

m; H length of the profile fin, m; d, outer diameter of the cooling channel, m; H, shield length, m. Indices: ext, outer; c, shield cell; in, inner fin; out, outer fin; ch, cooling channel; en, entrance surface of the cell.

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THERMAL CONDUCTIVITY OF FLUORIDES OF ALKALI EARTH METALS

B. M. Mogilevskii, V. F. Tumurova, A. F.
Chudnovskii, E. D. Kaplan, L. M. Puchkina,
and V. M. Reiterov

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A linear dependence is obtained between the thermal resistance and the temperatures for the monocrystalline fluorides CaF_2 , SrF_2 , BaF_2 , and MgF_2 . Anisotropy in MgF_2 has been discovered.

Thermal-conductivity measurements are an efficient method of studying the structural and energy properties of the crystal lattices of a class of ion laser compounds (the alkali earth fluorides) which are important in the practical aspect.

Monocrystals of the alkali earth fluorides are characterized over the range 80-300°K by a linear dependence of thermal resistance on temperature:

$$W = A_1 T + A_2 \quad (1)$$

with a negative value of the constant term A_2 (see Fig. 1a, b, where data of the measurements are given with an error of 5% with respect to steady-state procedure [1]). It is supposed that the negative quantity A_2 is the result of participation in heat transfer of optical branches evolved in the complex structure of fluorite. The coefficient of thermal conductivity can be represented in the form

$$\lambda = W^{-1} = \lambda_{ac} + \lambda_{opt} \approx \frac{B_1}{T} + \frac{B_2}{T^2}, \quad (2)$$

where

$$B_1 = A_1^{-1}, \quad B_2 = |A_2| \cdot (A_1)^{-2}. \quad (3)$$

The second term in Eq. (2) describes the four-phonon scattering processes of the optical mode, since three-phonon processes for these modes are suppressed because of limitations due to the laws of conservation of energy and momentum [2]. The numerical values of the coefficients A_1 and A_2 for various fluorides with the structure of fluorite in the sequence CaF_2 , SrF_2 , and BaF_2 are: $A_1 = 0.38 \cdot 10^{-3}$; $0.42 \cdot 10^{-3}$; and $0.6 \cdot 10^{-3}$ m/W; $A_2 = -14.5 \cdot 10^{-3}$; $-18 \cdot 10^{-3}$; and $-21.5 \cdot 10^{-3}$ m · deg/W. The measured values of thermal conductivity in CaF_2 , BaF_2 , and SrF_2 are higher by approximately 5% than the results of [3, 4], which probably is due to the higher purity of the samples.

In contrast to fluorides with the fluorite structure, MgF_2 has the anisotropic structure of rutile [5-7]. Anisotropy in the directions \perp and \parallel to the optical axis C[001] is manifested by measurements of the elec-

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trical conductivity [9, 12]. It is clearly expressed also in thermal conductivity: data \perp and \parallel to the direction of crystal growth differ by 40-50% (see Fig. 2a, b). Values of thermal conductivity for monocrystals of MgF_2 lie much higher than the values referred to a polycrystalline substance [8] and are described by Eq. (1) when $A_1(\perp) = 0.215 \cdot 10^{-3} \text{ m/W}$ and $A_2(\perp) = -(9.55 \pm 3.6) \cdot 10^{-3} \text{ m} \cdot \text{deg/W}$ (\perp to the direction of growth). Parallel to the direction of growth, the resistance to thermal flow is decreased: $A_1(\parallel) = 0.14 \cdot 10^{-3} \text{ m/W}$ and $A_2(\parallel) = -6 \cdot 10^{-3} \text{ m} \cdot \text{deg/W}$, i.e., $A_1(\parallel) = 0.65 A_1(\perp)$.

Similar to the lattice of rutile, MgF_2 can be represented as a dense hexagonal packing of fluorine ions, in part (one-half) of the octahedral voids of which are disposed magnesium cations. Octahedra of MgF_6 form chains extending along the C axis and have up to two common edges with other octahedra. For uncontaminated crystals, identification of the crystallographic alignments shows that the direction of growth deviates from the C axis by not more than 5° . The high degree of anisotropy of MgF_2 crystals is caused by the difference in the anharmonic characteristics of the interatomic bonds in the directions \perp and \parallel to the C axis (which is a screw axis of the fourth order).

In the anisotropic lattice of rutile, the thermal-conductivity tensor, reduced to the principal axis, comprises two independent components [2]: $\lambda_x = \lambda_y = \lambda_{\perp C}$ and $\lambda_z = \lambda_{\parallel C}$. In matrix form, the Fourier equation for thermal flow is

$$\vec{Q} = -\tilde{\lambda} \cdot \text{grad } T, \quad (4)$$

where $\tilde{\lambda}$ is the matrix of the thermal-conductivity coefficients. By measuring the thermal conductivity under adiabatic conditions (thermal flow, perpendicular to the direction of measurement, equal to zero) along a direction which deviates from the axis C by an angle φ , we have

$$\frac{|\vec{Q}|}{|\text{grad } T|} = \left[\frac{\cos^2 \varphi}{\lambda_{\parallel C}} + \frac{\sin^2 \varphi}{\lambda_{\perp C}} \right]^{-1}. \quad (5)$$

The measured thermal resistance depends on φ , and so

$$A_1(\varphi) = 0.14 \cdot 10^{-3} (1 + 0.55 \cdot \sin^2 \varphi) \text{ (m/W)}.$$

Comparison of the thermal conductivity of CaF_2 with the Leibfried-Schlemann formula [10], derived in [3], when $T = \theta_D$ gives

$$\lambda T = \frac{3 \sqrt[3]{4}}{10\pi^3} \left(\frac{k_B}{\hbar} \right)^3 \frac{M \theta_D^3 V_0^{1/3}}{\gamma^2}. \quad (6)$$

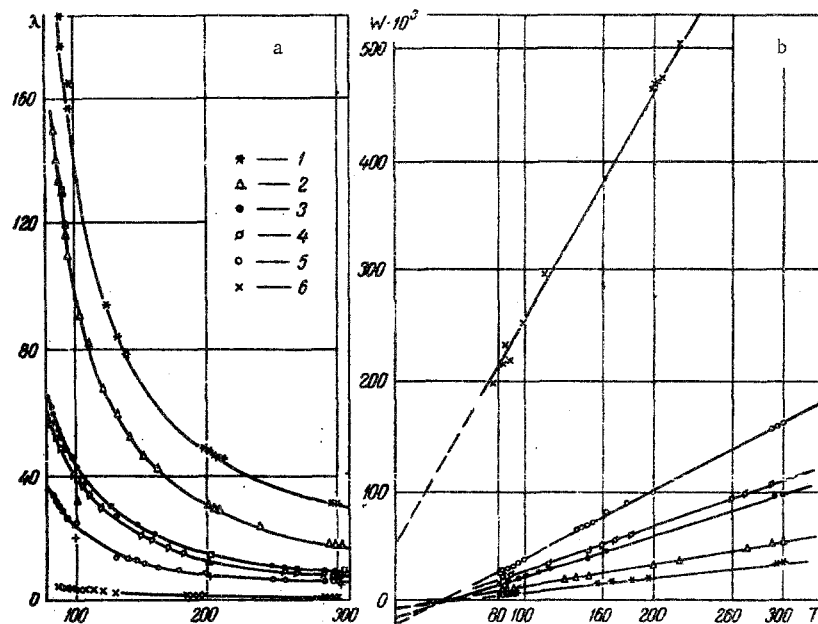


Fig. 1. Temperature dependence of thermal conductivity λ , $\text{W/m} \cdot \text{deg}$ (a) and thermal resistance W , $\text{m} \cdot \text{deg/W}$ (b) of pure crystals of the alkali-metal fluorides: 1) MgF_2 (\parallel); 2) MgF_2 (\perp); 3) CaF_2 ; 4) SrF_2 ; 5) BaF_2 ; 6) PbF_2 .

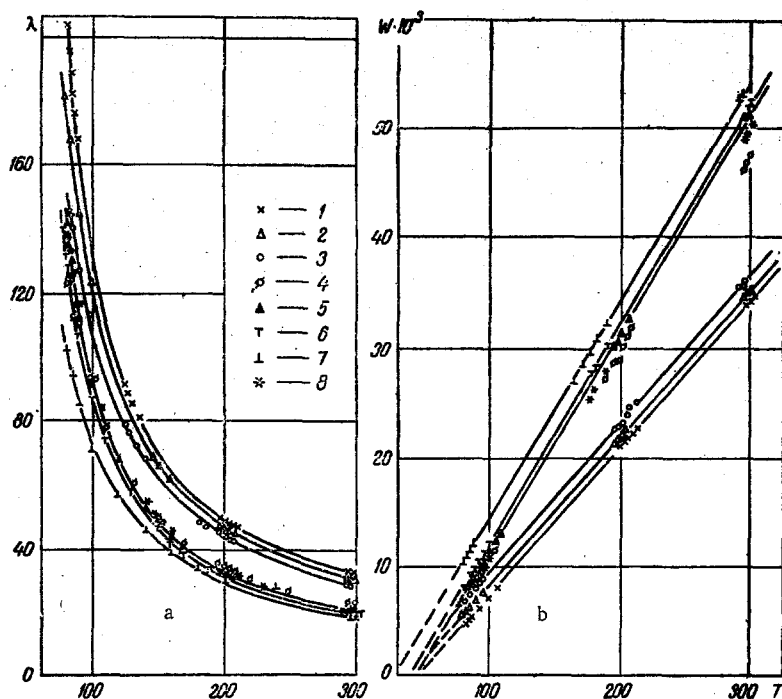


Fig. 2. Temperature dependence of thermal conductivity λ , W/m · deg (a) and thermal resistance W , m · deg/W (b) of crystals of MgF_2 with CaF_2 impurity: 1) MgF_2 (\parallel); 2) 0.1 mole % CaF_2 (\parallel); 3) 0.5 mole % CaF_2 (\parallel); 4) 1 mole % CaF_2 (\parallel); 5) MgF_2 (\perp); 6) 0.1 mole % CaF_2 (\perp); 7) 0.5 mole % CaF_2 (\perp); 8) 1 mole % CaF_2 (\perp).

In this case, the numerical coefficient in formula (6), according to Klemens estimates for alkali halide crystals, was decreased by a factor of four, and the quantities M and V_0 are related, respectively, to the average atomic weight and the average atomic volume of the particles constituting the lattice. The value of $\lambda T = 3.5 \cdot 10^3$ W/m, obtained in [3], satisfies the test quite well (when $T = \theta_d = 508^\circ K$). The use of the Leibfried-Schlemann formula, with the value occurring in it as discussed above, implies that CaF_2 is considered as a monatomic crystal with a certain average atomic mass. In this case, the whole of the spectrum of the crystal is taken into account equally in heat transfer. However, with the presence of six optical branches (out of nine) with a low dispersion [11, 12], in the description given by the Leibfried-Schlemann formula only 1/3 of the spectrum should be included and, consequently, the right-hand side of Eq. (6) should be multiplied by this number. As a result, $\lambda T = 4.2 \cdot 10^3$ W/m is also higher than the experimental values for the acoustic component in Eq. (2). The possible contribution of scattering to the optical fluctuations should reduce the value of λT . It must be noted that, concerning the values of the numerical coefficient in Eq. (6), there is no agreement in the literature. In [13], the revised value of this coefficient is less by a factor of 2.1, but in the recent paper by Klemens [14], it is less by a factor of 14 than in Eq. (6). Moreover, it is proposed in [14] to introduce into Eq. (6) a factor $N_c^{-1/3}$ into lattices with complex cells, where N_c is the number of atoms in an elementary cell (basis atoms). The experimental values of the numerical coefficient lie between these found theoretically in [10] and [14] (they differ mainly because of the difference in estimate of the constant of anharmonism).

For crystals with unknown parameters of anharmonicity and Debye temperatures, the use of Lindemann's rule can be recommended (for estimating θ_d). Then Eq. (6) reduces to the form suggested by Keyes [2]. Assuming that the constant coefficient in Keyes' formula varies weakly in structurally similar crystals, we can calculate the ratio of the product $\lambda T \sim T_{mp}^{3/2} D^{2/3} M^{-7/6}$ for the alkali earth fluorides:

$$\lambda_{\parallel C} T (MgF_2) : \lambda_{\perp C} T (MgF_2) : \lambda T (CaF_2) : \lambda T (SrF_2) : \lambda T (BaF_2) = 1.2 : 1.2 : 1 : 0.7 : 0.5 \quad (2.75 : 1.7 : 1 : 0.92 : 0.65).$$

Here, in the brackets, the experimental values are given of the ratios of the "purely acoustic" coefficients $B_1 = A_1^{-1}$. These ratios are close to those calculated for crystals with the fluorite structure and are significantly overestimated for the MgF_2 anisotropic lattice. The correlation between the values of the thermal conductivity and the lattice energies of the corresponding substances may be noted also.

Monocrystalline samples of PbF_2 were also investigated in the experiment, for which the law $W = (2.15T + 50) \cdot 10^{-3} \text{ m} \cdot \text{deg}/\text{W}$ was found. The high angular coefficient ($A_1 = 2.15 \text{ T} \cdot 10^{-3} \text{ m} \cdot \text{deg}/\text{W}$) confirms the lowering of the elasticity in the bonds. The PbF_2 is a crystal with a relatively high electrical conductivity with respect to the anion sublattice [15] and a low melting point ($T_{\text{mp}} = 855^\circ\text{C}$). Obviously, the inherent imperfection of the lattice and the residual impurities (the crystal is grown from chemically pure material) give rise to the appearance of a constant component of the thermal resistance. The anharmonic component of the thermal resistance is well recorded in the fluorite series (for verification by Keyes' formula, see above): $\lambda T (\text{CaF}_2) : \lambda T (\text{PbF}_2) = 1 : 0.2 (1 : 0.18)$. The theoretical estimate is outside the brackets and the experimental value is inside the brackets. Although the low-temperature form of PbF_2 (α -modification) belongs to the rhombic system, in contrast to the β -form of fluorite (above $\sim 200^\circ\text{C}$) [17], it is probable that the structural and energy deviation from the latter is small.

What has been said above refers to uncontaminated samples. Because of the unusualness of the thermal conductivity of MgF_2 , the problem was raised of studying the effect of an added impurity on the lattice heat transfer in rutile. The production of impure crystals of MgF_2 is accompanied by large technological difficulties, and the nominal content of impurity in the mixture may be strongly different from the actual content — in monocrystalline samples. In the experiment, some crystals with a nominal concentration — 0.1, 0.5, and 1 mole % CoF_2 — were investigated. The closeness of the radii of Mg^{2+} ($r = 0.74 \text{ \AA}$) and Co^{2+} ($r = 0.78 \text{ \AA}$) allows one to suppose a high degree of substitution in the lattice and a predominantly isotopic nature of the additional extrinsic thermal resistance. For subsequent estimates, we shall use the expression for the additional extrinsic thermal resistance W_N , caused by the change of mass of the substituting ion ($N_1 \ll 1$, $W_N < A_1 T$) [2]:

$$W_N = \frac{\pi}{6} \cdot \frac{\theta_D V_0}{\hbar v^2} N_1 \left(\frac{\Delta M}{M} \right)^2. \quad (7)$$

Having determined θ_D by Lindemann's rule, we obtain from Eq. (7) that $W_N = 5 \cdot 10^{-2} \cdot (\Delta M/M)^2 N$ $\text{m} \cdot \text{deg}/\text{W}$ and, consequently, for the mass defect corresponding to the Co^{2+} impurity, we have $W_N(\text{Co}^{2+}) = 1.7 \cdot 10^{-2} N \text{ m} \cdot \text{deg}/\text{W}$. Crystals with 0.1 and 0.5 mole % Co^{2+} give linear thermal resistance dependences, parallel with the corresponding dependences for pure crystals (\parallel and \perp to the axis C). If we consider an increment of the ordinates of thermal resistance of the samples, oriented along the direction of growth, then estimates of the impurity concentrations according to the isotopic law for $W_N(\text{Co}^{2+})$ give 0.035 mole % (for a nominal content of 0.1 mole %) and 0.1 mole % (for a nominal content of 0.5 mole %). For crystals oriented perpendicular to growth, the experimental values of the extrinsic thermal resistance are high by a factor of 1.25 to 1.5. Since $W_N \sim \theta_D^{-1}$ [see Eq. (7)], and $A_1 T \sim \theta_D^3$ [see Eq. (6)], it can be assumed that

$$\frac{W_N(\perp c)}{W_N(\parallel c)} \approx \left(\frac{A_1(\perp c)}{A_1(\parallel c)} \right)^{1/3} = 1.25.$$

This coincides fairly well with experiment. Because of rotation (up to 40°) of the axis C relative to the direction of growth (to the direction of measurement), a crystal with a nominal content of impurity of 1 mole % changes the thermal resistance according to a linear law, intermediate between the dependence of $W(T)$ for two mutually perpendicular directions of uncontaminated samples [close to $W(\perp C)$].

NOTATION

λ , thermal conductivity; W , thermal resistance; λ_{ac} , thermal conductivity due to acoustic oscillations; λ_{opt} , thermal conductivity due to optical oscillations; Q , thermal flux; M , molecular weight; θ_D , Debye temperature; V_0 , atomic volume; γ , Grüneisen's constant; D , density; T_{mp} , melting point; W_N , additional extrinsic thermal resistance; ΔM , change of mass of substituting ion; v , propagation velocity of long-wave lattice oscillations; N_1 , concentration of impurity in molar fractions; N , concentration of impurity in mole %.

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ELECTRIFICATION OF A PNEUMATIC TRANSPORT
FLOW AND A DIELECTRIC PIPE WITH HOMOGENEOUS
SURFACE PROPERTIES

V. N. Verevkin, R. A. Yailiyan,
and B. G. Popov

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The basic parameters of contact electrification are established for the interaction of a dispersed flow with the lateral surface of a pipeline; methods of determining the parameters experimentally are indicated, together with their practical application.

The formation and separation of contacts between systems of dispersed particles and the surfaces of industrial apparatuses, machine parts, transporting equipment (conveyers), bunkers, and silos take place in the course of many widely employed processes and commercial operations. After each contact a charge density σ_0 is created on the area of contact between the dispersed particle and the wall (solid surface); its value depends on the physicochemical properties of the surfaces in contact [1-3]. In systems in which the linear dimensions of the spot are 0.05 mm or under [4], no gas discharge occurs in the space between the separating surfaces. Electric exchange between the particle and the wall remains basically governed by the invariance of the parameters of the electric double layer: its thickness, the difference in work function corresponding to the transfer of ions or electrons from one phase to the other, and the electric induction vector. The particles in the flow touch the dielectric wall, which already bears a charge density σ (Fig. 1). Under the influence of the external field E due to the exchange charge density of the flow and as a result of the polarization of the particle, the contact area develops the following charge density [5]:

$$\sigma_1 = \alpha E. \quad (1)$$

The polarization coefficient α depends on the material, shape, and position of the particle at the moment of contact with the wall. The total induction vector in the electric double layer is governed by σ , σ_1 , and the charge density σ_T associated with the formation of the electric double layer:

$$\sigma_0 = \sigma_T + \alpha E + \sigma. \quad (2)$$

If electric exchange between the system of dispersed particles and the surface occurs as a result of contact between particles obeying Eq. (2), the following electrification current density will flow in each section of the surface:

$$j = \beta \sigma_T = \beta (\sigma_0 - \alpha E - \sigma). \quad (3)$$

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