The rare-earth centers in CsCdBr$_3$

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Abstract

CsCdBr$_3$ crystallizes in the quasi-linear CsNiCl$_3$ structure. It possesses linear chains of [CdBr$_6$]$^{4-}$ octahedra separated by parallel chains of Cs$^+$. Trivalent rare-earth (RE) ions substitute for the divalent Cd ions. The need for charge compensation leads to a number of RE centers, the most prominent of which is the symmetric pair center RE^{3+}–(Cd vacancy)–RE^{3+}. Madelung calculations were performed for a number of different centers giving a ranking for their chance of realization. Experimental evidence from optical spectroscopy and submillimeter ESR is given for the most likely centers. The symmetric pair center is of special interest for cooperative phenomena of RE^{3+} ions. This includes direct ion–ion interactions and interactions with or via the electronic excitations of the host lattice. Some experiments are discussed.   © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

CsCdBr$_3$ is not just another host material for rare-earth (RE) ions. It possesses a number of specific properties which are more of fundamental than of direct technological interest.

1. Trivalent RE ions substitute for divalent Cd ions. This requires charge compensation in a very dense crystal structure not offering the chance of charge compensation by interstitial ions such as, for example, in CaF$_2$. Charge compensation can only be realized by ion vacancies. The most discussed center of this kind is the symmetric pair center RE^{3+}–(Cd vacancy)–RE^{3+}. This was proposed in 1977 [1] on the basis of ESR experiments on CsCdBr$_3$:Gd^{3+}.
2. CsCdBr$_3$ has a quasi-linear structure with face-sharing [CdBr$_6$]$^{4-}$ octahedra separated by chains of [CsBr$_{12}$] anticubes. The symmetry of the Cd^{2+} sites is almost cubic with a slight trigonal distortion along the C$_3$ axis of the chain. The triangular basis of both chains, Cs and Cd, is identical. Therefore, the crystal readily tends to stacking faults continuing from one chain to the other.
3. [CdBr$_6$]$^{4-}$ complexes are strongly bound due to an essential contribution from covalent bonding. Theoretical calculations [2] show that the band structure in the region of the energy gap is mainly determined by this complex. Thus, the excitonic states of the lattice are excited states of this complex. The excitons can be delocalized as well as localized at stacking faults and at dopant RE ions.
4. As a result of the selection rules for optical transitions of the [CdBr$_6$]$^{4-}$ complex, the transitions from the valence to the lowest conduction band do not originate from the top of the valence band, but from lower branches. In this way, the optical band gap is much wider than the electronic one.
5. Because RE^{3+} ions substitute for Cd^{2+} in [CdBr$_6$]$^{4-}$ octahedra, they are directly embedded in the exciton-forming complex. This explains the strong interaction of the excitons with the RE ions. Experimental evidence will be given for this.

2. Optical and ESR spectra

From standard ESR spectra of CsCdBr$_3$:Gd^{3+}, we know of the existence of the symmetric pair centers RE^{3+}–(Cd vacancy)–RE^{3+} [1]. But the number of transitions found in

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