THERMAL CONDUCTIVITY OF BINARY DISORDERED CONTINUOUS SOLID SOLUTIONS

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A simplified model for the structure and an approximate method of computing the thermal conductivity of continuous solid solutions are proposed. The method is suitable for a check, extension of the measurement results, and prediction of the thermal conductivity of solid solutions.

Many elements (metals and nonmetals) and their chemical compounds (oxides, salts, carbides, nitrides, silicides, etc.) possess the capacity to form solid substitution solutions (unbounded solubility in the solid state).

The concentration dependence of the thermal conductivity of disordered continuous solid solutions has a characteristic peculiarity which is evidenced when comparing the composition–property diagram with the phase diagram (solubility diagrams). It is known (Fig. 1) that the dependence of the thermal conductivity of a continuous solid solution has a quite definite minimum at the 50% concentration of component atoms, ions, or molecules, while a qualitatively distinct monotonic behavior of the concentration dependence is observed in systems with practically insoluble components (mechanical mixtures). The presence of the minimum at the 50% component concentration, established experimentally, is explained qualitatively in solid-state theory by the distortions of the initial crystal lattice of the component A in the region surrounding the atom or molecule of the impurity component B. Distortions of the crystal lattice are considered as defects impeding heat transfer. The volume concentration of defects (distorted domains) of the initial component A in the crystal lattice varies in proportion to the impurity content (i.e., the component B) and reaches a maximum for an equal atomic or molar concentration of components. A further increase in the content of the component B can be considered as an impurity diminution (the component A) in the initial crystal lattice B, which will result in a growth of the thermal conductivity of the solid solution.

The complexity of a mathematical description of the heat-transport process in solid solutions and the contradiction and incompletenesss of the information about the nature of the energy interaction between the components explain the lack of reliable methods to compute the thermal conductivity in the solid state and produce a need for carrying out complex and tedious experimental investigations. The error acceptable in engineering computations (comparable to the measurement error) can be obtained, as a rule, by using two empirical coefficients in the computational relations [1-3].

The tendency to shorten tedious measurements and to search for simplified methods of generalization, interpolation, and extrapolation of experimental results explains the attempt to develop a combined approach to the description of the thermal conductivity of continuous solid solutions which will combine the fundamental representations of the molecular kinetic theory of the solid state with phenomenological (continual) models and methods of the theory of generalized conduction, tested on alloys with practically insoluble components in [4].

The lack of constraints, in principle, on the minimal size of a continuous medium in the theory of generalized conduction permitted its successful utilization for an analytical description of the heat-transport process in gas mixtures and liquid solutions, whose components can be mixed at the atomic or molecular level [4].

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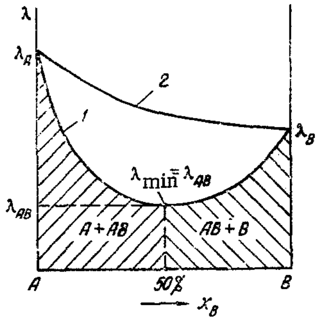

Fig. 1. Thermal conductivity–composition diagram: 1) system with unlimited solubility of the components in the solid state (continuous solid solutions); 2) system with components which are practically insoluble in the solid state, x_B in atomic %.

Let us consider the crystal lattice of any component, for example, A, with impurities of atoms of the component B. Rejecting a discrete image of the crystal lattice, let us consider the domain of lattice distortion around the impurity atom to be filled, just as is the rest of the undistorted lattice, by distinct continuous media (continuums) with different values of the coefficient of thermal conductivity: λ_{AB} and λ_A. The size of the distorted region and the degree of change in the properties of the continuous medium which fills it depend on the nature of the components and on their concentration.

Indeed, for a quite small impurity concentration, the size of the distortion domain can emerge outside the limits of the first coordination sphere, including the nearest atoms of the initial lattice surrounding the impurity atoms. An increase in the impurity concentration will result in closure of the distorted domains and then to mutual overlapping. The difference between the properties (thermal conductivity) of a continuous medium in the distortion zone from the properties of the initial components is inversely proportional to the impurity concentration and becomes maximal at the atomic or molecular concentrations of the components $x_A = x_B = 50\%$. At this point the thermal conductivity of a solution solid is $\lambda_{AB} = \lambda_{BA} = \lambda_{\min}$.

To simplify the subsequent analysis, let us consider (hypothesis 1) the thermal conductivity of a continuous medium to be constant in the distortion zone of a crystal lattice and to equal $\lambda_{AB} = \text{const} = \lambda_{\min}$. The hypothesis made permits consideration of a solid solution of 50% concentration as a special continuous medium (the substance AB) with thermal conductivity $\lambda_{AB} = \lambda_{\min}$, which forms a mixture A + AB with the initial components at the concentrations $0 < x_B < 50\%$ and a mixture AB + B for $50 < x_B < 100\%$.

Furthermore, let us assume (hypothesis 2) that the thermal conductivity of a solid solution with $x_A = x_B = 50\%$ is known (has been measured, as for any individual substance, or has been determined theoretically).

If the hypotheses made do not contain contradictions, in principle, then the dependence of the thermal conductivity of continuous solid solutions on both sides of the point $x_A = x_B = 50\%$ should be monotonic in character, which is in complete agreement with the whole set of experimental results (see Fig. 4) and is a qualitative foundation for the consistency of the hypotheses made. Further difficulties are thereby transferred to the method of determining the size of the distorted zone of the crystal lattice or (from the phenomenological viewpoint) to the determinination of the volume concentration of the component AB with the thermal conductivity $\lambda_{AB} = \lambda_{\min}$.

It is known that continuous solid substitution solutions form components with an identical kind of crystal lattice and very close atomic volumes (the difference is less than 15%). This latter permits considering the specific volumes per atom of the initial component and the impurity approximately equal. In such a case, the size (volume) of the distortion zone is expressed conveniently by a quantity which is a multiple of the coordination number N(x), i.e., the number of atoms (ions or molecules) of the initial component per atom of impurity. If $x_A = x_B = 50\%$, then

$$N(x) = N_{\min} = 1 \tag{1}$$

and is independent of the kind of crystal lattice.

Let us estimate the upper limit value lim N(x) of the number of atoms of the initial component per atom of impurity in different crystal lattices. If it is assumed in conformity with [5, 6] that the fundamental energy interaction between atoms at the sites of the crystal lattice occurs with the nearest neighbor atoms in the first coordination sphere, then the kind of lattice determines lim N(x) uniquely (Fig. 2).

Two important peculiarities exposed in the analysis of Fig. 2 should be noted: The limit values lim N(x) are independent of the kind of lattice; from physical considerations (the finite size of the distortion zone), the growth of the function N(x) with the diminution of the impurity concentration should be bounded by certain maximum values for any kind of lattice, i.e., $1 \leq N(x) \leq N_{\max}$.

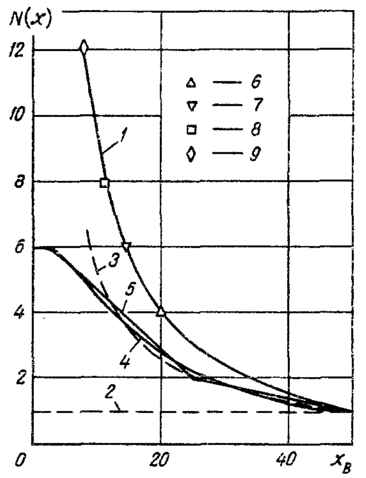

Fig. 2

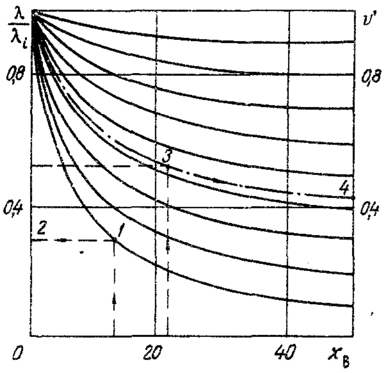

Fig. 3

Fig. 2. Derivation of the dependence N(x): 1, 2) maximum and minimum limit values of the coordination number N(x); 3) arithmetic mean (of the minimum and maximum limit) value of N(x); 4) kind of "smooth" function N(x) which satisfies conditions (1)-(5); 5) piecewise-linear approximation of N(x); 6, 7, 8, 9) values of N(x) for crystal lattices of diamond, simplest cubic, body-centered- and face-centered-cubic types, x in %.

Fig. 3. Nomogram for computation of the thermal conductivity of continuous solid solutions, x_B in atomic %.

The maximum value bounded by the first coordination sphere can vary between 4 and 12 depending on the kind of lattice.

In a first approximation it can be assumed that $N_{max} = 6$ (simplest cubic lattice), which thereby constrains the range of possible values of the function N(x) within the following limits:

$$1 \leq N(x) \leq 6. \tag{2}$$

Since the true form of the function N(x) is not determined by a priori considerations, there remains to seek it by either a sampling method or by taking account of the additional conditions which sharply contract the practically unbounded combinatorics of "suitable functions."

The problem of searching for the form of the function N(x) recalls, somewhat, the analogous problem of determining the approximate form of the even potential of intramolecular interaction in kinetic theory, where the form of the potential is specified by qualitative considerations, and its parameters are sought from a comparison between theoretical values and the results of measuring the transport coefficients or the state parameters. It is expedient to constrain the combinatorics of the possible functions by the imposition of a number of necessary conditions which the desired function should satisfy.

The finite size of the distortion zone for a low impurity concentration can be expressed by the condition

$$\text{when } x \to 0 \quad \frac{dN(x)}{dx} = 0. \tag{3}$$

According to the theory of generalized conduction, the condition

$$\text{when } x \to 50\% \text{ and } \lambda_{AB} \neq \lambda_A,\ \lambda_B \quad \frac{d\lambda(x)}{dx} \neq 0 \tag{4}$$

should be satisfied for a mixture of continuous media with different thermal conductivities. As is often done in a first approximation, we assume for the intermediate concentrations $0 \leq x_B \leq 50\%$ that the magnitude of the desired function N(x) will be close to some mean (for example, the arithmetic mean) between the upper limit (for a given impurity concentration) and the minimum values, i.e.,

$$\text{for } 0 < x < 50\% \quad N(x) \approx \frac{N_{\min} + \lim N(x)}{2}. \tag{5}$$

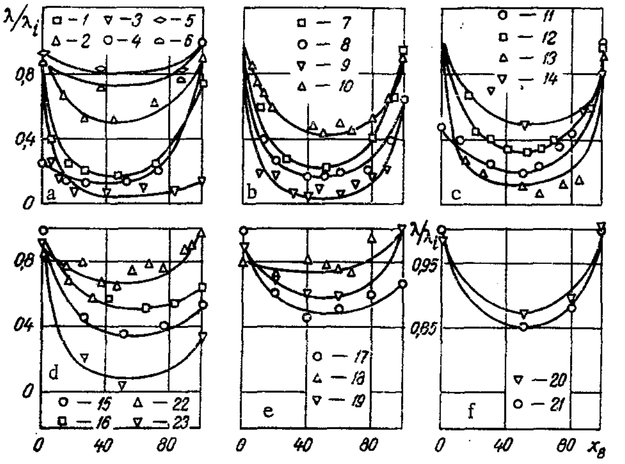

Fig. 4. Comparison between results of a computation and experimental results. Curves are from the computation. Experiment: 1) Ag–Au; 2) Pt–Pd; 3) Cu–Ni; 4) Pd–Ag (all for T = 273°K [7]); 5) W–Mo, T = 1200°K; 6) W–Mo; T = 2600°K [9]; 7) HgSe–HgTe; 8) Ge–Si; 9) In_2–GaAs; 10) PbTe–PbSe; 11) Mg_2Si–Mg_2Sn; 12) Mg_2Ge–Mg_2Sn; 13) Ga_2Se_3–Ga_2Te_3; 14) Bi_2Te_3–Bi_2Se_3 (all for T = 300°K [1, 2, 3]); 15) UO_2–PuO_2, T = 300°K [8]; 16) ZrC–ZrN, T = 300°K [10]; 17) TiC–HfC; 18) ZrC–HfC; 19) NbC–HfC, T = 300°K [10]; 20) $ZrC_{0.755}$–$NbC_{0.75}$, T = 1673°K; 21) the same for T = 2673°K [11]; 22) $ZrC_{0.92}$–$ZrN_{0.82}$ [13]; 23) $MoSi_2$–$ReSi_2$ [12]; T = 300°K; graph a is in atomic %; graphs b, c, d, e, f – x_B are in molecular %.

The form of the function N(x) satisfying the requirements (1)-(5) listed above is represented by curve 4 in Fig. 2. The approximate "smooth" function can be selected as a polynomial (curve 4 in Fig. 2)

$$N(x) \approx 6 - 3.318 \cdot 10^{-2}x^2 + 2.337 \cdot 10^{-3}x^3 - 7.743 \cdot 10^{-5}x^4 + 1.229 \cdot 10^{-6}x^5 - 7.639 \cdot 10^{-9}x^6, \tag{6}$$

whose numerical coefficients are determined by the boundary conditions (1)-(5) or by a simplified piecewise-linear approximation (the broken line 5 in Fig. 2):

$$\begin{aligned} &0 \leqslant x \leqslant 3\%, \quad N(x) = 6; \\ &3 \leqslant x \leqslant 25\%, \quad N(x) \approx 6 - \frac{2}{11}(x-3); \\ &25 \leqslant x \leqslant 50\%, \quad N(x) \approx 2 - 0.04\,(x - 25). \end{aligned} \tag{7}$$

By knowing the number of atoms (ions or molecules) of the initial component per impurity atom N(x), an expression for the volume concentration m_{AB} of the distorted zones in the crystal lattice, as though filled by a continuous medium with the thermal conductivity $\lambda_{AB} = \lambda_{min}$, can be obtained easily:

$$m_{AB} = 0.01\,[1 + N(x)], \quad 0 \leqslant m_{AB} \leqslant 1.0. \tag{8}$$

The chaotic structure of a two-component mixture of continuous media (the initial component and the distortion zones) and its corresponding ordered model for the computation of the thermal conductivity are determined by the impurity concentration. For a low impurity content (less than three atomic or molecular percent) the volume concentration of the distorted regions (8) is $m_{AB} < 0.2$ and the regions themselves are isolated, as a rule. The effective thermal conductivity of a system whose distorted domains are modeled in the form of impregnations which are not in contact in a continuous medium can be computed by means of the Eiken–Odelevskii formula [5]:

$$\lambda = \lambda_A \left(1 - \frac{m_{AB}}{\dfrac{1}{1-\nu'} - \dfrac{1-m_{AB}}{3}}\right), \quad \nu' = \frac{\lambda_{min}}{\lambda_A}. \tag{9}$$

As the impurity content grows (x > 3%) the distortion zones in the crystal lattice converge and enter into contact [2] to form a chaotic spatial system with interpenetrating components. The effective thermal conductivity of an ordered structure with interpenetrating components can be computed by means of the Dul'nev formula [6]

$$\lambda = \lambda_A \left[c^2 + \nu'(1-c)^2 + \frac{2\nu' c(1-c)}{\nu' c + 1 - c}\right], \quad \nu' = \frac{\lambda_{min}}{\lambda_A}, \tag{10}$$

where $c = f(m_{AB})$ is a geometric parameter of the ordered model [6], related uniquely to the volume concentration of the distortion zones m_{AB} by means of the cubic equation

$$2c^3 - 3c^2 + 1 = m_{AB}, \tag{11}$$

whose solution (first root) is

$$c = 0.5 + a\cos\frac{\varphi}{3}, \quad 270 \leqslant \varphi \leqslant 360^\circ, \quad 0 \leqslant m_{AB} \leqslant 0.5 \quad a = 1 \quad \varphi = \arccos(1 - 2m_{AB}), \quad 0.5 \leqslant m_{AB} \leqslant 1.0 \quad a = -1 \quad \varphi = \arccos(2m_{AB} - 1).$$

Thus, the computation of the thermal conductivity of continuous solid solutions can be performed as follows.

By means of the known (test) values of the thermal conductivity λ_{min} of a solid solution of 50 atomic or molecular %, and one of the initial components, λ_A, for example, we find the ratio $\nu' = \lambda_{min}/\lambda_A$ and then we calculate the volume concentration of the distortion zones m_{AB} in fractions of one by means of (6)-(8). Furthermore, depending on the impurity concentration, we determine the desired thermal conductivity of the solid solution with appropriate impurity concentration $0 < x_B < 50\%$ by means of (11) and (10) or (9).

The computation in the $50 < x_B < 100\%$ range is executed in an analogous manner with the replacement of the subscript of the components, i.e., $\nu' = \lambda_{min}/\lambda_B$ is calculated, $m_{BA} = f(x_A)$ is determined by means of (6)-(8), and then the desired magnitude of the effective thermal conductivity $\lambda = f(\lambda_B, m_{BA})$ is found from (9) or (10).

The computation is simplified substantially when a nomogram (Fig. 3) constructed by means of the scheme elucidated above is used.

EXAMPLE OF A COMPUTATION

Let us assume that the components $A(\lambda_A = 100$ W/m·K) and B form a continuous solid solution. The thermal conductivity of the alloy is known for $x_A = x_B = 50\%$, $\lambda_{AB} = \lambda_{min} = 10$ W/m·K. Calculate the thermal conductivity of the solid solution with concentration $x_B = 13$ atomic %.

We find $\nu' = 10/100 = 0.1$. All the desired values of the thermal conductivity of solid solutions in the domain $0 < x_B < 50\%$ lie on the curve $\nu' = 0.1$. The relative thermal conductivity of a solution of the desired composition is determined by the intersection of the $\nu' = 0.1$ curve with a perpendicular erected on the horizontal axis at the point $x_B = 13\%$ (point 1 in Fig. 3) and equal to $\lambda/\lambda_A = 0.3$ (point 2 in Fig. 3). The absolute desired value of the thermal conductivity of the solid solution ($x_B = 13\%$) is $\lambda = 0.3 \cdot 100 = 30$ W/m·K.

If the thermal conductivity of the solid solution $\lambda_{AB} = \lambda_{min}$ is unknown, then it can be determined by using the same nomogram for another known value of the thermal conductivity of a solid solution of the composition $0 < x_B < 50\%$. For example, by knowing that $x_B = 22\%$ $\lambda = 54$ W/m·K for $x_B = 22\%$, we find the intersection of perpendiculars erected at $x_B = 22\%$ on the horizontal axis and for $\lambda/\lambda_A = 54/100 = 0.54$ on the vertical axis (point 3 in Fig. 3). All the remaining values of the thermal conductivity of solid solutions of the system under consideration will be on the dashed-dot curve passing through point 3 and the corresponding value of $\nu' = 0.43$ or $\lambda_{min} = 43$ W/m·K (4).

A quantitative confirmation of the validity of the reasoning elucidated and of the method proposed for determining the thermal conductivity of continuous solid solutions was performed by comparing the computed and experimental values of the thermal conductivity of more than 30 binary systems of solid solutions of elements and chemical compounds (Fig. 4).

Despite the substantial differences in the nature of the components (metals, semiconductors, oxides, carbides, nitrides, silicides) and in the character of the thermal-energy carriers (electrons, phonons, combined transfer), not only the qualitative behavior of the concentration dependence of the thermal conductivity, but also the numerical results, agree completely in all the solid solutions considered. The shape of the discrepancy histograms of the computed and measured values of the thermal conductivity is almost a normal distribution curve. The root-mean-square discrepancy of the results of the computation and the experimental data for 150 points, which was about 10%, does not emerge outside the limits of the scatter zone for the experimental data obtained by different researchers for the same alloy, and is commensurate with the error in measuring the thermal conductivity [1, 8, 9-13]. No systematic discrepancies were detected in the whole range of component concentrations.

LITERATURE CITED

1. J. R. Drabble and E. J. Goldschmid, Thermal Conduction of Semiconductors, Pergamon (1951).
2. V. S. Oskotskii and I. A. Smirnov, Thermal Conductivity and Crystal Lattice Defects [in Russian], Nauka, Leningrad (1972).
3. B. M. Mogilevskii and A. F. Chudnovskii, Thermal Conductivity of Semiconductors [in Russian], Nauka, Moscow (1972).
4. G. N. Dul'nev and Yu. P. Zarichnyak, Inzh.-Fiz. Zh., 14, No. 3 (1968); 9, No. 6 (1966); 15, No. 4 (1968).

5. V. I. Odelevskii, Zh. Tekh. Fiz., 21, No. 11 (1951).
6. G. N. Dul'nev, Inzh.-Fiz. Zh., 9, No. 3 (1965).
7. V. S. Chirkin, Thermophysical Properties of Materials [in Russian], Fizmatgiz, Moscow (1959).
8. V. S. Chirkin, Thermophysical Properties of Nuclear Engineering Materials [in Russian], Atomizdat, Moscow (1968).
9. V. A. Vertogradskii, Author's Abstract of Candidate's Dissertation, Moscow Power Institute, Moscow (1972).
10. V. N. Paderno, Izv. Akad. Nauk SSSR, Neorgan. Mater., 3, No. 7 (1967).
11. B. A. Fridlender, Candidate's Dissertation, Leningrad Institute of Precision Mechanics and Optics, Leningrad (1974).
12. V. S. Neshpor and G. V. Samsonov, Fiz. Metl. Metalloved., 18, No. 2 (1964).
13. V. S. Neshpor, Yu. N. Vil'k and I. N. Denisina, Poroshkov. Metallurg., No. 1 (49) (1967).