THERMAL CONDUCTIVITY OF FLUORITE CONTAINING TRIVALENT METAL IMPURITIES

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The thermal conductivity of fluorite crystals containing rare-earth metal impurities was measured. It was shown that the structure of the defect centers has a strong effect on the magnitude and character of the heat transfer in these crystals.

Fluorite crystals which have been activated by trivalent metals (especially from the rare earth group — REM) are widely used in technology, most frequently in optical investigations. Thermal conductivity can successfully substitute for resonance and optical methods as an efficient technique for investigating defect states [1].

In this paper we address the problem of examining the special properties and structure of lattice defects in fluorite containing trivalent REM impurities — the metals Ce^{3+}, Sm^{3+}, Eu^{3+}, Dy^{3+}, Yb^{3+} — by analyzing thermal conductivity data.

Figure 1 shows the thermal conductivity of some doped CaF_2 crystals measured over the range 80 to 300°K by the steady-state method [2] with an accuracy of 5%. With the exception of the low temperature region in heavily doped samples (1 mole % Sm^{3+} and Dy^{3+} in Fig. 1), the thermal resistance of all the crystals in this temperature range follows a linear relation: $W = \lambda^{-1} = A_1T + A_2$. For samples with impurity concentrations N less than 0.2 mole %, the coefficient $A_1(N)$ coincides with $A_1(0)$ of a pure crystal within 5 to 10% [$A_1(0) = 0.38 \cdot 10^{-3}$ m/W]. Meanwhile, the coefficient $A_2(N)$ systematically increases with increasing impurity content; its magnitude is proportional to N. The parameter $W_N + A_2(N)-A_2(0)$ characterizes the contamination of the crystal by the impurities and its values for the various impurities are as follows: $W_N(Ce^{3+}, Sm^{3+}, Eu^{3+}, Dy^{3+}, Yb^{3+})$ = 72 ± 12; 85 ± 12; 120 ± 25; 145 ± 25; 155 ± $30 \cdot 10^{-3}$ N·m·deg/W. It is well known [3, 4] that the introduction of trivalent metal impurities into fluorite leads to the generation in the crystal — in proximity to the impurity atom — of interstitial fluorine ions which produce strong distortions of the lattice in their immediate vicinity. If interstitial fluorine atoms are included in the total mass of the scattering center and if it is assumed that the additional thermal resistance is associated only with localized mass defects [5], then it turns out that the experimental values of W_N are about 35 ± 5% of the calculated value for Ce^{3+} and Sm^{3+} (whereas $W_N \sim 50\%$ of the theoretical value for Dy^{3+}, Eu^{3+} and Yb^{3+}). However, samples containing trivalent yttrium (Y^{3+}) had a thermal resistivity of $W_N = 85 \pm 20 \cdot 10^{-3}$ N·m·deg/W which is about 30% greater than the theoretical values for the corresponding isotoped effects. These data show that the complexes formed by the trivalent REM and fluorine ions generate a deformed field which partly compensates for the isotope scattering effect. Such a compensation occurs in rare earth doped crystals [5, 6] and also, probably, in fluorite doped with REM; it is produced by localized loosening of the lattice [7] associated with the high energy of intracomplex binding in complicated structural defects, for example of the rhombohedral type [3].

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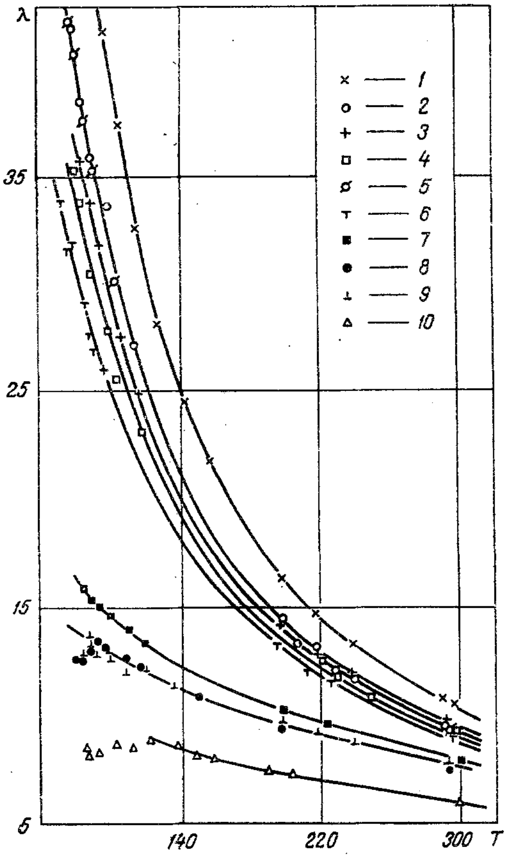

Fig. 1

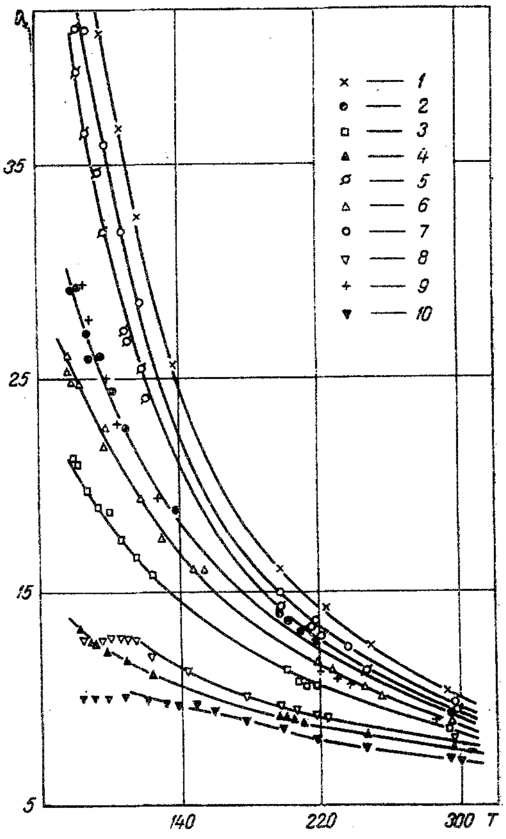

Fig. 2

Fig. 1. Thermal conductivity λ (W/m·deg) of fluorite crystals containing rare earth impurity ions: 1) CaF_2; 2) 0.1 mole % Ce^{3+}; 3) 0.1 Sm^{3+}; 4) 0.1 Yb^{3+}; 5) 0.1 Eu^{3+}; 6) 0.1 Dy^{3+}; 7) 0.5 Yb^{3+}; 8) 0.7 Yb^{3+}; 9) 1 Sm^{3+}; 10) 1 mole % Dy^{3+}.

Fig. 2. Thermal conductivity λ (W/m·deg) of fluorite crystals with YF_3 and WaF impurity: 1) CaF_2; 2) 0.3 mole % YF_3 + 0.3 mole % NaF; 3) 0.5 YF_3 + 0.5 NaF; 4) 1 YF_3 + 1 NaF; 5) 0.1 YF_3; 6) 0.2 YF_3; 7) 0.3 NaF; 8) 0.7 YF_3; 9) 1 NaF; 10) 1 mole % YF_3.

Samples containing 1 YF^{3+} are obviously dominated by defect centers having a higher symmetry (tetragonal or cubic) than in REM doped crystals coupled with a smaller intracomplex binding energy and, consequently, with an increasing effective cross section for scattering per unit impurity ion (the binding energy is 0.6eV for Dy^{3+} [8] and 0.45 eV for Y^{3+} [9]). As a result, the interstitial fluorine ion has such a strong deforming effect on the lattice that the impurity resistance W_N increases more rapidly than the isotope related effect. In contradiction to the explanation advanced above, Na^+ and O^{2-} impurities incorporated in the fluorite lattice also introduce vacancies [4], yet the experimental values of W_N ($19 \pm 2.5 \cdot 10^{-3}$ N·m·deg/W for CaF_2 with NaF impurity and $5 \cdot 10^{-3}$ m·deg/W for oxygen doped crystals in which the oxygen concentration is 0.6 mole % O^{2-}) can be readily explained by recourse to the isotope scattering effect.

In order to determine the amount of distortion of the lattice caused by interstitial fluorine ions, we investigated some samples which were doped by equal concentrations of Y^{3+} and Na^+ ions which compensate the Y^{3+} ions (see Fig. 2). For concentrations up to 0.5 mole % (Y^{3+} and Na^{3+}), the additional thermal resistance W_N (for $A_1 \approx 0.38 \cdot 10^{-3}$ m/W) was equal to $58 \pm 12 \cdot 10^{-3}$ N·m·deg/W, where N is the concentration in mole % of the (Y^{3+} + Na^+) complexes. Thus, the deformation of the CaF_2 lattice by Y^{3+} impurity leads to a contribution to the thermal resistivity comparable to 1/3 W_N (Y^{3+}) because of the effect of interstitial fluorine ions. Additional evidence for the significant role played by lattice deformation in the presence of trivalent REM ions is provided by measurements on samples containing divalent

Eu^{2+} impurities (the majority content was between 0.05 and 0.1 mole %). The removal of the interstitial cation decreases the additional thermal resistance W_N by almost 50% in comparison to its value in crystals doped with Eu^{3+}. From the data in Figs. 1 and 2 it follows that when the impurity concentration is high (for Y^{3+} and REM ions this means higher than 0.1 to 0.2 mole %), the slope of the coefficient A_1 is lower than in pure crystals ($A_1 \approx 0.24 \cdot 10^{-3}$ m/W for 1 mole % Sm^{3+} and Dy^{3+}) which is obviously related to a decrease in anharmonic interaction in crystals with a well developed defect structure [6]. On the other hand, the slope of the dependence of W_N on concentration N decreases (so that for $N \geq 0.5$ mole % of Yb^{3+}, $dW_N/dN \approx 35 \cdot 10^{-3}$ m·deg/W·1 mole%). Up until now phenomena occurring in defect systems containing large defect concentrations have not been studied extensively and they require theoretical interpretation.

At temperatures close to liquid nitrogen temperature, samples containing a high concentration of REM impurity exhibit properties of a resonance character (see the data for the sample containing 1 mole % Sm^{3+} and Dy^{3+} in Fig. 1) [1, 5] which is probably related to the large mass of the substitutional ions.

Samples containing Na^+ do not exhibit any resonance phenomena even when the content is as high as 2 mole %.

NOTATION

λ, thermal conductivity; W_N, heat resistance; T, absolute temperature; N, impurity content in mole %.

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