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Theoretical studies of electron-vibrational $4f^N$–$4f^{N-1}5d$ spectra in $LiYF_4:RE^{3+}$ crystals

B.Z. Malkin*, O.V. Solovyev, A.Yu. Malishev, S.K. Saikin

Department of Physics, Kazan State University, Kremlevskaya 18, 420008 Kazan, Russian Federation

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Abstract

The UV and VUV inter-configuration $4f^N$–$4f^{N-1}5d$ spectra of rare-earth ions in insulators consist of broad electron-vibrational bands which sometimes have a resolved fine structure. In the present work, the low-temperature absorption band shapes of the impurity Ce^{3+}, Pr^{3+} and Nd^{3+} ions in $LiYF_4$ crystals have been simulated in the framework of the microscopic theory operating with the real phonon spectrum of the host crystal lattice. The energy levels and wave functions of the ground ($4f^N$) and excited ($4f^{N-1}5d$) electronic configurations of rare-earth ions were obtained from the numerical diagonalization of the Hamiltonian containing energies of electrostatic Coulomb and exchange interactions between electrons, spin–orbit interactions and the crystal field interaction. Crystal field parameters and electron–phonon coupling constants were treated in the framework of the exchange charge model. Form-functions of the spectral bands proportional to the calculated integral intensities of electric dipole transitions are obtained as a sum of convolutions of spectral densities of multiphonon correlation functions and form-functions of zero-phonon lines with the widths determined by distributions of random lattice strains and non-radiative transition probabilities. The calculated values of the Huang–Rhys parameters of crystal field states in mixed $4f^{N-1}5d$ configurations vary in the range from 0.1 to 15 and correspond to intermediate or strong electron–phonon interactions. Results of simulations of the spectral envelopes agree satisfactorily with the experimental data available from the literature.

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Keywords: 4f–5d spectra; electron–phonon interaction; $LiYF_4$

1. Introduction

Studies of spectral properties and excitation dynamics in rare-earth-doped crystals allow to test theories of the electron–lattice interaction at different regimes of coupling strength (weak in the ground $4f^N$ electronic configuration and strong in the excited $4f^{N-1}5d$ configuration). Investigations of mixed $4f^{N-1}5d$ configurations started from the pioneer works by Feofilov [1] and Kaplyanskii and Feofilov [2] on the spectra of impurity divalent rare-earth ions in alkaline-earth fluorides. The quantitative features of the structural form of electron-vibrational $4f^N$–$4f^{N-1}5d$ spectra for divalent rare-earth ions in alkali-halides were discussed by Wagner and Bron [3] using a simplified model of electron–lattice interaction. As it has been shown by Kaplyanskii and Przhevuskii [4] by piezo-spectroscopic measurements, deformation potentials of $4f^{N-1}5d$ states exceed ones for $4f^N$ states by an order of magnitude.

New possibilities of taking VUV spectra with the use of synchrotron radiation demonstrated by Yen et al. [5,6] were widely explored during last 10 years. Systematic experimental studies of the $4f^N$–$4f^{N-1}5d$ excitations and respective $4f^{N-1}5d$–$4f^N$ emission, theoretical modeling of energy-level patterns and transition intensities in the $4f^N$–$4f^{N-1}5d$ spectra were carried out for a lot of systems. Trends in the atomic parameters were systematized by Reid et al. [7]. An original theory of 4f–5d spectra of impurity rare-earth ions based on simulations of molecular orbitals in large clusters of ions in dielectric crystals was derived by Ogasawara et al. [8].

*Corresponding author. Tel.: +7 8432 315342; fax: +7 8432 387418.
E-mail address: Boris.Malkin@ksu.ru (B.Z. Malkin).

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