ELSEVIER

Journal of Alloys and Compounds 275–277 (1998) 181–185

Journal of ALLOYS AND COMPOUNDS

Local lattice structure, crystal field and energy level patterns in $CsCdBr_3:Tm^{3+}$ crystals

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Abstract

In $CsCdBr_3$, Tm^{3+} substitutes for 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 Tm^{3+} ions. © 1998 Elsevier Science S.A.

Keywords: Crystal field; $CsCdBr_3:Tm^{3+}$; Local lattice deformation

1. Introduction

Dopant trivalent rare earth (RE) ions substitute for Cd^{2+} ions in the quasi-one-dimensional double bromides $CsCdBr_3$ forming optical centers with various mechanisms of charge compensation. Symmetric dimer centers, where the excess positive charge of a pair of RE^{3+} ions is compensated by a 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 $CsCdBr_3$ codoped with Ho and Tm [3], and Pr and Tm [4]. Although the spectral properties of $CsCdBr_3$ crystals activated by different 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 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 $^3H_6$ with the results of the EPR measurements [8] we identify unambiguously one of the energy level schemes as belonging to the symmetric dimer center Tm^{3+}–Cd^{2+} vacancy–Tm^{3+} which substitutes for three adjacent Cd^{2+} ions in the linear chain of confacial $(CdBr_6)^{4-}$ 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 Tm^{3+} single-ion centers of C_{3v} symmetry (which may be of the type Tm^{3+}–Cd^{2+} vacancy–Cd^{2+}–Tm^{3+}) with energies only slightly different from those of the symmetric dimer. The absence of a second 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 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 Tm^{3+} ion in the $^1G_4$ 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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0925-8388/98/$19.00
PII: S0925-8388(98)00299-0

similar mechanism of phonon-induced shifts of crystal-field levels of paramagnetic ions was described many years ago [9].

2. Experimental

The crystals were grown in a sealed quartz ampoule by the Bridgeman technique from the starting materials CsBr (Merck, suprapure), $CdBr_2$ (Cerac, 99.9%) and $TmBr_3$ (Cerac, 99.9%). 0.5% of the Cd^{2+} ions were substituted by Tm^{3+}. The materials were mixed as powders in a dry inert atmosphere in a glove box and filled into the ampoule. During the growing procedure the ampoule was filled with a slight Br_2 atmosphere to avoid incorporation of other anions into the crystal. Single crystals of good optical quality were obtained with the crystallographic axis parallel to the axis of the ampoule. The crystals easily cleaved along the crystal axis giving surfaces of good optical quality. Further details of the crystals are given in Ref. [6].

The site-selective excitation and fluorescence spectra were recorded using a tunable dye laser pumped by a N_2 laser and a 3m McPherson monochromator. The fluorescence was detected by a cooled Hamamatsu R943-05 photomultiplier in the photon-counting technique and registered by a multichannel analyzer. The crystals were immersed in superfluid helium at 1.6 K or in gaseous helium at 4.2 K. To determine the symmetries of the crystal-field levels polarized spectra were recorded in excitation as well as in emission.

Four different centers could be found from the spectra, two centers of trigonal symmetry, having doublet and singlet crystal-field states, and two centers of lower symmetry. The lowest and the first excited crystal-field components of the ground state $^3H_6$ are singlets with a gap of $11.7\pm0.3\ cm^{-1}$ for one of the trigonal centers and $9.7\pm0.3\ cm^{-1}$ for the other. In the lower symmetry spectra this gap equals $13\pm0.3\ cm^{-1}$. The submillimeter EPR spectra of our samples are given in Ref. [8]. At helium temperatures two resonance lines were observed corresponding to magnetic dipole transitions between the lowest crystal-field singlet states with zero magnetic field splittings of 336 and 292 GHz (11.2 and $9.7\ cm^{-1}$). The identification of the spectra of the trigonal centers with the symmetric dimer center and with the single-ion center is possible due to the resolved specific triplet and doublet hyperfine structure of the corresponding EPR signals. The energy levels of these centers are presented in Table 1 together with the results for the symmetric dimer given in Ref. [4]. It can be seen that for most of the crystal-field states the experimental data coincide (taking into account possible shifts in the frequency scales), but some of the crystal-field states obtained in Ref. [4] and marked by "?" in Table 1 are neither confirmed by our measurements nor by our calculations (see below).

3. Local structure of the symmetric dimer center

As we are mainly interested in the relative positions of the Tm^{3+} ions and their nearest neighbours, we considered explicitly only the displacements of the nearest 50 ions around the symmetric dimer center Tm^{3+}–Cd vacancy–Tm^{3+} from their equilibrium positions in the perfect lattice (the ion coordinates in a rectangular system of coordinates with the z-axis along the crystal axis, in units of the lattice constants $a=7.675$ Å, $c=6.722$ Å, $x=0.1656$ [10], are given in Table 2). These ions belong to the first (12 Br^-), second (2 Cd^{2+}), third (12 Cs^+), and fourth (24 Br^-) coordination shells of the impurity ions. The numerical values of the ion displacements presented in Table 2 were obtained by minimizing the potential energy of the cluster in the harmonic approximation.

The energy of the inter-ion interaction was assumed to be the sum of Coulomb and non-Coulomb terms. The effective ion charges (in units of the proton charge e: $Z(Cd^{2+})=1.56$, $Z(Cs^+)=0.84$, $Z(Br^-)=-0.8$) and the non-Coulomb force constants, corresponding to interactions between the nearest neighbours Cd^{2+}–Br^-, Cs^+–Br^-, and Br^-–Br^-, were obtained by fitting the calculated phonon frequencies at the Γ-point of the Brillouin zone to experimental data [11,12].

According to the results of minimizing the energy of the relaxed lattice with respect to the ion displacements (see Table 2), the distance between the Tm^{3+} ions attracted by the Cd^{2+} vacancy diminishes from 6.722 to 5.943 Å. This value is consistent with the energy of the magnetic dipole–dipole interaction between the Tm^{3+} ions in the symmetric dimer determined from the EPR spectra, and is very close to the distance of 5.93 Å between the Gd^{3+} ions, determined in Ref. [13]. In the perfect lattice the radius of the first Cd^{2+}–Br coordination shell is 2.77 Å; in the symmetric dimer center the six Br^- ions nearest to the vacancy are forced outwards, but the displacements of the Tm^{3+} ions along the dimer axis are so large that the corresponding Tm^{3+}–Br distance decreases to 2.65 Å: on the contrary, the terminal triangles of the Br^- ions lag behind the impurity ions and the corresponding inter-ion distance increases to 2.83 Å. These values are close to the distances (2.64 and 2.86 Å) between the Yb^{3+} and the nearest Br^- ions in the intrinsic dimer units in $Cs_3Yb_2Br_9$ [14]. However, the harmonic approximation fails when the ion displacements are so large and the results of our calculations are to be considered as rather crude estimates.

4. Crystal-field parameters

The main contributions to the crystal-field splitting of RE ions in a field of C_{3v} symmetry can be obtained by a parametrized one-electron Hamiltonian of the form

Table 1
Energy levels of Tm^{3+} in $CsCdBr_3$ (values in cm^{-1})

$^{2S+1}L_J$	Irr. repr.	Symmetric dimer center			Single ion	
		E_{exp} (this work)	E_{exp} (Ref. [4])	E_{calc}	E_{exp} (this work)	E_{calc}
$^3H_6$	A_1	0	0	0	0	0
	A_2	11.7	11.4	11.4	9.7	9.4
	E	76.7	74.8	73.5	75.0	78.6
	A_1	101.2	99.0	94.3	99.5	91.5
	E	122.6	120.0	112	121.0	119
	A_2	237.6	226.7	207	236.0	213
	E	298.4	294.2	292	296.0	298
	A_1			319	320.0	314
	E	327.6	323.0	326	340.0	326
$^3F_4$			5536.0?			
	E	5557	5559.5	5557	5559	5564
	A_1	5563	5565.3	5557	5564	5561
	E	5750	5752.8	5766	5749	5770
	A_2^a			5794		5797
	E	5801	5805.0	5795	5802	5802
	A_1^a		5875.6?	5835		5842
$^3H_5$	E	8193.0	8195.3	8193	8191	8195
	A_2^a	8244.5		8243		8246
	E^a	8251.0	8248.6	8257	8252	8261
	E^a		8318.0	8368		8370
	A_1^a			8368		8377
	E^a		8407.3	8439		8441
	A_2^a			8454		8453
$^3H_4$	E	12499	12495	12499	12504.5	12500
	A_1^a	12508	12516	12519		12525
	E^a		12557	12551		12556
	A_2^a	12602	12634	12612		12632
	E^a	12653	12648	12624		12622
	A_1^a		12773?	12718		12721
$^3F_3$	E (A_2^a)	14348	14341	14348	14346	14350
	A_2 (E^a)	14352	14364	14383	14354	14387
	E	14374	14377	14392	14376	14394
	A_2^a			14394		14398
	A_1	14399	14406	14408	14405.5	14406
			14441?			
$^3F_2$	E^a		14803?	14936		14937
	A_1	15024	15035	15024	15024	15029
	E^a			15055		15055
$^1G_4$	E	20805	20808	20805	20811	20810
	A_1	20834	20837	20826	20840	20827
	E	21266	21269	21270	21267.5	21269
	A_2	21314	21318	21319		21316
	E	21328	21332	21333	21330.5	21343
	A_1	21418	21422	21410	21420	21417
$^1D_2$	A_1^a			27358		27359
	E	27387	27388	27387		27390
	E^a		27413?	27443		27444

[a] Theoretically predicted symmetry.

$$H = B_2^0 O_2^0 + B_4^0 O_4^0 + B_6^0 O_6^0 + B_4^3 O_4^3 + B_6^3 O_6^3 + B_6^6 O_6^6 \quad (1)$$

where O_p^k are the Stevens operators. We do not know any ‘‘ab initio’’ calculations of the crystal-field parameters B_p^k for RE ions in a bromine coordination. If the inter-ion distances in the host lattice are known, it should be possible to obtain preliminary estimates of these parameters by the semi-phenomenological exchange charge model [15]. In this model the crystal field can be represented as a sum

$$B_p^k = B_{pZ}^k + B_{pS}^k \quad (2)$$

where the contributions of the electrostatic field by the point charges of the ions are given by

Table 2
Local lattice structure of the Tm^{3+} symmetric dimer center (the Cd^{2+} vacancy sits on the site with coordinates (0 0 0))

Ion	Coordinate			Displacement		
	x/a	y/a	z/c	$\delta x/E$	$\delta y/E$	$\delta z/E$
Tm^{3+}	0	0	$\pm 1/2$	0	0	∓ 0.390
Br^-	$\pm x\sqrt{3}$	0	$\pm 3/4$	∓ 0.146	0	∓ 0.127
Br^-	$\pm x\sqrt{3}$	0	$\mp 1/4$	± 0.115	0	∓ 0.011
Cs^+	$\mp 1/\sqrt{3}$	0	$\pm 3/4$	∓ 0.114	0	± 0.026
Cs^+	$\pm 1/\sqrt{3}$	0	$\pm 1/4$	∓ 0.075	0	∓ 0.143
Cd^{2+}	0	0	± 1.0	0	0	∓ 0.023
Br^-	$\mp x\sqrt{3}\pm\sqrt{3}/2$	$\pm 1/2$	$\pm 1/4$	± 0.024	± 0.033	± 0.013
Br^-	$\pm x\sqrt{3}\mp\sqrt{3}/2$	$\pm 1/2$	$\pm 3/4$	± 0.014	∓ 0.027	± 0.004

$$B_{pZ}^{k} = -e^{2}K_{p}^{k}(1-\sigma_{p})\langle r^{p}\rangle\sum_{i}Z(i)\frac{O_{p}^{k}(\vartheta(i),\varphi(i))}{R(i)^{p+1}} \tag{3}$$

and the contributions of the exchange charge field are equal to

$$B_{pS}^{k} = \frac{2}{7}(2p+1)K_{p}^{k}e^{2}\sum_{i}(G_{s}S_{s}(i)^{2} + G_{\sigma}S_{\sigma}(i)^{2} + \gamma_{p}G_{\pi}S_{\pi}(i)^{2})\frac{O_{p}^{k}(\vartheta(i),\varphi(i))}{R(i)} \tag{4}$$

Here, $\gamma_2 = 3/2$, $\gamma_4 = 1/3$, $\gamma_6 = -3/2$ and K_p^k are numerical factors [15], σ_p are the shielding factors, $\langle r^p\rangle$ are the moments of the radial wave function of the 4f electrons and $R(i)$, $\theta(i)$ and $\varphi(i)$ are the spherical coordinates of the lattice ion with charge $eZ(i)$. In the simplest case $G_s = G_\sigma = G_\pi = G$ is the only dimensionless parameter of the model. The overlap integrals $S(i)$ have been computed using the radial 4f wave function of the Tm^{3+} ion from Ref. [16] and the 4s, 4p wave functions of the Br^- ion given in Ref. [17]. Similarly to Ref. [18] the dependencies of the overlap integrals on the inter-ion distance R (Å) are approximated by the following expressions:

$$S_{s} = \langle 4f, m=0|4s\rangle = 0.1067\exp(-0.4847R^{1.8036})$$

$$S_{\sigma} = \langle 4f, m=0|4p, m=0\rangle = 0.06415\exp(-0.28545R^{1.9204})$$

$$S_{\pi} = \langle 4f, m=1|4p, m=1\rangle = 0.8366\exp(-1.8445R^{0.9992}) \tag{5}$$

Using the Ewald method to calculate the lattice sums and taking into account the local lattice deformation we obtained the following crystal-field parameters for the symmetric Tm^{3+} dimer (values are in cm^{-1}): $B_2^0 = -227.6(1-\sigma_2) - 0.8G$; $B_4^0 = -19.2(1-\sigma_4) - 3.23G$; $B_4^3 = 530.1(1-\sigma_4) + 107.9G$; $B_6^0 = 0.29(1-\sigma_6) + 0.71G$; $B_6^3 = 5(1-\sigma_6) + 6.4G$; $B_6^6 = 7.2(1-\sigma_6) + 9.7G$. The value of the model parameter $G = 17$ has been determined from the total splitting of the ground state $^3H_6$ using the generally adopted shielding factors $\sigma_4 = \sigma_6 = 0$ and $\sigma_2 = 0.6$. We should like to draw attention to the relatively large values of the terms corresponding to overlap and covalency effects in comparison to the case of RE ions in fluorine or chlorine coordination. The calculated crystal-field parameters were used as starting values for the fitting procedures constrained by the conditions that the calculated energy gaps between the two lowest crystal-field singlets and the effective g-factors of these quasi-doublets in the symmetric dimers and in the single-ion centers had to agree with the experimental data. Similarly to the authors of Ref. [5] we find it more descriptive to give the crystal-field Hamiltonian (1) in terms of the cubic and trigonal components, as represented in the expression below by the first and second line, respectively

$$H = -\frac{2}{3}B_4(O_4^0 - 20\sqrt{2}O_4^3) + \frac{16}{9}B_6\left(O_6^0 + \frac{35\sqrt{2}}{4}O_6^3 + \frac{77}{8}O_6^6\right) + \delta B_2^0O_2^0 + \delta B_4^0O_4^0 + \delta B_6^0O_6^0 + \delta B_6^6O_6^6 \tag{6}$$

The initial and final values of the crystal-field parameters for the Tm^{3+} centers as compared with the corresponding parameters of the Ho^{3+} centers (determined in Ref. [8]) are given in Table 3. Despite the large trigonal distortion of the nearest bromine octahedron, the main features of the crystal-field splitting of the RE ions in $CsCdBr_3$ are determined by the cubic component of the crystal field. The calculated energy levels of the Tm^{3+} ions presented in Table 1 were obtained by diagonalizing simultaneously the spin–orbit interaction ($\zeta = 2663$ cm^{-1}) and the crystal-field Hamiltonian (5) in the space of the ^3H, ^3F, ^3P, ^1I, ^1G, ^1D states with fitted baricenters of the free-ion multiplets. The splittings of all free-ion states of Tm^{3+}, except $^1G_4$, for

Table 3
Crystal-field parameters for Tm^{3+} and Ho^{3+} in $CsCdBr_3$ (values in cm^{-1})

	Symmetric dimer center			Single ion	
	Tm^{3+}, exchange charge model	Tm^{3+}	Ho^{3+} [8]	Tm^{3+}	Ho^{3+} [8]
B_4	125.2	125.25	150.67	122.2	144.25
B_6	5.2	6.95	9.83	6.86	12.96
δB_2^0	−105	−81.4	−75.6	−79.1	−73.6
δB_4^0	9.4	1.5	6.14	−6.8	4.87
δB_6^0	3.1	−1.1	−4.73	1.4	−12.19
δB_6^6	83.6	−13	−18.36	−50	−118.5

both types of impurity centers are satisfactorily described by our final sets of crystal-field parameters. But in the case of ${}^1G_4$ the results of our calculations are in drastic disagreement with the measured energies. Particularly, the calculated total splitting is about 1.5 times less than the measured one. To make the calculated energies consistent with the observed spectra we had to multiply by 1.85 all matrix elements of the Hamiltonian (6) in the space of states belonging to the ${}^1G_4$ multiplet. These ‘‘correct’’ results are given in Table 1. We would like to point out that a similar strong dependence of the crystal-field parameters on the free-ion state was also found in the cubic RE elpasolites with bromine sublattices [19]. In no way can corrections of this magnitude be obtained from the two-electron correlation crystal field [20].

5. Discussion

It seems that excitonic emissions in the near ultraviolet and visible regions can generally be observed in crystals containing Cd^{2+} ions in an octahedral bromine coordination [21]. The radiative lattice states may be attributed to excitations of the halogen 4p electrons to the empty Cd^{2+} 5s states in the $(CdBr_6)^{4-}$ complex (from the valence to the conduction band). In $CsCdBr_3$ the lowest excitonic absorption and emission bands are observed in the region of the ${}^1G_4$ state (which is mixed with the ${}^3H_4$ and ${}^3F_4$ states by spin–orbit interaction) [4,22]. In this case we have to complete the matrix of the crystal-field Hamiltonian (6) by the matrix

$$\begin{aligned}\langle {}^1\mathrm{G}_4 m|\Delta H|{}^{2S+1}L_J m'\rangle = \tfrac{1}{2}\sum_{m'',\mathrm{e}} [(&E({}^1\mathrm{G}_4 m) - E({}^3\mathrm{H}_6 m'') \\ &- \hbar\omega_\mathrm{e})^{-1} + (E({}^{2S+1}L_J m') \\ &- E({}^3\mathrm{H}_6 m'') - \hbar\omega_\mathrm{e})^{-1}] \\ &\langle {}^1\mathrm{G}_4 m,\mathrm{g}|V|{}^3\mathrm{H}_6 m'',\mathrm{e}\rangle \\ &\langle {}^3\mathrm{H}_6 m'',\mathrm{e}|V|{}^{2S+1}L_J m',\mathrm{g}\rangle \qquad (7)\end{aligned}$$

which corresponds to virtual scattering of lattice excitons with energies $\hbar\omega_e$ by the localized 4f electrons. Here g and e stand for the ground and excited states of the lattice and V is the interaction energy linear in the exciton annihilation and creation operators. Due to the resonance denominator (the first term on the right-hand side) these terms may cause an anomalous enhancement of the crystal-field splitting. The existence of a strong interaction between RE ions and electronic lattice excitations in $CsCdBr_3$ is confirmed by the observed peculiarities in the quantum up-conversion processes [6] and in the non-radiative relaxation as well [22].

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