. Averaging is performed as follows:

$$\langle f \rangle = \frac{1}{4\pi}\int\limits_0^{\pi}\int\limits_0^{2\pi} d\theta\, d\varphi \sin\theta f(\theta, \varphi). \tag{5}$$

Calculations based on formula (4) are trivial for elastically isotropic bodies, in which the elastic-wave velocities are independent of direction: $I = 1/v_L^3 + 2/v_S^3$, where v_L and v_S are the longitudinal- and transverse-wave phase velocities, respectively. If material is anisotropic, integration over angular variables of form (5) cannot be perform analytically at any crystallographic symmetry of material, and the precise result of averaging can be found only numerically.

Analytical expressions for the I value were obtained in [4, 5] in the form of power-law series, using the approximate theory of elastic waves in crystals. They make it possible to calculate I with any specified accuracy. The formulas obtained are inconvenient because they are expressed in terms of intermediate quantities specific for a given theory, and calculations must be carried out each time for crystals with different symmetries.

The purpose of this study was to derive approximate expressions for I containing directly the components of the tensor of elastic moduli c_{iklm} (21 moduli for triclinic crystals with the lowest symmetry). These expressions make it possible to estimate the I values and, therefore, Debye temperature Θ (3) with minimum computational expenditures. The solutions have the form of power-law series up to the terms quadratic in deviations of c_{iklm} from elastic moduli c_{iklm}^0 of an isotropic medium, the elastic properties of which are most close to those of the material under consideration. As an example, the obtained general expressions are applied to materials with cubic symmetry.

EQUATION FOR $(\Lambda^{-3/2})_t$

Squared elastic-wave phase velocities are eigenvalues of the Green–Christoffel symmetric tensor Λ [4]:

$$\Lambda \mathbf{u}_b = v_b^2 \mathbf{u}_b, \quad b = 0, 1, 2, \tag{6}$$

where $\Lambda_{im} = \lambda_{iklm} n_k n_l$. Here, $\lambda_{iklm} = c_{iklm}/\rho$, where c_{iklm} is the fourth-rank tensor of elastic moduli, ρ is the crystal density, $\mathbf{n}$ is the unit vector of the phase normal, and $\mathbf{u}_b$ are the vector amplitudes of the isonormal waves. Subscript 0 in (6) is related to a quasi-longitudinal wave, and subscripts 1 and 2 are related to quasi-transverse waves.

To pass to reciprocal cubed velocity, we introduce the tensor

$$\alpha = \Lambda^{-3/2}, \quad \alpha^2 = \Lambda^{-3} = (\Lambda^{-1})^3. \tag{7}$$

Then,

$$\alpha \mathbf{u}_b = \frac{1}{v_b^3} \mathbf{u}_b, \quad b = 0, 1, 2. \tag{8}$$

In Eq. (8), eigenvalues of tensor α, which is a half-integer power of tensor Λ, are chosen to be positive. Obviously, the sum of reciprocal cubed velocities is the trace $\alpha_t = (\Lambda^{-3/2})_t$ of tensor α. In this case, $I = \langle \alpha_t \rangle$.

To derive the equation to which the α_t value satisfies, we will use some properties of reciprocal tensors [4]. Having denoted the determinant of tensor α as $|\alpha|$, we note that at $|\alpha| \neq 0$ the tensor $\bar{\alpha}$, which is reciprocal to tensor α, is defined as $\bar{\alpha} = |\alpha| \alpha^{-1}$. The following relations are valid:

$$\bar{\alpha}_t = \frac{1}{2}\left[(\alpha_t)^2 - (\alpha^2)_t\right],$$

$$\bar{\bar{\alpha}}_t = \frac{1}{2}\left[(\bar{\alpha}_t)^2 - (\bar{\alpha}^2)_t\right] = \frac{1}{2}\left[(\bar{\alpha}_t)^2 - (\overline{\alpha^2})_t\right].$$

At the same time, $\bar{\bar{\alpha}} = |\alpha| \alpha$ and $\bar{\bar{\alpha}}_t = |\alpha| \alpha_t$. Therefore,

$$(\bar{\alpha}_t)^2 - 2|\alpha|\alpha_t - (\overline{\alpha^2})_t = 0,$$

$$\frac{1}{4}\left[(\alpha_t)^2 - (\alpha^2)_t\right]^2 - 2|\alpha|\alpha_t - (\overline{\alpha^2})_t = 0.$$

Let us take into account relations (7). Then, $(\alpha^2)_t = (\Lambda^{-3})_t$ and $(\overline{\alpha^2})_t = (\overline{\Lambda^{-3}})_t = (\Lambda^3)_t / |\Lambda|^3$. In addition, $|\alpha| = |\Lambda|^{-3/2}$. As a result, we arrive at

$$\frac{1}{4}\left[(\alpha_t)^2 - (\Lambda^{-3})_t\right]^2 - \frac{2\alpha_t}{|\Lambda|^{3/2}} - \frac{(\Lambda^3)_t}{|\Lambda|^3} = 0. \tag{9}$$

Equation (9) is a quartic equation with respect to α_t, with coefficients expressed in terms of the invariants of tensor Λ; the latter is assumed to be specified.

EXPANSION OF COEFFICIENTS INTO SERIES

Let us represent the Green–Christoffel tensor Λ as the sum of the main part Λ_0 and small additive $\Lambda' = \Lambda - \Lambda_0$. This partition is ambiguous, and the question of the proper choice of Λ_0 will be discussed below.

Having restricted ourselves to linear and quadratic terms, we expand the coefficients in Eq. (9), containing Λ, in series in powers of Λ':

$$\begin{aligned} \Lambda^3 &= (\Lambda_0 + \Lambda')^3 \approx \Lambda_0^3 + \Lambda_0^2\Lambda' + \Lambda_0\Lambda'\Lambda_0 \\ &+ \Lambda'\Lambda_0^2 + \Lambda'^2\Lambda_0 + \Lambda'\Lambda_0\Lambda' + \Lambda_0\Lambda'^2, \\ (\Lambda^3)_t &\approx (\Lambda_0^3)_t + 3(\Lambda_0^2\Lambda')_t + 3(\Lambda_0\Lambda'^2)_t, \end{aligned} \tag{10}$$

$$\begin{aligned} \Lambda^{-1} &= (1 + \Lambda_0^{-1}\Lambda')^{-1}\Lambda_0^{-1} \approx \Lambda_0^{-1} - \Lambda_0^{-1}\Lambda'\Lambda_0^{-1} \\ &+ \Lambda_0^{-1}\Lambda'\Lambda_0^{-1}\Lambda'\Lambda_0^{-1}, \end{aligned}$$

$$\begin{aligned} \Lambda^{-3} &\approx \Lambda_0^{-3} - \Lambda_0^{-3}\Lambda'\Lambda_0^{-1} - \Lambda_0^{-2}\Lambda'\Lambda_0^{-2} - \Lambda_0^{-1}\Lambda'\Lambda_0^{-3} \\ &+ \Lambda_0^{-2}\Lambda'\Lambda_0^{-2}\Lambda'\Lambda_0^{-1} + \Lambda_0^{-1}\Lambda'\Lambda_0^{-3}\Lambda'\Lambda_0^{-1} \\ &+ \Lambda_0^{-1}\Lambda'\Lambda_0^{-2}\Lambda'\Lambda_0^{-2} + \Lambda_0^{-3}\Lambda'\Lambda_0^{-1}\Lambda'\Lambda_0^{-1} \\ &+ \Lambda_0^{-2}\Lambda'\Lambda_0^{-1}\Lambda'\Lambda_0^{-2} + \Lambda_0^{-1}\Lambda'\Lambda_0^{-1}\Lambda'\Lambda_0^{-3}, \end{aligned} \tag{11}$$

$$\begin{aligned} (\Lambda^{-3})_t &\approx (\Lambda_0^{-3})_t - 3(\Lambda_0^{-4}\Lambda')_t + 3(\Lambda_0^{-3}\Lambda'\Lambda_0^{-2}\Lambda')_t \\ &+ 3(\Lambda_0^{-4}\Lambda'\Lambda_0^{-1}\Lambda')_t. \end{aligned}$$

For the determinant of tensor Λ, we have [4]

$$|\Lambda| = |\Lambda_0 + \Lambda'| = |\Lambda_0| + (\bar{\Lambda}_0\Lambda')_t + (\Lambda_0\bar{\Lambda}')_t + |\Lambda'|.$$

Since

$$\begin{aligned} \bar{\Lambda}' &= \bar{\Lambda}'_t + \Lambda'^2 - \Lambda'_t\Lambda' = \frac{1}{2}\left[(\Lambda'_t)^2 - (\Lambda'^2)_t\right] \\ &+ \Lambda'^2 - \Lambda'_t\Lambda', \end{aligned}$$

we have

$$\begin{aligned} |\Lambda| &\approx |\Lambda_0| + (\bar{\Lambda}_0\Lambda')_t + \frac{1}{2}\Lambda_{0t}\left[(\Lambda'_t)^2 - (\Lambda'^2)_t\right] \\ &+ (\Lambda_0\Lambda'^2)_t - \Lambda'_t(\Lambda_0\Lambda')_t. \end{aligned} \tag{12}$$

We choose Λ_0 as the Green–Christoffel tensor of an isotropic medium: $\Lambda_0 = a + (d - a)\mathbf{n} \otimes \mathbf{n}$. Its eigenvalues are a, a, and d. Later we will take the values of scalars a and d such that the elastic properties of this medium differ minimally from those of the anisotropic material under consideration. For an arbitrary power n of this tensor, we have $\Lambda_0^n = a^n + (d^n - a^n)\mathbf{n} \otimes \mathbf{n}$; therefore, the traces of tensors in (10) and (11) take the form

$$\begin{aligned} (\Lambda^3)_t &\approx 2a^3 + d^3 + 3a^2\Lambda'_t + 3(d^2 - a^2)\mathbf{n}\Lambda'\mathbf{n} \\ &+ 3a(\Lambda'^2)_t + 3(d - a)\mathbf{n}\Lambda'^2\mathbf{n}, \end{aligned} \tag{13}$$

$$(\Lambda^{-3})_t \approx \frac{2}{a^3} + \frac{1}{d^3} - \frac{3}{a^4}\Lambda'_t - 3\left(\frac{1}{d^4} - \frac{1}{a^4}\right)\mathbf{n}\Lambda'\mathbf{n}$$
$$+ \frac{6}{a^5}(\Lambda'^2)_t + 3\left(\frac{1}{a^4 d} + \frac{1}{a^3 d^2} + \frac{1}{a^2 d^3} + \frac{1}{ad^4} - \frac{4}{a^5}\right)\mathbf{n}\Lambda'^2\mathbf{n} \quad (14)$$
$$+ 3\left(\frac{2}{a^5} + \frac{2}{d^5} - \frac{1}{a^4 d} - \frac{1}{a^3 d^2} - \frac{1}{a^2 d^3} - \frac{1}{ad^4}\right)(\mathbf{n}\Lambda'\mathbf{n})^2.$$

In addition, $|\Lambda_0| = a^2 d$, $\bar{\Lambda}_0 = |\Lambda_0|\Lambda_0^{-1} = ad - a(d-a)\mathbf{n}\otimes\mathbf{n}$, and (12) is written as

$$|\Lambda| \approx a^2 d + ad\Lambda'_t - a(d-a)\mathbf{n}\Lambda'\mathbf{n}$$
$$+ \frac{d}{2}\left[(\Lambda'_t)^2 - (\Lambda'^2)_t\right] + (d-a)(\mathbf{n}\Lambda'^2\mathbf{n} - \Lambda'_t\mathbf{n}\Lambda'\mathbf{n}).$$

As a result, the powers of the determinant $|\Lambda|$, entering Eq. (9), are presented by the series

$$|\Lambda|^{-3/2} \approx \frac{1}{a^3 d^{3/2}}\left\{1 - \frac{3}{2}\frac{\Lambda'_t}{a} + \frac{3}{2}\left(\frac{1}{a} - \frac{1}{d}\right)\mathbf{n}\Lambda'\mathbf{n}\right.$$
$$+ \frac{3}{8a^2}\left[3(\Lambda'_t)^2 + 2(\Lambda'^2)_t\right] - \frac{3}{2}\left(\frac{1}{a^2} - \frac{1}{ad}\right)\left(\mathbf{n}\Lambda'^2\mathbf{n}\right. \quad (15)$$
$$\left.\left. + \frac{3}{2}\Lambda'_t\mathbf{n}\Lambda'\mathbf{n}\right) + \frac{15}{8}\left(\frac{1}{a} - \frac{1}{d}\right)^2(\mathbf{n}\Lambda'\mathbf{n})^2\right\},$$

$$|\Lambda|^{-3} \approx \frac{1}{a^6 d^3}\left\{1 - 3\frac{\Lambda'_t}{a} + 3\left(\frac{1}{a} - \frac{1}{d}\right)\mathbf{n}\Lambda'\mathbf{n}\right.$$
$$+ \frac{3}{2a^2}\left[3(\Lambda'_t)^2 + (\Lambda'^2)_t\right] - 3\left(\frac{1}{a^2} - \frac{1}{ad}\right)(\mathbf{n}\Lambda'^2\mathbf{n} \quad (16)$$
$$\left. + 3\Lambda'_t\mathbf{n}\Lambda'\mathbf{n}) + 6\left(\frac{1}{a} - \frac{1}{d}\right)^2(\mathbf{n}\Lambda'\mathbf{n})^2\right\}.$$

Finally, the desired α_t value can be written in the form of expansion

$$\alpha_t = \frac{1}{v_0^3} + \frac{1}{v_1^3} + \frac{1}{v_2^3} \approx k_0 + k_1 + k_2, \quad (17)$$

where the unknown terms k_0, k_1, and k_2 must be determined on the assumption that k_0 does not contain Λ'; k_1 contains terms linear in Λ'; and k_2 contains terms quadratic in Λ'.

To determine the k_0, k_1, and k_2 values, we substitute relations (13)–(17) into Eq. (9), grouping the terms with different powers of Λ'. For k_0, which is a zero approximation of the α_t value, we obtain the following quartic equation, similar to (9):

$$\frac{1}{4}\left(k_0^2 - \frac{2}{a^3} - \frac{1}{d^3}\right)^2 - \frac{2k_0}{a^3 d^{3/2}} - \left(\frac{2}{a^3 d^3} + \frac{1}{a^6}\right) = 0. \quad (18)$$

One can easily make sure that $2a^{-3/2} + d^{-3/2}$ is one of its roots. This conclusion is in agreement with the fact that the trace of tensor $\Lambda_0^{-3/2} = a^{-3/2} + (d^{-3/2} - a^{-3/2})\mathbf{n}\otimes\mathbf{n}$, related to the isotropic medium whose eigenvalues are $a^{-3/2}$, $a^{-3/2}$, and $d^{-3/2}$, is the same. Thus,

$$k_0 = \frac{2}{a^{3/2}} + \frac{1}{d^{3/2}}. \quad (19)$$

Having grouped the terms linear in Λ' and taking into account (19), we obtain the following linear equation for the k_1 additive, which refines the α_t value (17):

$$2(a^{3/2} + d^{3/2})^2\left(\frac{2}{a^{9/2}d^3}k_1 + \frac{3}{a^7 d^3}\Lambda'_t\right.$$
$$\left. + 3\frac{a^{5/2} - d^{5/2}}{a^7 d^{11/2}}\mathbf{n}\Lambda'\mathbf{n}\right) = 0,$$

hence,

$$k_1 = -\frac{3}{2a^{5/2}}\Lambda'_t + \frac{3}{2}\left(\frac{1}{a^{5/2}} - \frac{1}{d^{5/2}}\right)\mathbf{n}\Lambda'\mathbf{n}. \quad (20)$$

Similarly, a linear equation for the next additive k_2 can be obtained by considering the terms quadratic in Λ', taking into account (19) and (20), from which we find

$$k_2 = \frac{15}{8a^{7/2}}(\Lambda'^2)_t + \frac{3}{4}\left(\frac{2}{ad^{5/2}} + \frac{2}{a^2 d^{3/2}}\right.$$
$$\left. + \frac{2}{a^{5/2}d + a^3\sqrt{d}} - \frac{5}{a^{7/2}}\right)\mathbf{n}\Lambda'^2\mathbf{n} + \frac{3}{8}\left(\frac{5}{a^{7/2}} + \frac{5}{d^{7/2}}\right. \quad (21)$$
$$\left. - \frac{4}{ad^{5/2}} - \frac{4}{a^2 d^{3/2}} - \frac{4}{a^{5/2}d + a^3\sqrt{d}}\right)(\mathbf{n}\Lambda'\mathbf{n})^2.$$

Simple but cumbersome calculations performed to derive k_2 are omitted.

Thus, a sum of reciprocal cubed isonormal-wave velocities with phase normal $\mathbf{n}$ can be approximately calculated using formula (17), which contains the terms determined according to (19)–(21).

In accordance with [4], we will write the parameters of an isotropic medium whose elastic properties are most close to those of the anisotropic material characterized by the tensor λ_{iklm}:

$$a = \frac{1}{30}(3\lambda_{ikik} - \lambda_{iikk}), \quad d = \frac{1}{15}(2\lambda_{ikik} + \lambda_{iikk}). \quad (22)$$

The tensor Λ', entering expressions (19)–(21), can be written as

$$\Lambda'_{im} = \Lambda_{im} - (\Lambda_0)_{im} = \lambda'_{iklm}n_k n_l,$$
$$\lambda'_{iklm} = \lambda_{iklm} - \lambda^0_{iklm}, \quad (23)$$

where $\lambda^0_{iklm} = c^0_{iklm}/\rho$ and c^0_{iklm} are the tensor of the isotropic-medium elasticity moduli. Note that the components of tensor λ'_{iklm} can be written in the Voigt notation as follows:

$$\lambda'_{\beta\gamma} = \begin{cases} \lambda_{\beta\gamma} - d & \text{if} \quad \beta\gamma \in \{11, 22, 33\} \\ \lambda_{\beta\gamma} - a & \text{if} \quad \beta\gamma \in \{44, 55, 66\} \\ \lambda_{\beta\gamma} - c & \text{if} \quad \beta\gamma \in \{12, 13, 23\} \\ \lambda_{\beta\gamma} & \text{else,} \end{cases} \tag{24}$$

where $c = d - 2a = (2\lambda_{iikk} - \lambda_{ikik})/15$. According to (22),

$$a = \frac{1}{15}(\lambda_{11} + \lambda_{22} + \lambda_{33} + 3\lambda_{44} + 3\lambda_{55} + 3\lambda_{66} - \lambda_{12} - \lambda_{13} - \lambda_{23}),$$
$$d = \frac{1}{15}(3\lambda_{11} + 3\lambda_{22} + 3\lambda_{33} + 4\lambda_{44} + 4\lambda_{55} + 4\lambda_{66} + 2\lambda_{12} + 2\lambda_{13} + 2\lambda_{23}), \tag{25}$$
$$c = \frac{1}{15}(\lambda_{11} + \lambda_{22} + \lambda_{33} - 2\lambda_{44} - 2\lambda_{55} - 2\lambda_{66} + 4\lambda_{12} + 4\lambda_{13} + 4\lambda_{23}).$$

It is important that the following equalities are valid at this choice of parameters a and d [4]:

$$\left\langle \Lambda'_t \right\rangle = 0, \quad \left\langle \mathbf{n}\Lambda'\mathbf{n} \right\rangle = 0, \quad \lambda'_{iikk} = 0, \quad \lambda'_{ikki} = 0. \tag{26}$$

AVERAGING OVER THE PHASE-NORMAL DIRECTIONS

The parameter I, which enters formula (3) for the Debye temperature, is obtained at averaging of α_t (17) over the directions of phase normal $\mathbf{n}$:

$$I = \langle \alpha_t \rangle \approx \frac{2}{a^{3/2}} + \frac{1}{d^{3/2}} + \langle k_2 \rangle. \tag{27}$$

Here, we take into account that $\langle k_0 \rangle = k_0$ (because k_0 (19) is independent of $\mathbf{n}$) and that $\langle k_1 \rangle = 0$, in view of relations (20) and (26). Thus, within zero approximation, I is the sum of reciprocal cubed elastic-wave velocities $2a^{-3/2} + d^{-3/2}$ in an effective isotropic medium, and the first approximation disappears because the parameters a and d are chosen so that the elastic properties of this medium differed minimally from those of an anisotropic material. To calculate the following approximation, one must average k_2 (21); i.e., average scalars $(\Lambda'^2)_t$, $\mathbf{n}\Lambda'^2\mathbf{n}$, and $(\mathbf{n}\Lambda'\mathbf{n})^2$. Taking into account relation (23), we obtain

$$\left\langle (\Lambda'^2)_t \right\rangle = \lambda'_{iklm}\lambda'_{mpqi} \left\langle n_k n_l n_p n_q \right\rangle,$$
$$\left\langle \mathbf{n}\Lambda'^2\mathbf{n} \right\rangle = \lambda'_{iklm}\lambda'_{mpqr} \left\langle n_i n_k n_l n_p n_q n_r \right\rangle, \tag{28}$$
$$\left\langle (\mathbf{n}\Lambda'\mathbf{n})^2 \right\rangle = \lambda'_{iklm}\lambda'_{pqrs} \left\langle n_i n_k n_l n_m n_p n_q n_r n_s \right\rangle,$$

where the averaged products of the components of the phase-normal unit vector have the form (δ_{ik} is the Kronecker delta)

$$\left\langle n_k n_l n_p n_q \right\rangle = \frac{1}{15}(\delta_{kl}\delta_{pq} + \delta_{kp}\delta_{lq} + \delta_{kq}\delta_{lp}),$$
$$\left\langle n_i n_k n_l n_p n_q n_r \right\rangle = \frac{1}{105}(\delta_{ik}\delta_{lp}\delta_{qr} + \delta_{ik}\delta_{lq}\delta_{pr} + \delta_{ik}\delta_{lr}\delta_{pq} + \ldots), \tag{29}$$
$$\left\langle n_i n_k n_l n_m n_p n_q n_r n_s \right\rangle = \frac{1}{945}(\delta_{ik}\delta_{lm}\delta_{pq}\delta_{rs} + \delta_{ik}\delta_{lm}\delta_{pr}\delta_{qs} + \delta_{ik}\delta_{lm}\delta_{ps}\delta_{qr} + \ldots).$$

Only some terms are given in relations (29); in fact, the second and the third relations contain 15 and 105 terms, respectively. However, the tensor λ'_{iklm} is symmetric with respect to permutations of pairs of indices and permutations of indices in each pair $\lambda'_{iklm} = \lambda'_{lmik} = \lambda'_{kilm} = \lambda'_{ikml}$; therefore, (28) will have similar terms, related to one of the following eight groups:

$$\begin{aligned} A &= (\mu\nu)_t = \lambda'_{ikkl}\lambda'_{limm}, & B &= (\mu^2)_t = \lambda'_{ikkl}\lambda'_{lmmi}, \\ C &= (\nu^2)_t = \lambda'_{ikll}\lambda'_{kimm}, & D &= \mu_t\nu_t = \lambda'_{ikki}\lambda'_{llmm}, \\ E &= (\mu_t)^2 = \lambda'_{ikki}\lambda'_{lmml}, & F &= (\nu_t)^2 = \lambda'_{iikk}\lambda'_{llmm}, \\ P &= \lambda'_{iklm}\lambda'_{iklm}, & Q &= \lambda'_{iklm}\lambda'_{ilkm}, \end{aligned} \tag{30}$$

where symmetric second-rank tensors $\mu_{ik} = \lambda'_{illk}$ and $\nu_{ik} = \lambda'_{ikll}$ are introduced. As a result,

$$\left\langle (\Lambda'^2)_t \right\rangle = \frac{1}{15}(B + P + Q),$$
$$\left\langle \mathbf{n}\Lambda'^2\mathbf{n} \right\rangle = \frac{1}{105}(4A + 4B + C + 2P + 4Q), \tag{31}$$
$$\left\langle (\mathbf{n}\Lambda'\mathbf{n})^2 \right\rangle = \frac{1}{945}(32A + 32B + 8C + 4D + 4E + F + 8P + 16Q).$$

It should be noted that tensors μ and ν are trace-free in view of the latter two relations (26): $\mu_t = \lambda'_{ikki} = 0$ and $\nu_t = \lambda'_{iikk} = 0$. Therefore, $D = E = F = 0$ in (31).

The remaining invariants A, B, C, P, and Q, formed by the products of the components of tensor λ'_{iklm}, have the form

$$\begin{aligned} A = {} & (\lambda'_{11} + \lambda'_{55} + \lambda'_{66})(\lambda'_{11} + \lambda'_{12} + \lambda'_{13}) \\ & + (\lambda'_{22} + \lambda'_{44} + \lambda'_{66})(\lambda'_{22} + \lambda'_{12} + \lambda'_{23}) \\ & + (\lambda'_{33} + \lambda'_{44} + \lambda'_{55})(\lambda'_{33} + \lambda'_{13} + \lambda'_{23}) \\ & + 2(\lambda_{16} + \lambda_{26} + \lambda_{45})(\lambda_{16} + \lambda_{26} + \lambda_{36}) \\ & + 2(\lambda_{15} + \lambda_{35} + \lambda_{46})(\lambda_{15} + \lambda_{25} + \lambda_{35}) \\ & + 2(\lambda_{24} + \lambda_{34} + \lambda_{56})(\lambda_{14} + \lambda_{24} + \lambda_{34}), \end{aligned}$$

$$B = (\lambda'_{11} + \lambda'_{55} + \lambda'_{66})^2 + (\lambda'_{22} + \lambda'_{44} + \lambda'_{66})^2 + (\lambda'_{33} + \lambda'_{44} + \lambda'_{55})^2 + 2(\lambda_{16} + \lambda_{26} + \lambda_{45})^2 + 2(\lambda_{15} + \lambda_{35} + \lambda_{46})^2 + 2(\lambda_{24} + \lambda_{34} + \lambda_{56})^2,$$

$$C = (\lambda'_{11} + \lambda'_{12} + \lambda'_{13})^2 + (\lambda'_{22} + \lambda'_{12} + \lambda'_{23})^2 + (\lambda'_{33} + \lambda'_{13} + \lambda'_{23})^2 + 2(\lambda_{16} + \lambda_{26} + \lambda_{36})^2 + 2(\lambda_{15} + \lambda_{25} + \lambda_{35})^2 + 2(\lambda_{14} + \lambda_{24} + \lambda_{34})^2, \quad (32)$$

$$P = \lambda'^2_{11} + \lambda'^2_{22} + \lambda'^2_{33} + 2\lambda'^2_{12} + 2\lambda'^2_{13} + 2\lambda'^2_{23} + 4\lambda'^2_{44} + 4\lambda'^2_{55} + 4\lambda'^2_{66} + 4\lambda^2_{14} + 4\lambda^2_{15} + 4\lambda^2_{16} + 4\lambda^2_{24} + 4\lambda^2_{25} + 4\lambda^2_{26} + 4\lambda^2_{34} + 4\lambda^2_{35} + 4\lambda^2_{36} + 8\lambda^2_{45} + 8\lambda^2_{46} + 8\lambda^2_{56},$$

$$Q = \lambda'^2_{11} + \lambda'^2_{22} + \lambda'^2_{33} + 4\lambda'_{12}\lambda'_{66} + 4\lambda'_{13}\lambda'_{55} + 4\lambda'_{23}\lambda'_{44} + 2\lambda'^2_{44} + 2\lambda'^2_{55} + 2\lambda'^2_{66} + 8\lambda_{14}\lambda_{56} + 4\lambda^2_{15} + 4\lambda^2_{16} + 4\lambda^2_{24} + 8\lambda_{25}\lambda_{46} + 4\lambda^2_{26} + 4\lambda^2_{34} + 4\lambda^2_{35} + 8\lambda_{36}\lambda_{45} + 4\lambda^2_{45} + 4\lambda^2_{46} + 4\lambda^2_{56},$$

where primed components are calculated in correspondence with formulas (24).

The final expression for I is obtained using (27), (21), and (31):

$$I \approx \frac{2}{a^{3/2}} + \frac{1}{d^{3/2}} + \frac{1}{8a^{7/2}}(B + P + Q) + \frac{1}{140}\left(\frac{2}{ad^{5/2}} + \frac{2}{a^2d^{3/2}} + \frac{2}{a^{5/2}d + a^3\sqrt{d}} - \frac{5}{a^{7/2}}\right) \times (4A + 4B + C + 2P + 4Q) + \frac{1}{315}\left(\frac{5}{a^{7/2}} + \frac{5}{d^{7/2}} - \frac{4}{ad^{5/2}} - \frac{4}{a^2d^{3/2}} - \frac{4}{a^{5/2}d + a^3\sqrt{d}}\right) \times (4A + 4B + C + P + 2Q), \quad (33)$$

where the parameters a and d are found using formulas (25) and the invariants A, B, C, P, and Q are determined from formulas (32). The Debye temperature at 0 K can be obtained by substituting I (33) into relation (3); thus, this value is expressed directly in terms of 21 elastic moduli $c_{\beta\gamma}$ of the material with arbitrary anisotropy ($\lambda_{\beta\gamma} = c_{\beta\gamma}/\rho$). The relative error in calculating the I value is determined by the contribution of the third approximation and its order corresponds to cubed relative average quadratic elastic anisotropy [4].

CALCULATIONS FOR CUBIC CRYSTALS

The calculations according to general formula (33) do not present any difficulties for anisotropic bodies of any crystallographic symmetry. Let us focus here on the crystals of the cubic system, which have the highest symmetry as compared to the crystals of other systems. Their elastic properties are characterized by three independent moduli, λ_{11}, λ_{12}, and λ_{44}:

$$\lambda_{11} = \lambda_{22} = \lambda_{33}, \quad \lambda_{12} = \lambda_{13} = \lambda_{23}, \quad \lambda_{44} = \lambda_{55} = \lambda_{66},$$

while other moduli are zero. In accordance with (25), one can find the parameters of an isotropic medium whose elastic properties are the closest to those of cubic crystals:

$$a = \frac{1}{5}(\lambda_{11} - \lambda_{12} + 3\lambda_{44}), \quad d = \frac{1}{5}(3\lambda_{11} + 2\lambda_{12} + 4\lambda_{44}), \quad c = \frac{1}{5}(\lambda_{11} + 4\lambda_{12} - 2\lambda_{44}). \quad (34)$$

Then, the nonzero components of the difference fourth-rank tensor λ'_{iklm} (24) are as follows:

$$\lambda'_{11} = \lambda'_{22} = \lambda'_{33} = \lambda_{11} - d = \frac{2}{5}\lambda', \quad \lambda'_{12} = \lambda'_{13} = \lambda'_{23} = \lambda_{12} - c = -\frac{1}{5}\lambda', \quad \lambda'_{44} = \lambda'_{55} = \lambda'_{66} = \lambda_{44} - a = -\frac{1}{5}\lambda', \quad (35)$$

where

$$\lambda' = \lambda_{11} - \lambda_{12} - 2\lambda_{44} \quad (36)$$

characterizes the deviation of the elastic properties of a cubic crystal from the isotropic-medium properties. Taking into account (32), we calculate the invariants of tensor λ'_{iklm}:

$$A = B = C = 0, \quad P = Q = \frac{6}{5}\lambda'^2. \quad (37)$$

As a result, the main calculation formula (33) is simplified and can be written as

$$I \approx \frac{2}{a^{3/2}} + \frac{1}{d^{3/2}} + \frac{\lambda'^2}{70}\left(\frac{7}{a^{7/2}} + \frac{4}{d^{7/2}} + \frac{4}{ad^{5/2}} + \frac{4}{a^2d^{3/2}} + \frac{4}{a^{5/2}d + a^3\sqrt{d}}\right), \quad (38)$$

where a and d are determined according to (34) and λ' is found using (36).

The elastic moduli c_{11}, c_{12}, and c_{44} and densities ρ near 0 K for some materials belonging to the cubic system are listed in Table 1 [6]. Their molar masses M are also given. The materials are arranged in ascending order of their relative mean quadratic elastic anisotropy

$$\Delta = \sqrt{\frac{\langle(\Lambda'^2)_t\rangle}{\langle(\Lambda^2)_t\rangle}} = \frac{2|\lambda'|/\sqrt{5}}{\sqrt{(\lambda_{11} + 2\lambda_{44})^2 + 2(\lambda_{12} + \lambda_{44})^2 + 2\lambda^2_{11} + 4\lambda^2_{44}}}.$$

Table 1. Theoretically calculated and experimental values of the Debye temperature at 0 K for some materials belonging to the cubic system

Material	Elastic moduli, GPa			ρ, g/cm^3	M, g/mol	Δ	$\Theta^{(0)}$, K	$\Theta^{(2)}$, K	Θ (precise), K	Θ_{exp}, K
	c_{11}	c_{12}	c_{44}							
Tungsten	532.6	204.9	163.1	19.317	183.84	0.0010	384.4	384.4	384.4	383
Aluminum	114.3	61.9	31.6	2.733	26.981	0.0343	431.6	430.5	430.5	433
Vanadium	232.4	119.4	46.0	6.051	50.941	0.0357	400.5	399.2	399.3	399
Tantalum	266.3	158.2	87.4	16.696	180.94	0.0854	268.3	264.4	263.9	245
Gold	201.6	169.7	45.4	19.488	196.96	0.102	173.2	164.6	161.6	162.3
Palladium	234.1	176.1	71.2	12.132	106.42	0.120	290.9	279.1	275.7	271
Silver	131.5	97.3	51.1	10.635	107.86	0.160	245.1	231.7	226.5	227.3
Lead	55.5	45.4	19.4	11.599	207.2	0.162	117.7	109.5	105.2	105
Nickel	261.2	150.8	131.7	8.968	58.693	0.171	502.3	481.9	476.0	477
Copper	176.2	124.9	81.8	9.018	63.546	0.187	376.5	354.1	344.5	347

The Debye temperature was calculated based on the reported data within the zero approximation by substituting the values $I \approx I^{(0)} = 2a^{-3/2} + d^{-3/2}$, which correspond to an effective isotropic medium (column $\Theta^{(0)}$), into formula (3). In the next approximation, the I value refined according to (38) (column $\Theta^{(2)}$) was substituted. The most accurate I and Θ estimates were obtained by computer-aided numerical averaging of the sum $1/v_0^3 + 1/v_1^3 + 1/v_2^3$, while the elastic-wave velocities were determined as solutions to the characteristic equation $\left|\Lambda - v^2\right| = 0$ for cubic crystals (penultimate column). The experimental values of the Debye temperature at 0 K, taken from [7], are reported in the last column in Table 1.

Table 2. Relative deviations of the approximate $\Theta^{(0)}$ and $\Theta^{(2)}$ values of the Debye temperature from the accurate Θ values, calculated numerically using formulas (3) and (4)

Material	$\lvert\Theta^{(0)} - \Theta\rvert/\Theta$, %	$\lvert\Theta^{(2)} - \Theta\rvert/\Theta$, %	$\lvert\Theta - \Theta_{exp}\rvert/\Theta_{exp}$, %
Tungsten	~0	~0	0.37
Aluminum	0.26	~0	0.58
Vanadium	0.30	0.03	0.08
Tantalum	1.7	0.19	7.7
Gold	7.2	1.9	0.43
Palladium	5.5	1.2	1.7
Silver	8.2	2.3	0.35
Lead	11.9	4.1	0.19
Nickel	5.5	1.2	0.21
Copper	9.3	2.8	0.72

The relative deviations (in percents) of successive temperature approximations $\Theta^{(0)}$ and $\Theta^{(2)}$ from the Θ value, calculated using numerical averaging of the sum of reciprocal cubed velocities, are listed in Table 2. It can be seen that these deviations increase with an increase in the degree of material anisotropy, reaching in the case of lead 10 and ~4% for $\Theta^{(0)}$ and $\Theta^{(2)}$, respectively. At the same time, the relative deviation of the theoretical Θ value from the experimental measured Θ_{exp} values generally does not exceed 1% and equals 7.7 and 1.7% only in some cases (tantalum and palladium, respectively).

CONCLUSIONS

Approximate expressions (3), (32), and (33) for estimating the Debye temperature at 0 K were derived. These expressions contain directly the elastic moduli of a solid $c_{\beta\gamma}$ (or $\lambda_{\beta\gamma} = c_{\beta\gamma}/\rho$, where $\beta, \gamma = 1, \ldots 6$) and can be applied for materials of any crystallographic symmetry. Note that relation (33) is presented in the form of a series (up to quadratic terms) in deviations of moduli $c_{\beta\gamma}$ from elastic moduli $c^0_{\beta\gamma}$ of an effective isotropic medium. The formulas obtained can be used for fast estimating of the Debye temperature at 0 K, which does not require time-consuming numerical averaging of the $1/v_0^3 + 1/v_1^3 + 1/v_2^3$ value over the directions of the phase normals of isonormal elastic waves.

CONFLICT OF INTEREST

The author declares that he has no conflicts of interest.

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