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Theoretical studies of nonradiative 4f–4f multiphonon transitions in dielectric crystals containing rare earth ions

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Abstract

Detailed calculations have been performed of multiphonon relaxation rates of optical excitations in Nd-doped $LiYF_4$ and Pr-doped $CsCdBr_3$ crystals in the frameworks of the exchange charge model of the crystal fields and rigid ion harmonic models of lattice dynamics. It is shown that the empirical energy gap low emerges from the exponential diminishing of spectral densities of n-phonon correlation functions with the increase of an order n. Calculated transition probabilities for 2-, 3-phonon processes agree with experimental data. However, for energy gaps exceeding the maximum phonon energy more than twice, the existing theory which neglects the lattice anharmonicity brings about underestimated relaxation rates.

Keywords: Electron–phonon interaction; Multiphonon transitions; Neodymium; Praseodymium; $LiYF_4$; $CsCdBr_3$

1. Introduction

Nonradiative decay rates between crystal field energy levels belonging to different manifolds of rare earth (RE) ions are predominantly determined by the energy gap and the particular host crystal lattice. To describe the experimental data, the energy gap law for the probabilities of nonradiative transitions at low temperatures was introduced [1,2]

$$W = (1/\tau_0)\exp(-a\Delta E/\hbar\omega_M), \quad (1)$$

where a and τ_0 are empirically fitted parameters, ω_M is the highest phonon frequency of the host medium, and ΔE is the energy gap between the populated state and the next lower lying energy level of a RE ion (usually this gap is considered as the difference between energies of the lowest crystal field state of the upper multiplet and the highest crystal field state of the lower multiplet). The minimum number of phonons n needed to bridge the gap ($\Delta E = \hbar[(n-1)\omega_M + \Omega]$), $0 < \Omega < \omega_M$) denotes the order of the process. The theoretical derivation of the energy gap law in the framework of linear mechanism of the electron–phonon interaction [3] based on the substitution of an exponent e^{-an} for $1/n!$ (where n is the number of phonons emitted by the ion) is not satisfactory. Pukhov and Sakun worked out the microscopic model of nonradiative multiphonon transitions using terms of nth order in the Hamiltonian of electron–phonon interaction to calculate the probability of a process that involved n phonons [4]. We consider here this nonlinear mechanism of nonradiative transitions in the framework of a cluster model taking into account interactions between the RE ion and a finite number of its ligands in the first coordination shell. Making use of this model allows calculations of multiphonon transition probabilities without introducing any additional fitting parameters except those involved in the description of the crystal field interaction. The main goal of the present work is to check whether the existing theory is able to predict reliable estimations of multiphonon relaxation rates of impurity RE ions in dielectric crystals.

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