CRYSTALLOGRAPHY

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Abstract

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A GENERAL FORMULA FOR THE DEBYE TEMPERATURE OF CRYSTALS

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As is known, the Debye temperature θ is an important characteristic of the physical properties of a solid. Its calculation, according to Debye theory, reduces to finding the sum of the reciprocal cubes of the three phase velocities of propagation of elastic waves, averaged over all directions of the wave normal $\mathbf{n}$*

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

For isotropic media I is obtained at once, but in the presence of anisotropy the calculation of this quantity is a very complicated problem. Even for such highly symmetric crystals as cubic ones, despite the development of a number of special computational methods, the calculations are so cumbersome that they have to be carried out by means of electronic computers ([1]) for each particular crystal separately. For less symmetric crystals the computational difficulties increase still more. Therefore, up to now θ has been calculated only for very few crystals (excluding the cubic and hexagonal syngonies).

In ([2, 3]) a method was proposed for calculating the Debye temperature that is, in principle, suitable for any crystals and that makes it possible to reduce the calculations many times over in comparison with all earlier methods. The present work gives a further development of this method, leading to still more substantial simplifications.

For a given $\mathbf{n}$, the squares of the phase velocities are the eigenvalues of the tensor

$$\Lambda = (\Lambda_{kl}) = \frac{\rho}{1}(c_{ikjl} n_i n_l)$$

$$\Lambda \mathbf{u} = v^2 \mathbf{u}. \tag{2}$$

Here c_{ijkl} is the tensor of elastic constants; ρ is the density of the medium; n_i are the components of the unit vector of the wave normal $\mathbf{n}$; $\mathbf{u}$ is the displacement vector of the wave. Thus v_0^2 (quasi-longitudinal wave) and v_1^2, v_2^2 (quasi-transverse waves) are the roots of the characteristic equation of third degree

$$|v^2 - \Lambda| = 0. \tag{3}$$

We shall construct an approximate theory by starting from a comparison of the given crystal with the isotropic medium nearest to it *on the average*. The tensor $\Lambda^0 = a + b\mathbf{n} \cdot \mathbf{n}$ for such a medium, according to ([4], [2]), is determined by the relations

$$a = \frac{1}{2}\langle \Lambda_c - \mathbf{n}\Lambda\mathbf{n}\rangle, \qquad b = \frac{1}{2}\langle 3\mathbf{n}\Lambda\mathbf{n} - \Lambda_c\rangle. \tag{4}$$

Here $\mathbf{n} \cdot \mathbf{n}$ is a dyad, $(\mathbf{n} \cdot \mathbf{n})_{ik} = n_i n_k$, $\Lambda_c = \Lambda_{kk}$, $\mathbf{n}\Lambda\mathbf{n} = n_k \Lambda_{kl} n_l$. According to (4),

$$\Lambda = a + b(\mathbf{n} \cdot \mathbf{n} + \alpha), \qquad \langle \alpha_c \rangle = \langle \mathbf{n}\alpha\mathbf{n}\rangle = 0. \tag{5}$$

* Angle brackets denote averaging over all directions of the unit vector $\mathbf{n}$.

Denoting $v^2 = a + b\xi$, we obtain instead of (3) the following equation for ξ*:

$$\xi^3 - (1 + \alpha_c)\xi + (\alpha_c - n\alpha n + \bar{\alpha}_c)\xi - (n\bar{\alpha}n + |\alpha|) = 0, \tag{6}$$

and instead of (2)

$$(\mathbf{n} \cdot \mathbf{n} + \alpha)\mathbf{u} = \xi\mathbf{u}.$$

Putting here $\mathbf{u} = \mathbf{n} + \mathbf{u}'$, $\mathbf{u}'\mathbf{n} = 0$, we obtain

$$\xi = 1 + n\alpha n + n\alpha\mathbf{u}', \tag{7}$$

after which (2) can be reduced to the form (see ([5], [2]))

$$\mathbf{u}' = \beta\mathbf{k} - \mathbf{k}\mathbf{u}' \cdot \beta\mathbf{u}', \qquad \mathbf{k} = [\mathbf{n}[\alpha\mathbf{n}, \mathbf{n}]], \tag{8}$$

$$\beta = \frac{1 + n\alpha n + \tau_c - \tau}{(1 + n\alpha n)(1 + n\alpha n + \tau_c) + \bar{\tau}_c}, \qquad \tau = (\mathbf{n} \cdot \mathbf{n} - 1)\alpha. \tag{9}$$

In view of the relative smallness of the tensor α and of the quantities connected with it, $\mathbf{k}$, $n\alpha n$, α_c, $\overline{n\alpha n}$, τ, etc., equation (8) admits a very simple approximate solution by iteration. In the first approximation $\mathbf{u}'_{(1)} = \beta\mathbf{k}$; in the second $\mathbf{u}'_{(2)} = \beta\mathbf{k} - \mathbf{k}\beta\mathbf{k}\cdot\beta^2\mathbf{k}$, etc. At the same time, by definition, it is clear that in this way we obtain the displacement toward the quasi-longitudinal wave. According to (7), we have respectively

$$\xi_0 = 1+\varepsilon, \qquad \varepsilon_{(1)} = n\alpha n + n\alpha\beta\mathbf{k}, \qquad \varepsilon_{(2)} = n\alpha n + n\alpha\beta\mathbf{k} - \mathbf{k}\beta\mathbf{k}\cdot n\alpha\beta^2\mathbf{k}. \tag{10}$$

The expression for $\varepsilon_{(1)}$ is valid up to terms of the third order in α inclusive, $\varepsilon_{(2)}$ up to the 5th order in α, and, in general, $\varepsilon_{(k)}$ up to order $(2k+1)$ in α. Taking this into account, from (8)–(10) we obtain

$$\varepsilon_{(1)} = \sigma + \mathbf{k}^2 + \mathbf{k}\alpha\mathbf{k} - \sigma\mathbf{k}^2, \qquad \sigma = n\alpha n, \tag{11}$$

$$\begin{aligned}\varepsilon_{(2)} = \varepsilon_{(1)} &+ \mathbf{k}^2(\sigma^2 - \bar{\tau}_c - \mathbf{k}^2) - (2\sigma+\tau_c)\mathbf{k}\alpha\mathbf{k} + \mathbf{k}\alpha\mathbf{k}(3\sigma^2 + 3\sigma\tau_c \\ &+ (\tau_c)^2 - \bar{\tau}_c) + \mathbf{k}^2[7\sigma^3 + 12\sigma^2\tau_c + 6\sigma(\tau_c)^2 + 3\sigma\bar{\tau}_c + \tau_c\bar{\tau}_c \\ &+ (\tau_c)^3 - 3\mathbf{k}\alpha\mathbf{k} + 3\sigma\mathbf{k}^2].\end{aligned} \tag{12}$$

Since $v^2 = a + b\xi$, it follows from (1) that

$$\begin{aligned}I &= \left\langle (a+b\xi_0)^{-3/2} + (a+b\xi_1)^{-3/2} + (a+b\xi_2)^{-3/2} \right\rangle \\ &= a^{-3/2}\left\langle (1+r_1\tilde{\xi}_1)^{-3/2} + (1+r_1\tilde{\xi}_2)^{-3/2} \right\rangle + c^{-3/2}\left\langle (1+r_2\varepsilon)^{-3/2} \right\rangle,\end{aligned} \tag{13}$$

where $c = a+b$, $r_1 = b/a$, $r_2 = b/c$. Using the binomial expansion, we obtain in the first approximation

$$\begin{aligned}I_1 = a^{-3/2}&\left\langle 2 - \frac{3}{2}r_1(\tilde{\xi}_1 + \tilde{\xi}_2) + \frac{15}{8}r_1^2(\tilde{\xi}_1^2 + \tilde{\xi}_2^2) - \frac{35}{16}r_1^3(\tilde{\xi}_1^3 + \tilde{\xi}_2^3)\right\rangle \\ &+ c^{-3/2}\left\langle 1 - \frac{3}{2}r_2\varepsilon + \frac{15}{8}r_2^2\varepsilon^2 - \frac{35}{16}r_2^3\varepsilon^3\right\rangle\end{aligned} \tag{14}$$

and in the second approximation

$$\begin{aligned}I_2 = I_1 + \frac{63}{256}\Big[a^{-3/2}&\left\langle 10r_1^4(\tilde{\xi}_1^4 + \tilde{\xi}_2^4) - 11r_1^5(\tilde{\xi}_1^5 + \tilde{\xi}_2^5)\right\rangle \\ &+ c^{-3/2}\left\langle 10r_2^4\varepsilon^4 - 11r_2^5\varepsilon^5\right\rangle\Big].\end{aligned} \tag{15}$$

Since, according to (6), $\xi_0 + \xi_1 + \xi_2 = 1 + \alpha_c$, $\xi_0(\xi_1+\xi_2) + \xi_1\xi_2 = \bar{\alpha}_c - \tau_c$, then $\tilde{\xi}_1 + \tilde{\xi}_2 = \alpha_c - \varepsilon$, $\tilde{\xi}_1\tilde{\xi}_2 = \bar{\alpha}_c - \tau_c - (1+\varepsilon)(\alpha_c - \varepsilon)$. With the aid of

the latter formulas all sums $\tilde{\xi}_1^k + \tilde{\xi}_2^k$ are expressed in terms of ε. For example, $\tilde{\xi}_1^2+\tilde{\xi}_2^2 = (\tilde{\xi}_1+\tilde{\xi}_2)^2-2\tilde{\xi}_1\tilde{\xi}_2$, $\tilde{\xi}_1^3+\tilde{\xi}_2^3 = (\tilde{\xi}_1+\tilde{\xi}_2)^3-3\tilde{\xi}_1\tilde{\xi}_2(\tilde{\xi}_1+\tilde{\xi}_2)$, etc. As a result, the expressions entering into (14) are reduced to polynomials with respect to the components n_k up to the 12th degree inclusive, and in (15) to polynomials up to the 20th degree. Thus the problem is reduced to averaging products of components of the unit vector n_k,

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* A bar over a tensor denotes the reciprocal tensor.

which can be done elementarily, although for a large number of factors the calculations for crystals of lower symmetries will be cumbersome.

All the relations given above are universal in character and are suitable for crystals of any symmetry. To obtain formulas for a crystal of a particular type, one must substitute into (4)–(15) the corresponding expressions for the tensor Λ (see, for example, ([6,2])). As an illustration, let us apply the general relations (11)–(15) to the case of cubic crystals, for which $a = c_{44}/\rho + 0.2c_3$, $b = (c_{12}+c_{44})/\rho + 0.4c_3$, $c_3 = (c_{11}-c_{12}-2c_{44})/\rho$. In the first approximation we obtain

$$I_1 = a^{-3/2}\left\{2 + r_{ar}b\left[0.1r_1(1-0.06r_a) + \frac{57.2-8.4r_a+0.48r_b}{1001}\right]\right\} + \\ +c^{-3/2}\left\{1 - \frac{r_{br}c}{1001}\left[57.2(1-r_2)+0.5r_b - r_c(7.2-6.7r_2)\right]\right\}, \qquad (16)$$

where $r_a = c_3/a$, $r_b = c_3/b$, $r_c = c_3/c$.

Restricting ourselves in the second approximation (15) to terms no higher than the 4th order, we obtain

$$I_2 = I_1 + \frac{r_b^4}{1001}\left[a^{-3/2}(0.17r_1+0.26r_1^2+4.18r_1^3+5.72r_1^4) - \right. \\ \left. -c^{-3/2}(0.17r_2+0.7r_2^2+5.86r_2^3-5.28r_2^4)\right]. \qquad (17)$$

The results of calculating the Debye temperature by formulas (16), (17) for several well-studied cubic crystals ([1]) are presented in Table 1. The first two rows contain the results of calculations by formulas (16) and (17); the third row gives experimental data, and the fourth row gives the results of calculations by other authors. The crystals are arranged in order of increasing mean elastic anisotropy ([4,2]). It is seen from the table that even the incomplete second approximation gives results that are not inferior in accuracy to the data shown in the last row, which were obtained by various authors (see ([1])) by means of very laborious and cumbersome calculations, sometimes using electronic computers. For lithium, which together with sodium and thorium belongs to the cubic crystals with the highest anisotropy, the results of calculations by

Table 1

	Al	Au	LiF	Ag	NaCl	Cu	KBr	Li
θ_1	428.4	163.8	735.2	230.1	322.1	351.4	177.9	382.6
θ_2	428.4	162.4	734.6	227.9	321.4	347.3	172.0	366.4
θ_{exp}	375–	164.6	722–	225.3	320	343.8	174	369
	426	–	743	–		–		
		164.8		226.5		346.7		
θ_a	427.4	161.6	734–	226.4	321–	344.4	171.7	334.6
	–	–	734.6	–	321.9	–	–	–
	428.7	162.2		227.1		345.4	172.8	338.4

our formulas agree with experiment much better than the data of other authors. Application of the general formulas (11), (15) to crystals of lower symmetry will make it possible to calculate the Debye temperature for them as well, something that previously had been practically inaccessible because of excessive computational difficulties.

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Note: Figure translations are in progress. See original paper for figures.