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PREDICTION OF THE THERMOPHYSICAL PROPERTIES OF SOLIDS

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Proceeding from the established interrelations between thermophysical, elastic, and structural characteristics, the article analyzes the possibility of predicting the thermophysical properties of solids.

Prediction of the thermophysical properties of materials (heat capacity, thermal conductivity, coefficient of thermal expansion, etc.) is of considerable scientific and practical interest. It is known from solid-state physics [1] that

$$\alpha = \gamma C_v/(3\beta^2 r N_A z). \tag{1}$$

Here, according to [2], we have:

$$\gamma/(r\beta^2) = (m + 4)\,\delta/(2V_{el}E). \tag{2}$$

Substituting (2) into (1), we have

$$C_v/\alpha = 6V_{el}N_A Ez/[(m + 4)\,\delta]. \tag{3}$$

Furthermore, we take into account [3]:

$$E = AkT_{mp}N/V_{el}, \tag{4}$$

where A is a dimensionless coefficient, where for compounds with predominantly ionic type of chemical bonds A = 64, for metals A = 90. Then we have from (3) and (4):

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$$C_v/\alpha = 6ANRT_{\mathrm{mp}}\, z/[(m+4)\,\delta]. \tag{5}$$

In the case of metals ($z = 1$, $m = 2$) it follows from formula (5) that

$$C_v/\alpha = 747T_{\mathrm{mp}}N/\delta. \tag{6}$$

For face-centered and hexagonal lattices $N/\delta = \sqrt{2}$, i.e., $C_V/\alpha = 1057T_{\mathrm{mp}}$; for body-centered lattices $N/\delta = 3\sqrt{3/4}$ [2], i.e., $C_V/\alpha = 972T_{\mathrm{mp}}$. It was necessary to verify whether these interrelations, i.e., formulas (6), correspond to the experimental data. The results of the investigations of the dependence of the ratio C_V/α on $T_{\mathrm{mp}}N/\delta$ for metals are presented in Fig. 1a. It can be seen that this dependence is really close to linear. The dots corresponding to the metals K, Li, Al, Ca, Ag, Cd, Zn, Cs, Na, Rb, Fe, Cr, Pt, Nb, and Ta lie close to the straight line; only Mo, W, Ti, V, and Au noticeably diverge from it. It is interesting to note that W and Mo correspond very well to formula (3) and considerably less well to formula (6), i.e., these metals obey formula (4) only very approximately. As regards the metals Ti and V, their considerable deviation from the straight line in Fig. 1a is due to the fact that the experimental values of α according to different authors differ considerably from each other [4]. In the case of Au it is known that it obeys the other regularities less well, too [4]; this is due to the peculiarities of its phonon spectrum. And, finally, it must also be borne in mind that the initial formula (1) is approximate, and that it does not always apply that $m = 2$ (or that $m = 10$ for complex substances [2]).

For complex substances with predominantly ionic type of chemical bonds and adopting $m = 10$, we have from (5):

$$C_v/\alpha = 228T_{\mathrm{mp}}Nz/\delta = 228T_{\mathrm{mp}}z^2N_1/\delta. \tag{7}$$

Since in handbooks isobaric heat capacity (C_p) is usually given, and since for solids $C_p \approx C_V$ (at low temperatures), we investigated the dependence of the ratio C_p/α on $T_{\mathrm{mp}}z^2N_1/\delta$. The obtained results are presented in Fig. 1b from which it can be seen that formula (7) is in good agreement with the experimental data. It must be borne in mind that for some substances, e.g., NiO and CaO, T_{me} has not been completely determined. This may also be the cause of the noticeable deviation of the dots belonging to these compounds from the straight line in Fig. 1b.

Formula (7) is of considerable interest because it permits an evaluation of the ratio C_V/α when the ratio N_1/δ is known (which is constant for each structural type) and when T_{mp} is known, which is usually known or can be predicted [3], or it is experimentally determined (which is much simpler and more accessible than the experimental determination of C_V and α). It is well known that the ratio C_V/α is contained in a number of important formulas, e.g., in Grüneisen's formula for calculating the vibration frequency of atoms, in Schwarz's formula for calculating the energy of crystals, etc. Moreover, formula (7) makes it possible to evaluate α, too, because the heat capacity can be determined when the Debye temperature is known, and this, as will be shown below, can be predicted. Finally, it must be borne in mind that the present article deals chiefly with polycrystals of the cubic system because in the case of lower systems all the formulas under consideration agree less with experiments. Even in the case of the cubic system, on account of the above, formula (7) does not always give C_V/α with great accuracy. Its advantage is that it makes it possible to evaluate C_V/α easily and rapidly on the basis of x-ray data or even without them because crystal structures can be predicted [5]. We note that the ratio C_V/α is almost independent of the temperature. This is clear from an analysis of formulas (3) and (5), and it is also experimentally confirmed [6].

For relatively simple crystal structures the heat capacity can be calculated by the generally known formula

$$C_v = 234Rz\,(T/\theta)^3, \tag{8}$$

where $T \ll \theta$. Formula (8) is used as a rule for determining θ when C_V is known. Since the experimental determination of C_V is laborious and requires special equipment (especially in the range of low temperatures), the inverse problem is of considerable interest: to calculate C_V when θ is given. Among the known formulas for determining θ, the following expression is most in agreement with the experimental values of [7]:

$$\theta = 172\sqrt{kT_{\mathrm{mp}}z/M}\;\sqrt[3]{\delta/V_{\mathrm{el}}}\,. \tag{9}$$

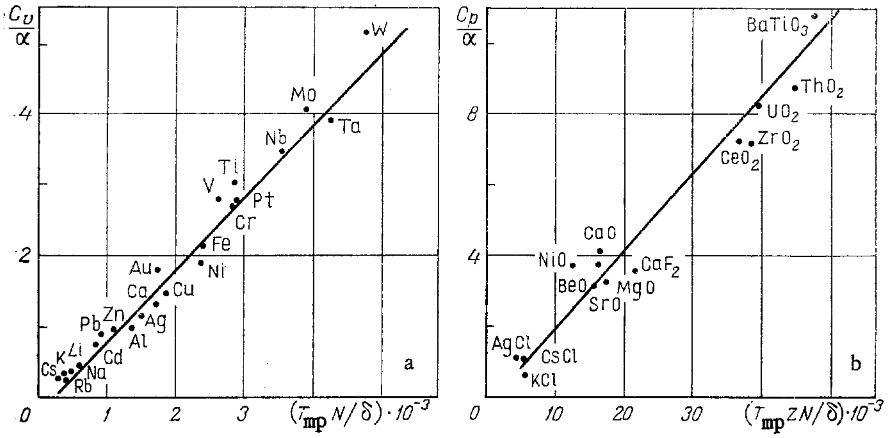

Fig. 1. Dependence of the ratio of heat capacity [MJ/(mole·K)] to the coefficient of linear expansion (K^{-1}) on the product of the melting point (K) by the structural factor N/δ and the number of atoms in a formula unit: a) for metals; b) for complex substances.

It can also be represented in the form

$$\theta = 172\sqrt{kT_{mp}z/M}/r, \tag{10}$$

where in the case of complex substances r has to be understood to mean the minimal distance between the centers of the ions which play the dominating part in the propagation of sound waves. It was noted in [8] that such ions are usually anions (on condition that the ionic radius of the cation is smaller than of the anion). If the radii of the ions differ considerably (by a factor of 1.5 or more), then we can with fairly good approximation take it that $r = 2r_i$, where r_i is the ionic radius of the larger ion. This opens up great prospects for predicting the θ of materials because the prediction of T_{mp} is possible. If the sizes of the ionic radii differ little from each other, then the approximation $r \approx 2r_i$ becomes rather crude. In such cases it is expedient to use formula (9). Formulas (9) and (10) make it possible easily to evaluate the values of θ, and in the case of a cubic system the error usually does not exceed 10%. It must be pointed out that Sindh and Tolpadi [9] dealt with a method of determining θ based on complex computer calculations which quite frequently yields a somewhat greater accuracy than calculation by formulas (9) and (10). However, for that the values of the elastic constants must be available, but they are far from always being known. The advantage of formulas (9) and (10) is that they make it possible to evaluate θ, also for substances that have not yet been synthesized. This is of considerable interest, not only for calculating C_V by formula (8), and then α by formula (7), but also for evaluating one of the most important thermophysical characteristics, the thermal conductivity of solids. A number of formulas are known for calculating the coefficient of lattice thermal conductivity λ, where θ figures directly and indirectly [10]. One of the most widely used formulas is the Leibfried–Schlohmann formula [10]:

$$\lambda = 2{,}4k^3\theta^3 M_a/(\Gamma^2 T h^3). \tag{11}$$

The constant Γ can be determined from Grüneisen's law

$$\alpha = \Gamma C_v x/(3V), \tag{12}$$

if the isothermal compressibility x and the molar volume V are known. As regards the ratio C_V/α, it can be evaluated by formula (7). However, the value of x is far from being always known. Then we use formula (3), and proceeding from it and from the generally known formulas $V_{el} = VN/(N_A z)$ and $x = 3(1 - 2\mu)/E$, we find easily that

$$\alpha = (m+4)C_v x\delta/[18(1-2\mu)VN]. \tag{13}$$

It follows from (12) and (13) that

$$\Gamma = (m+4)\,\delta/[6(1-2\mu)\,N]. \tag{14}$$

It is known that Γ is an important physical parameter. Formula (14) makes it possible to determine Γ fairly simply if μ is known (it usually changes within fairly narrow limits for certain classes of substances [2]). By formula (14) we calculated the values of Γ for Cu, Al, Fe, Ni, Ag, Mg, Mo, Nb, Ta, Zn, Au, Pt, MgO, CaO, NaCl, KCl, $BaTiO_3$, $CaTiO_3$ and compared them with the values of Γ obtained by formula (12). Agreement between them was perfectly good for all substances except Nb and MgO for which the divergences amounted to approximately 50%. The reason for these discrepancies is that when $\mu \geqq 0.4$ (e.g., Nb), even a slight inaccuracy in determining μ leads to a considerable error for Γ as can be easily seen from (14). In the case of MgO, $\mu = 0.35$ and, in addition, it must be borne in mind that with this compound α depends to a considerable extent on the previous history. Thus, when $\mu \leqq 0.3$ (which is the case, e.g., with most ceramic materials [2]), formula (14) may be used for evaluating Γ with acceptable accuracy.

In conclusion, it should be noted that formula (3) is a useful complement to Grüneisen's fundamental law. It is well known that the microscopic theory and the thermodynamic theory complement each other. In this case, these complements are very useful because problems that are not solved by one theory are successfully solved with the aid of the other theory. For instance, in distinction to formula (12), formula (3) makes it possible (except for C_V and α) to predict the thermal stresses in materials when $T > \theta$. In fact, when $T > \theta$, $C_V \approx 3Rz$, and then, proceeding from (3), we can easily predict the magnitude of the product αE which determines the magnitude of the thermal stresses in materials.

Although the discussed interrelations do not always permit predictions with good accuracy, they are nevertheless of considerable interest because they make it possible to shorten considerably some laborious experimental investigations in the search for materials with specified thermophysical characteristics. The accuracy of prediction is connected to a considerable extent with the nature of the chemical bonds in solids.

NOTATION

α, linear coefficient of thermal expansion; C_V and C_p, molar heat capacities with constant volume and constant pressure, respectively; β and γ, coefficients in the expression of potential energy of the oscillator; m, parameter characterizing the potential of the repulsive forces; r, interatomic distance; N_A, Avogadro's number; z and N, number of atoms in a formula unit and in an elementary cell, respectively; N_1, number of formula units in an elementary cell; V_{el} and V, volume of an elementary cell and molar volume, respectively; $\delta = V_{el}/r^3$, structural coefficient; E, Young's modulus; k, Boltzmann constant; R, universal gas constant; T_{mp}, melting point, K; h, Planck constant; θ, characteristic Debye temperature, K; M, molar mass; M_a, atomic mass; Γ, Grüneisen constant; x, isothermal compressibility; μ, Poisson ratio; T, absolute temperature.

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