Total separation of all the GTM effects in one experiment permits posing the problem of calculating the maximal quantity of secondary parameters characterizing electronic models of semiconductors. In this connection, it is quite important to us to consider henceforth optimal methods of calculating these parameters under minimal a priori assumptions.

NOTATION

V_{1-4}, V_{2-5}, emf's on the transverse (Hall) and longitudinal probes; V_α, thermal emf; V_ρ, ohmic voltage drop; V_H, V_E, V_{RL}, $V_{NE}^{\perp}$, emf's of the transverse Hall, Ettingshausen, Righi–Leduc, and Nernst–Ettingshausen effects; $V_{\alpha P}$, $V_{\alpha N}$, and $V_{\alpha MRL}$, emf of the longitudinal Peltier, Nernst, and Maggi–Righi–Leduc effects; $V_{\Delta\rho}$ and $V_{NE}^{\parallel}$, emf of the longitudinal magnetic resistance and Nernst–Ettingshausen effects; $V_{\alpha P}$, $V_{NEP}^{\perp}$, and V_{RLP}, secondary thermal emf and TM effects caused by the Peltier heat; $A_{NE}^{\perp}$, A_{RL}, A_E, coefficients of the Nernst–Ettingshausen, Righi–Leduc, and Ettingshausen effects; E, H, electric and magnetic field intensities. Indices 0, H = 0.

LITERATURE CITED

1. A. I. Ansel'm, Introduction to the Theory of Semiconductors [in Russian], Fizmatgiz, Moscow (1962).
2. P. S. Kireev, Physics of Semiconductors [in Russian], Vysshaya Shkola, Moscow (1969).
3. I. S. Lisker, Author's Abstract of Doctoral Dissertation, Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR (1970).
4. I. S. Lisker, Calculating Systems, No. 29 [in Russian], Nauka, Novosibirsk (1968), p. 3.

THERMAL CONDUCTIVITY OF RARE EARTH FLUORIDE CRYSTALS

B. M. Mogilevskii, V. F. Tumpurova,
and A. F. Chudnovskii

UDC 536.21

Thermal resistance of LaF_3 and HoF_3 monocrystals is linearly dependent on temperature. In LaF_3 crystals a deviation from the linear law was observed at T > 170°K in the direction of higher thermal-conductivity values. In doped $LaF_3:Eu^{2+}$ in the region T > 170°K thermal resistance is lower than in pure specimens.

Halogenides of the rare earth elements are used in electrochemical devices as solid electrolytes. This has stimulated study of their structure and physical properties [1, 2]. Most data have been gathered on lanthium fluoride LaF_3. The crystalline structure of LaF_3 and other similar rare earth fluorides of the tisonite series has remained a matter of discussion. Oftedal [3] established a hexagonal structure with spatial group $D_{6h}^3(P6_3/mcm)$ by the x-ray diffraction method. Nuclear magnetic resonance studies [4,5] indicated a hexagonal cell with group $C_{6v}^3(P6_3/cm)$. Optical measurements defined the trigonal space group $D_{3d}^4(P\bar{3}cl)$. Data on the isomorphic CeF_3 favor the trigonal structure [6, 7]. In pure LaF_3 crystals thermal resistance shows no anisotropy (just as electrical conductivity [8]) and changes by a linear law (measurements performed by the technique of [15] with error of 5%) $W = 1.9 \cdot 10^{-3}$ T (m·deg/W) up to 170°K. Above this temperature nonlinearity sets in in the direction of higher thermal-conductivity values (Fig. 1a, b). The Leibfried–Schlömann expression for thermal conductivity of pure crystals [9] with the Klemens correction [10] (decreasing the numerical coefficient of the Leibfried–Schlömann formula by a factor of 14) gives good agreement with ex-

---

Agrophysical Scientific-Research Institute, Leningrad. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 30, No. 1, pp. 135-138, January, 1976. Original article submitted December 19, 1974.

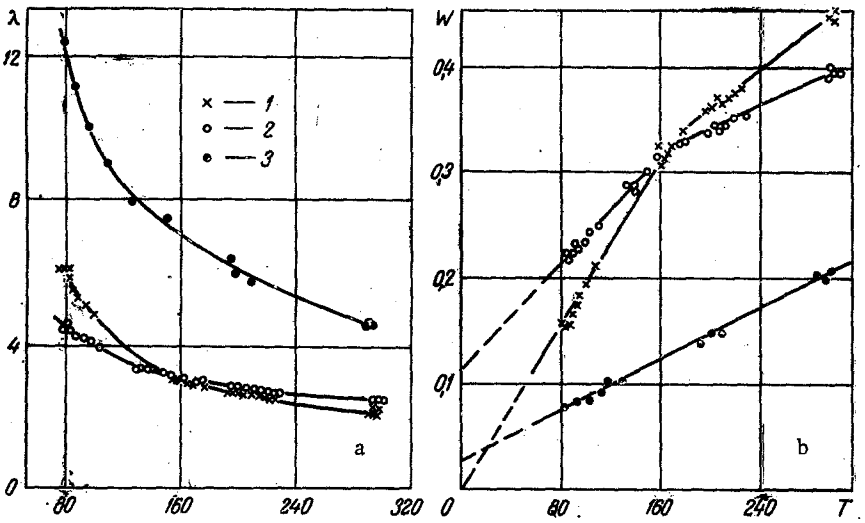

Fig. 1. Thermal conductivity λ (W/m•deg) versus temperature (°K) (a) and thermal resistance W (m•deg/W) versus temperature (b): 1) LaF_3; 2) LaF_3 + 0.8 mol.% Eu^{2+}; 3) HoF_3.

periment (divergence of 10%). Using the Case criterial value [11] ($\lambda T \sim T_m^{3/2} D^{2/3}/M^{1/6}$) for comparison of data on pure CaF_2 [12], LaF_3, and HoF_3 [in the latter case, $W = (0.765T + 19) \cdot 10^{-3}$ (m•deg/W); see Fig. 1a, b] we obtain

$$\lambda T\,(CaF_2) : \lambda T\,(LaF_3) : \lambda T\,(HoF_3) = 1 : 0.48 : 0.4 \text{ (calculation);}$$

$$1 : 0.2 : 0.5 \text{ (experiment).}$$

The divergence of calculated and experimental data for LaF_3 indicates significant increase in anharmonicity in the tisonite lattices, natural in view of the differences in the cubic (CaF_3) and trigonal (LaF_3) structures. In the doped LaF_3 specimens, alloyed with 0.8 mol.% Eu^{2+}, the angular slope of the thermal resistance is lower than in the pure crystal: $W(LaF_3{:}Eu^{2+}) = 1.2 \cdot 10^{-3}T + 0.12$ (m•deg/W). The high value of the constant component of the linear law W = f(T) with decrease in slope is a phenomenon characteristic of strongly doped systems with fluorite structure [12] and evidently expresses the fact of intense defect-anharmonic interaction upon change in the lattice spectrum. In the temperature range T > 170°K in both impure and pure specimens the rate of thermal resistance growth is attenuated. The addition to the linear decrease in thermal resistance for pure specimens is described by the formula

$$\Delta W\,(LaF_3) = -1.1 \cdot 10^3 \exp\left(-\frac{0.075\,\text{eV}}{K_B T}\right)\left(\frac{\text{m}\cdot\text{deg}}{\text{W}}\right), \tag{1}$$

and for doped specimens

$$\Delta W\,(LaF_3 : Eu^{2+}) = -0.5 \cdot 10^3 \exp\left(-\frac{0.075\,\text{eV}}{K_B T}\right)\left(\frac{\text{m}\cdot\text{deg}}{\text{W}}\right). \tag{2}$$

The higher values of thermal conductivity (at T > 160°K) in doped LaF_3, as compared to the pure specimens, indicates strong disorder or high defect rate in the material (see, for example, data on amorphization of the materials As_2Se and Se [13, 14]).

According to [8] (experiments on thermal expansion) Schottky defects are formed in LaF_3: molecular ion $[LaF_2^+]$ and ion $[F^-]$ vacancies, the interaction between which obeys the law

$$[LaF_3] \rightleftarrows [LaF_2^+] \times [F^-]. \tag{3}$$

The relative concentration of Schottky defects is described by the expression

$$\frac{N_S}{N} = \exp\left(-\frac{E_s}{K_B\,T}\right), \tag{4}$$

where $E_S = E_{S0} + \gamma K_B T$ with $E_{S0} = 0.069$ eV, $\gamma = 4.05$. From the closeness of the exponential terms in Eq. (4) and Eqs. (1) and (2) it follows that the cause of the deviation from linearity of the law $W \sim T$ is strong defect formation (at room temperature the crystal contains about 0.3 mol.% molecular vacancies). The effect of natural defects on thermal conductivity is analogous to that of the introduced impurity Eu^{2+} — the rate of growth of thermal resistance is decreased. With the thermal phonon path length independent of temperature, the drop in thermal conductivity should be retarded. It remains unclear why this braking occurs at such high thermal-conductivity values of about 3 W/m•deg, corresponding to path lengths $\geqslant 15$ A° ($C \simeq 14.71$ A°). In estimating the path length in tisonite crystals the propagation velocity of long-wave oscillations was taken as about $2.5 \cdot 10^3$ m/sec in correspondence with a Debye temperature of 360°K (the literature contains no data on sound velocity). As a rule, amorphous-like behavior of thermal conductivity sets in at λ values almost an order lower than those found in LaF_3 [11]. Introduction of Eu^{2+} leads to the appearance of additional fluorine vacancies (the negative unit charge of an Eu^{2+}-center replacing an La^{3+} is compensated by a positively charged anion vacancy).

The number of LaF_2^+ molecular ion vacancies which strongly scatter thermal oscillations then decreases (since $[F^-] \times [LaF_2^+] = \mathrm{const}$). This is probably the cause of the slight increase in thermal conductivity of doped crystals over pure ones (by about 10%). If we assume that in the doped crystals the concentration of molecular ion vacancies is negligibly small, we find their dimensions to be about 5-10 A°. A certain contribution from constant impurity thermal resistance ($19 \cdot 10^{-3}$ m•deg/W) (possibly due to crystal contamination) was noted in the HoF_3 crystals. However, anomalies like those in LaF_3 were absent.

It should also be noted that despite the structural anisotropy in tisonite crystals, no anisotropy in thermal conductivity was observed (nor does it exist in electrical conductivity [13]).

NOTATION

λ, thermal conductivity, W/m•deg; $W = \lambda^{-1}$, thermal resistance; N_S, total Schottky defect concentration; N, number of formula units in specimen.

LITERATURE CITED

1. A. C. Lilly, B. C. Laroy, C. O. Tiller, and B. J. Whiting, J. Electrochem. Soc., 120, 1673 (1973).
2. B. C. Laroy, A. C. Lilly, and C. O. Tiller, J. Electrochem. Soc, 120, 1678 (1973).
3. I. Oftedal, Z. Phys. Chem., B, 5, 272 (1929).
4. L. O. Anderson and W. G. Proctor, Z. Kristallogr., 127, 366 (1968).
5. L. O. Anderson and G. Johanson, Z. Kristallogr., 127, 386 (1968).
6. K. Lee, Sol. State Commun., 7, 367 (1969).
7. C. O. Tiller, A. C. Lilly, and B. C. Laroy, Phys. Rev. B, 8, 4787 (1973).
8. A. Sher, R. Solomon, K. Lee, and M. W. Muller, Phys. Rev., 144, 593 (1966).
9. G. Liebfried and E. Schlömann, Nachrichten Akad. Wisten Göttingen, 11a, 4 (1954).
10. M. Roufosee and P. G. Klemens, Phys. Rev. B, 7, 5379 (1973).
11. B. M. Mogilevskii and A. F. Chudnovskii, Semiconductor Thermal Conductivity [in Russian], Nauka, Moscow (1972).
12. B. M. Mogilevskii, V. F. Tumpurova, and A. F. Chudnovskii, Inzh.-Fiz. Zh., 27, 287 (1974).
13. L. Stourac, B. T. Kolomiec, and V. P. Silo, Czech. J. Phys., B, 18, 92 (1968).
14. L. Stourac, A. Vasko, J. Srb, C. Musil, and F. Strla, Czech. J. Phys., B, 18, 1067 (1968).
15. E. D. Devyatkova, A. V. Petrov, I. A. Smirnov, and B. Ya. Moizhes, Fiz. Tverd. Tela, 2, 738 (1960).