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# Local lattice structure, crystal field and energy level patterns in $\text{CsCdBr}_3:\text{Tm}^{3+}$ crystals

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## Abstract

In  $\text{CsCdBr}_3$ ,  $\text{Tm}^{3+}$  substitutes for  $\text{Cd}^{2+}$ . It predominately forms symmetric dimer centers and single-ion centers, both of trigonal symmetry. The energy level schemes of both centers were determined by EPR and site-selective laser spectroscopy. To describe the spectra term dependent crystal-field parameters were deduced on the basis of a microscopic model taking into account the local lattice deformation induced by the impurity centers and the quasi-resonant virtual scattering of intrinsic lattice excitations by the  $\text{Tm}^{3+}$  ions. © 1998 Elsevier Science S.A.

**Keywords:** Crystal field;  $\text{CsCdBr}_3:\text{Tm}^{3+}$ ; Local lattice deformation

## 1. Introduction

Dopant trivalent rare earth (RE) ions substitute for  $\text{Cd}^{2+}$  ions in the quasi-one-dimensional double bromides  $\text{CsCdBr}_3$  forming optical centers with various mechanisms of charge compensation. Symmetric dimer centers, where the excess positive charge of a pair of  $\text{RE}^{3+}$  ions is compensated by a  $\text{Cd}^{2+}$  vacancy between them, are preferentially formed. Due to the close proximity of the optically active ions in the dimers these crystals are studied extensively as promising materials for up-conversion lasers [1,2]. In particular, efficient energy-transfer processes were observed in  $\text{CsCdBr}_3$  codoped with Ho and Tm [3], and Pr and Tm [4]. Although the spectral properties of  $\text{CsCdBr}_3$  crystals activated by different  $\text{RE}^{3+}$  ions have been thoroughly studied [5–7], the identification of the spectral lines with specific impurity centers still has a hypothetical character. A microscopic theoretical description of the splittings of the  $\text{RE}^{3+}$  states in the crystal field does not yet exist, and the mechanisms of the ion–lattice interaction and quantum up-conversion are not yet elucidated.

In this paper the energy levels of the two dominating optical centers with different charge compensation have been obtained by site-selective laser spectroscopy. By

comparing the crystal-field splitting of the ground state  $^3\text{H}_6$  with the results of the EPR measurements [8] we identify unambiguously one of the energy level schemes as belonging to the symmetric dimer center  $\text{Tm}^{3+}-\text{Cd}^{2+}$  vacancy– $\text{Tm}^{3+}$  which substitutes for three adjacent  $\text{Cd}^{2+}$  ions in the linear chain of confacial  $(\text{CdBr}_6)^{4-}$  octahedra. The distorted local structure of the crystal lattice around the isolated symmetric dimer is determined in a quasi-molecular model for the impurity center. The obtained inter-ionic distances were used to find an initial set of crystal-field parameters using the exchange charge model. These parameters were refined by a least-square fit to the experimental data of the crystal-field and Zeeman splittings.

We present here also the energy level scheme for one of the  $\text{Tm}^{3+}$  single-ion centers of  $\text{C}_{3v}$  symmetry (which may be of the type  $\text{Tm}^{3+}-\text{Cd}^{2+}$  vacancy– $\text{Cd}^{2+}-\text{Tm}^{3+}$ ) with energies only slightly different from those of the symmetric dimer. The absence of a second  $\text{Tm}^{3+}$  ion in the nearest neighbourhood of this center is confirmed by EPR experiments [8]. Analysis of the optical spectra has shown that the crystal-field parameters of the  $\text{Tm}^{3+}$  ions in the dimer and single-ion centers are strongly term-dependent. We assume that the observed selective increase of the crystal field, particularly affecting the  $\text{Tm}^{3+}$  ion in the  $^1\text{G}_4$  state which is positioned in the gap between the lowest intrinsic absorption and emission bands of the host lattice, is caused by quasi-resonant virtual scattering of lattice excitons; a

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