THERMAL CONDUCTIVITY AND STRUCTURAL CHARACTERISTICS OF CaF_2 CRYSTALS DOPED WITH NaF AND YF_3

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The thermal conductivity of CaF_2 single crystals containing different amounts of yttrium and sodium was investigated at temperatures of 80-300°K. An anomaly due to resonance was found in the initial region of experimental temperatures.

Alkali-earth fluorides find wide application in various branches of optics. An investigation of fluorite crystals doped with trivalent metals is very important, since such impurity systems have desirable technical qualities. A method of investigating defect states which is becoming more and more popular is the measurement of thermal conductivity. In the present investigation we studied heat transfer in pure and doped CaF_2 crystals in the range 80-300°K. The method of measurement was the well-known steady-state method (error of measurement 5%), whose basic features were described in [1]. The most reliable thermal conductivity data for CaF_2 are given in [2, 3]. Our values for the thermal conductivity at room temperature were approximately 3-5% lower than the results of [2], but 5% higher than the data of [3], although the temperature dependences were similar. These differences are probably due to the different degrees of purity of the crystals. The thermal conductivity of Na-doped specimens is shown in Fig. 1a, and the thermal resistance is shown in Fig. 1b. Figure 1b indicates that the thermal resistance of undoped CaF_2 varies linearly with temperature: $W = A_1T + A_2$, where $A_1 = 0.38 \cdot 10^{-3}$ m/W, and $A_2 = -14.5 \cdot 10^{-3}$ m·deg /W. According to [2], at the Debye temperature the thermal conductivity of CaF_2 is predicted satisfactorily by the Leibfried–Schlomann formula [4] with $\gamma_G = 1.8$ and $v = 3.51 \cdot 10^3$ m/sec. With reduction of temperature umklapp processes [2] become more and more important and lead to an exponential increase in the thermal conductivity. In view of the linear variation of W, Slack's viewpoint [2] is not very convincing. It is more plausible to postulate that a contribution to the heat transfer is made by the optical branches, which give rise to an additional thermal conduction component. In the complex spectrum of fluorite the optical branches are very pronounced and constitute a substantial part (2/3) of the spectrum. Three-phonon processes (particularly fusion processes) for optical phonons are inhibited by the limitations imposed by the laws of conservation of energy and momentum [5] and the leading role is taken over by four-phonon processes, whose scattering rate is related to the temperature by a square law.

The thermal conductivity, conforming to the law $W = A_1T + A_2$, has the form

$$\lambda = \lambda_{ac} + \lambda_{opt} \simeq \frac{B_1}{T} + \frac{B_2}{T^2}, \tag{1}$$

where $B_1 = 1/A_1 = 2.6 \cdot 10^3$ W/m, $B_2 = |A_2|/A_1^2 = 9.9 \cdot 10^4$ W·deg/m. The second term on the right side of (1) is the thermal conductivity representing energy transfer by optical phonons. It is probable that umklapp processes, discussed in [2], actually take place only at temperatures lower than nitrogen temperatures. For instance, Slack [2] reported that b was constant in the exponential law $\lambda \sim \exp[\theta_D/bT]$ only when $T \leq 0.1\,\theta_D$ ($b \simeq 2.83$-3). The quantity $|A_2|$ is hardly suitable for accurate calculation of the contribution of optical transfer. The presence of foreign admixtures and the small amount of isotopic scattering [2] should reduce the absolute value of $|A_2|$ (see Table 1, which gives the results of a spectrographic impurity analysis for three investigated pure specimens with almost equal thermal conductivity). The effect of Na is

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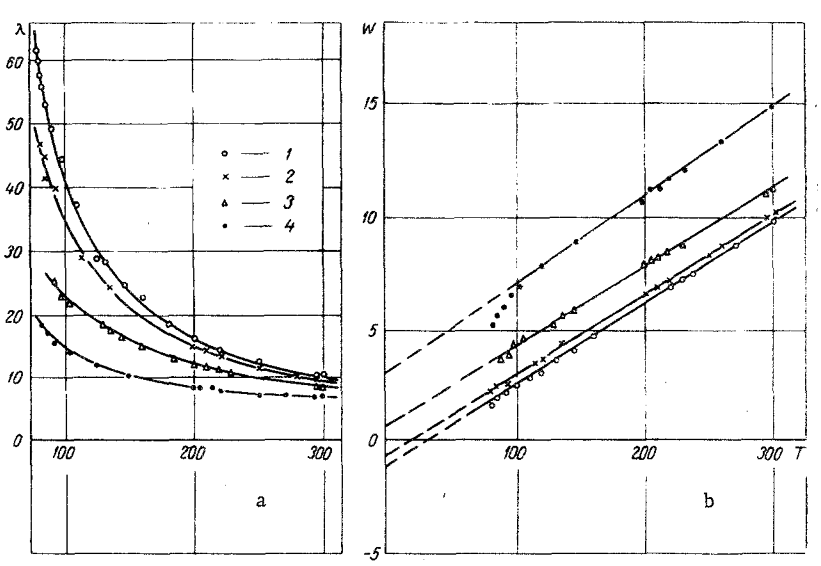

Fig. 1. Temperature dependence of thermal conductivity (a) and thermal resistance (b) of NaF-doped CaF_2: 1) pure CaF_2; 2) 0.3 mole %; 3) 1 mole %; 4) 2 mole %. λ in W/m · deg, W in 10^{-2} m · deg/W, T in °K.

illustrated by Fig. 1a, b. The gradient of the relationship W(T) is the same in the doped crystals; only the ordinate A_2 at $T = 0$ is altered. The effect of the impurity is typical of that of a dopant in low concentrations, at which the additional thermal resistance increases in proportion to the dopant concentration. As is known [4], in the region of high temperatures on the assumption of a Rayleigh law for phonon scattering by point defects we have:

$$\frac{\lambda}{\lambda_0} = \frac{\operatorname{arctg} Z}{Z}, \tag{2}$$

where Z is a parameter which depends on the dopant content: $Z = (\omega_D/\sqrt{D_a})\sqrt{1/T}$; D_a is the proportionality constant in the law representing the rate of scattering of long-wave longitudinal vibrations (τ_a^{-1}) due to anharmonic interactions: $\tau_a^{-1} = D_a\omega^2 T$; I is the Rayleigh scattering parameter with scattering rate $\tau_I^{-1} = I\omega^4$:

$$I = \frac{V_0 L_I}{4\pi v^3} N_I (1 - N_I). \tag{2a}$$

At low dopant concentrations $(z \ll 1)$ we obtain from (2) a linear relation for W with

$$A_1 = \frac{2\pi^2 \hbar v D_a}{k_B^2 \theta_D}, \tag{3a}$$

$$A_2 = \frac{\pi}{6} \frac{\theta_D V_0}{\hbar v^2} N_I (1 - N_I) L_I. \tag{3b}$$

The cofactor D_a takes account of normal and umklapp processes, and D_a is independent of temperature in the absence of "freezing out" of umklapp processes. At low dopant concentrations $(N_I \ll 1)$ $A_2 \sim N_I$. There is sense in comparing the empirical differences $A_2(N_I) - A_2(0)$, i.e., the change in the constant A_2 relative to an undoped specimen (see Fig. 2), with expression (3b). This difference increases linearly with increase in the amount of Na introduced (we investigated specimens with 0.3, 1, and 2 mole % Na): $A_2(N_I) - A_2(0) = 1.8 \cdot 10^{-2} N_I$ % (m · deg/W). When the numerical values ($V_0 = 4.1 \cdot 10^{-29}$ m^{-3}) are substituted in (3b) we have: $A_2 = 8.5 \cdot 10^{-2} L_I N_I$ % (m · deg/W). The total deformation at the site of the defect can be attributed to isotopic "deformation" due to a local change of mass $\Delta M = M_D - \overline{M}$, the deformation field of the defect, and the local change in the force constants. As a result, L_I acquires the form [6]

$$L_I = \left(\frac{\Delta M}{\overline{M}}\right)^2 + d\varepsilon^2. \tag{4}$$

The coefficient d (which depends on the anharmonicity parameter) has a value of 2500-3000. It is known [7] that the impurity Na^+ ion occupies the cationic sites of the fluorite lattice, and the insufficient positive

TABLE 1. Results of Spectrographic Impurity Analysis (in mole %) of Three Pure CaF_2 Specimens

№	Si	Mn	Mg	Fe	Al	Cu	Na	Pb	Ba	Sr
1	0,001	0,001	0,003	0,001	0,001	—	—	—	0,001	0,01
2	0,001	0,001	0,01	0,001	0,001	—	0,01	—	0,001	0,1
3	0,001	—	0,003	0,001	0,001	—	0,01	—	0,001	0,03

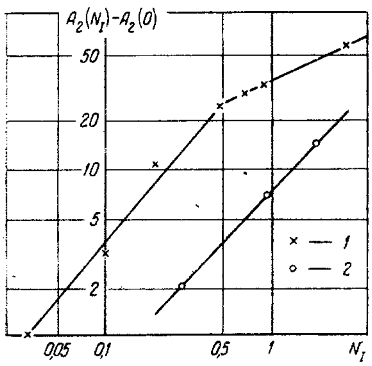

Fig. 2. Additional impurity resistance of CaF_2 as function of dopant concentration: 1) for YF_3-doped specimens; 2) for NaF-doped specimens. $A_2(N_I) - A_2(0)$ in $0.24 \cdot 10^{-2}$ m·deg/W; N_I, %.

charge is compensated by an anionic vacancy in the fluorine sublattice. The complex of the sodium ion with the anionic vacancy has high binding energy (~0.6 eV) and dissociates only at high temperatures ($T \geq 700$-$800°K$). Thus, in estimates of the total change in defect mass we must take into account the fact of complex formation. The resultant value of L_I due to change in mass is ~0.2, which predicts the experimental data fairly well. The minor role of the deformation term proper [the second term in (4)] is probably due to association of defects. In [8] estimates of impurity scattering in semiconductors were made with the aid of relation (3b) multiplied by a coefficient whose value depended on the relative contributions of umklapp and normal scattering processes (with due allowance for the special role of normal processes). Experimental data for a large number of semiconductors of the $A^{III}B^{V}$ and fourth groups give a value close to 2 for this coefficient. The difference in the spectra of fluorite and these semiconductors hardly justifies the introduction of the additional cofactor, defined in [8], into (3b). In any case, the use of this coefficient (greater than 1) would mean that impurity scattering in Na-doped specimens is less than purely isotopic scattering. If this is so, the reason for the reduction of the Rayleigh cross section would be the interference of the matrix elements representing isotopic and deformation scattering. Such an effect is manifested in defect regions in which there are changes in the local mass and force constants of different sign (for instance, an increase in mass accompanied by weakened binding, or the converse [9]).

An unexpected slight reduction of the thermal resistance is observed in the low-temperature region of the relation W(T) for a specimen containing 2% Na. The reason for this has not been established, and the explanation will require the extension of the experiments into the low-temperature region.

The thermal resistance of a Y-doped CaF_2 specimen behaves in a peculiar way. For a Y content less than 0.2 mole % the variation of W with temperature is still linear (see Fig. 3a and b). The difference parameter $A_2(N) - A_2(0)$ increases in approximate proportion to the dopant concentration

$$A_2(N) - A_2(0) = (8{,}5 \pm 1{,}2) \cdot 10^{-2} N_I \ \% \quad (\text{m} \cdot \text{deg/W}). \tag{5}$$

Calculation of the isotopic term in (4) gives $(\Delta M/\overline{M})^2 \approx 0.7$. The right side of (5) is higher than theoretical estimates of A_2, although the introduction of a cofactor greater than 1 (in accordance with [8]) leads to better agreement with experiment. A possible increase in the experimental scattering cross section in comparison with theory can be attributed to the pronounced distortion of the lattice in the region of the interstitial fluorine anion, which compensates the excess charge of the Y^{3+} ion situated at the cationic site [7]. That the interstitial anions will cause extreme deformation of the lattice is indicated by their large size (in comparison with the cations), their low mobility (even at 1000°K it differs from that of the vacancies by a factor of 10 [7]), and the anomalous reduction of electrical conductivity of the crystals with increase in Y content in the range 0.01-1.5 mole % (this reduction is probably due to strong interdefect interaction). As a result, the deformation parameter $d\varepsilon^2$ has a value close to that of the isotopic term: $d\varepsilon^2 \approx 0.3$ ($|\varepsilon| \simeq 10^{-2}$). The associative bond between Y^{3+} ions and adjacent interstitial anions (situated in the octahedral interstices) reduces the deformation, which otherwise would be even greater.

The behavior of the thermal resistance is significantly altered when the Y content exceeds 0.5 mole %. Firstly, the gradient A_1 is reduced to $0.27 \cdot 10^{-3}$ m/W for specimens with 0.5, 0.7, and 1 mole % and to $0.23 \cdot 10^{-3}$ m/W for a specimen containing 3 mole %. Secondly, the rate of increase of the thermal

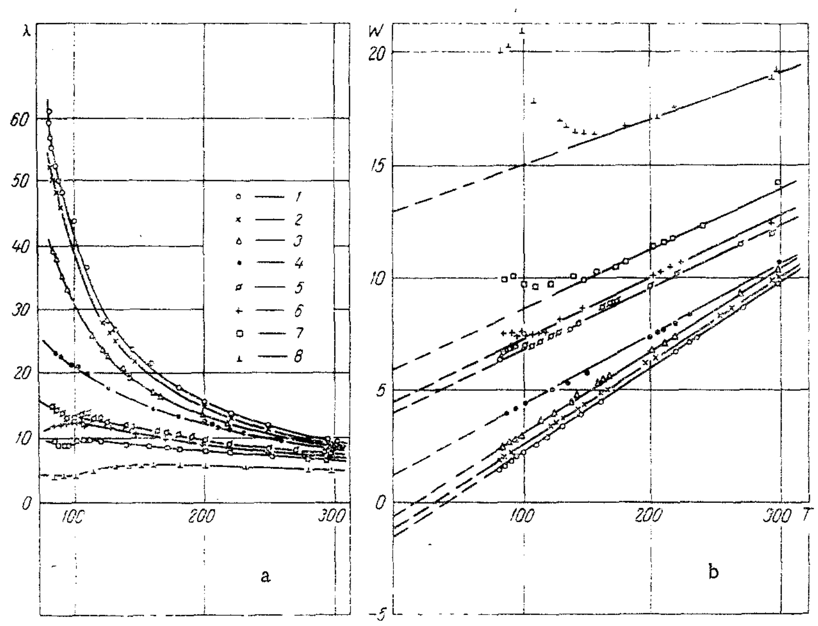

Fig. 3. Temperature dependence of thermal conductivity (a) and thermal resistance (b) of YF_3-doped CaF_2: 1) pure CaF_2; 2) 0.03; 3) 0.1; 4) 0.2; 5) 0.5; 6) 0.7; 7) 1; 8) 3 mole %.

resistance with increase in dopant content is reduced. The difference parameter $A_2(N) - A_2(0)$ (with $N_I = 0.5, 0.7$, and 1 mole %) acquires the form (see Fig. 3)

$$A_2(N) - A_2(0) \simeq 3{,}8 \cdot 10^{-2} + 3{,}6 \cdot 10^{-2} N_I \, \% \text{ (m·deg/W)}. \tag{6}$$

In other words, the differential scattering cross section (proportional to dW/dN_I) is almost halved in comparison with the value at lower concentrations [compare with (5)]. The reduced gradient of the isotherms of the impurity component of the thermal resistance at higher dopant contents is correlated with similar observations in semiconductors [10]. This reduction is due to mutual overlapping of locally deformed regions. This may also occur in the present case. The weakening of the temperature dependence of the thermal resistance causes some difficulty. In fact, according to (2), if the rate of anharmonic scattering is independent of N_I or does not decrease with increase in N_I, then $\partial W(N_I)/\partial T \geq dW(0)/\partial T$, i.e., the rate of change of the thermal resistance with temperature is greater in doped specimens than in pure crystals. The reduction of this rate may be due to reduction of anharmonic scattering when impurities are present. This is to be expected, for instance, whenever the additional phonon—phonon interaction with some regions of the spectrum (probably optical) disappears owing to alteration of these regions in doped materials. The linear, or almost linear, relationship (6) can be interpreted in the following way. Yttrium-doped specimens, like CaF_2 doped with rare earths, contain defect centers of various symmetry types. In the simplest situation they are cubical, tetragonal, and trigonal centers. Dissociated Y^{3+} ions correspond to cubic centers, complexes of Y^{3+} with F^- in the nearest interstitial position correspond to tetragonal centers, and two associated dipoles situated alongside one another ($Y^{3+} + F^-$) correspond to the trigonal centers [11]. The degree of dissociation depends on the concentration and temperature. At the experimental temperatures there are apparently complex defects of the last two types, the cross sections for which will be different. We assume that the scattering cross section of dissociated (tetragonal) centers is σ_1 (with concentration N_1), and that of the associated centers is σ_2. Owing to the pronounced weakening of the elastic and Coulomb fields of associated defects $\sigma_1 > \sigma_2$. The total impurity thermal resistance W_N then consists of two terms: $W_N = A_2(N) - A_2(0) \sim (N_I - N_1)\sigma_2 + N_1\sigma_1$. According to the law of mass action,

$$\frac{N_1^2}{N_I - N_1} = \frac{1}{g} \exp\left[-\frac{v_a}{k_B T}\right] = k_1. \tag{7}$$

The activity coefficients are taken as 1 (on the assumption of noninteraction of the defects). It follows from (7) that $N_1 = (k_1/2)(\sqrt{1 + 4N_I/k_1} - 1)$ and when $4N_I \ll k_1$ $N_1 \simeq N_I$, $W_N \sim N_I\sigma_1$. However, when $4N_I \gg k_1$, $N_1 \simeq \sqrt{N_I k_1}$

$$W_N \sim \sqrt{N_I k_1}\,(\sigma_1 - \sigma_2) + N_I \sigma_2. \tag{8}$$

The result of the condition $4N_I \gg k_1$ is that the first term in (8) increases slightly with dopant content, whereas the second term is proportional to the total concentration. Finally, $dW_N/dN_I \sim \sigma_2$ (when $\Delta\sigma = \sigma_1 - \sigma_2 \sim \sigma_2$). In addition, if two-stage dissociation of the centers occurs, so that cubic defects with concentration N_c are formed, then by introducing another law of the same type as (7) with dissociation constant k_2, we obtain $W \sim N_c\sigma_c + N_{tr}\sigma_{tr} + N_{tg}\sigma_{tg}$, where the subscripts c, tr, and tg refer to the concentrations and scattering cross sections of cubic, tetragonal, and trigonal centers: $\sigma_c > \sigma_{tr} > \sigma_{tg}$. We assume that $k_2 > k_1$. Then, when $N_I \ll k_1$ $W_N \sim N_I\sigma_c$, but when $N_I \gg k_2^2/k_1$ ($\sigma_c = \sigma_1 > \sigma_{tr} \approx \sigma_{tg} = \sigma_2$) $W_N \sim \sqrt[4]{N_I k_1 k_2^2}(\sigma_1 - \sigma_2) + N_I\sigma_2$. The increase in the first term with dopant content becomes even slower in comparison with (8). In the experiment [see (6)] this term was regarded as almost constant. Yttrium-doped specimens show anomalies due to resonance in the initial region of experimental temperatures (80-120°K). These anomalies are particularly distinct when $N_I > 0.5$ mole %. Resonance dips in the thermal conductivity have been described by various authors [6]. Klein [12] gives an expression characterizing the scattering rate near resonance for a wide class of defect states (transitions between local modes, scattering on quasi-local levels, etc.)

$$\tau_R^{-1} = \frac{C_1\omega^{2n}}{(\omega^2 - \omega_R^2)^2 + C_2\omega^{2n+2}} \,. \tag{9}$$

The coefficient C_2 can depend on the temperature. We assume that in the resonance region ($\omega = \omega_R$) the scattering rate τ_R^{-1} is very high and exceeds the sum of all the other scattering rates $\tau_R^{-1} \gg \tau_a^{-1} + \tau_I^{-1} = \tau_\Sigma^{-1}$. In the region far from resonance, however, τ_R^{-1} is small. Then the total thermal conductivity, calculated in the isotropic approximation from the formula

$$\lambda = \frac{k_B v^2}{2\pi^2}\left(\frac{kT}{\hbar v}\right)^3 \int\limits_0^{\frac{\theta_D}{T}} \frac{x^4 \exp x}{(\exp x - 1)^2}\,\tau_\Sigma(x)\;dx, \tag{10}$$

where $x = \hbar\omega/k_BT$, will be reduced in the resonance region by an amount $\Delta\lambda$

$$|\Delta\lambda| = \frac{k_B v^2}{2\pi^2}\left(\frac{k_B T}{\hbar v}\right)^3 \frac{x_R^4 \exp x_R}{(\exp x_R - 1)^2}\,\tau_\Sigma(x_R)\,\Delta x_R \,. \tag{11}$$

The subscript R indicates resonance quantities. In $\Delta x_R = \hbar\Delta\omega_R/k_BT$ the frequency interval $\Delta\omega_R$ characterizes the width of the spectral region "cut off" from heat transfer by resonance scattering. The width of this region can be calculated by including (9) in the over-all scattering rate and analyzing its change close to resonance. For simplicity we take n = 1 in (9) and write $C_1 = C_0\omega_R^3$. We have: $|\Delta\omega_R|/\omega_R \approx C_2 [\tau_\Sigma(\omega_R)/\tau_t]^{1/2}$, where τ_t^{-1} is the total scattering rate at frequency $\omega = \omega_R$ ($\tau_t^{-1} = \tau_\Sigma^{-1}(\omega_R) + \tau_R^{-1}(\omega_R) \approx \tau_R^{-1}(\omega_R)$). We assume also that τ_R^{-1} is independent of temperature, and τ_Σ^{-1} is determined predominantly by anharmonic scattering processes ($\tau_\Sigma^{-1} \approx \tau_a^{-1}$). The maximum of function (11) (i.e., the maximum of function $x_R^{5/2}\mathrm{sh}^{-2}(x_R/2)$) corresponds to $x_R \simeq 1.8$, and the value of $\Delta\lambda_{max}$ is given by

$$\left|\frac{\Delta\lambda_{\max}}{\lambda_R}\right| \approx 0{,}25C_2\left(\frac{\lambda_R V_0}{k_B v^2\tau_t}\right)^{-\frac{1}{2}} . \tag{12}$$

Here λ_R is the extrapolated value of the "normal" (determined by τ_Σ) thermal conductivity at the resonance point.

Since $C_1 \sim N_I$, and $\tau_c^{-1} \approx C_1C_2^{-1}\omega_R^{-2}$ it is to be expected that (12) will increase in proportion to $\sqrt{N_I}$. The resonance anomaly in the thermal conductivity is situated in the initial region of measurement temperatures and is not completely included. Hence, it is difficult to determine the exact position of resonance on the temperature scale and the value of $|\Delta\lambda_{max}|$. The available data, however, suggest that the increase in $|\Delta\lambda_{max}/\lambda_R|$ with concentration is more rapid than by a $\sqrt{N_I}$ law. If we assign the resonance point to 80-100°K, we obtain for the resonance frequency $\nu_R = \omega_R/2\pi = 3\text{-}3.7 \cdot 10^{12}$ sec^{-1}. What is the nature of the quasi-local mode? It is hardly likely to be a case of electronic transitions, since, firstly, the increase in interimpurity interaction with increase in dopant content would affect the characteristics of such a transition and, secondly, the results of γ irradiation of yttrium-doped crystals show that there are no changes in thermal conductivity in the resonance region. Yet γ irradiation would affect the electron distribution among the impurity centers. There was a small reduction (by 10%) of thermal conductivity in the region of nitrogen temperatures due to γ irradiation (0.6-0.8 MeV in a dose of $6 \cdot 10^6$ R) only in specimens containing 0.1 mole %. Pure specimens and crystals with a high dopant content do not show any change in thermal conductivity outside the limits of experimental error. We can postulate that resonance is of isotopic nature and is due to a local increase in mass. In a simple cubic lattice with small ω_R/ω_D

ratios the resonance condition is [6,13]: $(\omega_R/\omega_D)^2 \approx M/3(\Delta M)$, where ΔM is the difference in mass between the substituent ion and the "proper" ion of mass M. For Y replacing Ca we have $\Delta M/M = 1.25$ and, hence, $\omega_R \simeq 0.5\omega_D$ (in the experiment $T_R \approx 100°K$, $\omega_R \approx 0.2\omega_D$). The resonance condition is over-simplified and is probably unsuitable for the fluorite structure. More accurate calculations, carried out only for NaCl lattices so far, are required [13]. Another important factor is the presence of the interstitial fluorine ion, which will alter the resonance picture considerably.

NOTATION

λ	is the thermal conductivity;
W	is the thermal resistance ($W = \lambda^{-1}$);
θ_D	is the Debye temperature;
γ_G	is the Gruneisen constant;
λ_0	is the thermal conductivity of pure specimen;
V_0	is the molecular volume;
N_I	is the molecular defect concentration;
$N_I\%$	is the defect concentration in mole per cent;
L_I	is the local deformation parameter;
M_D	is the defect mass;
$\bar{M}$	is the mean mass of host molecule;
ε	is the relative difference between defect radius and radius of host atoms;
y	is the number of possible orientations of defect complex;
v_a	is the binding energy of complex;
ω_D	is the Debye frequency;
v	is the mean velocity of propagation of phonons;
C_0, C_2	are the dimensionless quantities.

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