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EPR Identification of coupled Yb^{3+} ion pairs in optically bistable compound $CsCdBr_3$:Yb

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Abstract

Electron Paramagnetic Resonance (EPR) studies on ytterbium ions in weakly doped $CsCdBr_3$ are reported. Analysis of the characteristic features of the observed EPR spectra and their angular dependence shows that Yb^{3+} ions substitute for Cd^{2+} ions in D_{3d} point site symmetry mainly to form weakly antiferromagnetically coupled symmetric pair complexes of the type Yb^{3+}–V_{Cd}–Yb^{3+}, with interionic separation of around 5.9 Å and J exchange coupling value of -0.0016 cm^{-1}. Several weaker resonance lines are also observed which are assigned to single ion Yb^{3+} centers in perturbed sites of lower symmetry.

Keywords: Insulators; Crystal growth; Crystal structure and symmetry; Exchange and superexchange; Electron paramagnetic resonance

1. Introduction

The interesting phenomenon of intrinsic optical bistability (IOB) originating from rare earth ion pairs has been observed at low temperature in the dimer isostructural systems $Cs_3Y_2Br_9$:10% Yb^{3+} and Cs_3Lu_2Br:10% Yb^{3+} [1,2] and more recently in a quasi one-dimensional compound $CsCdBr_3$:1% Yb^{3+} [3]. The studies on these materials suggest that intense bistable pair luminescence can result from co-operative non-linearities mediated by local field effects. These non-linearites arise from strong ion–ion coupling within well-isolated dimer units and energy migration in the Yb^{3+} pairs has a degrading effect on bistable emission. Thus, a precise knowledge of ion–ion coupling mechanisms in such pairs is of fundamental interest and could help to better understand and optimise bistable luminescence. Electron Paramagnetic Resonance (EPR) spectroscopy is a powerful technique to probe such ion–ion interactions in the ground state of a coupled paramagnetic system. In the present work, EPR studies have been performed on IOB compound $CsCdBr_3$:1.3% Yb^{3+}. The host $CsCdBr_3$ crystallises in the hexagonal structure of space group $P6_3/mmc$ (D_{6h}^4) consisting of linear chains of face sharing $(CdBr_6)^{4-}$ octahedra parallel to the crystallographic c-axis with Cs^+ ions occupying sites between the chains. Point symmetries are D_{3h} for Cs^+ and D_{3d} for Cd^{2+}. A striking feature of $CsCdBr_3$ is that when rare-earth (RE^{3+}) ions such as Yb^{3+} are incorporated in the Cd^{2+} lattice position, they enter nearly exclusively as charge compensated ion-pair centres, even at low dopant concentration. The main RE center is a symmetric in chain RE^{3+}–V_{Cd}–RE^{3+} pair complex identified by McPherson and Henling by EPR experiments on Gd^{3+} [4,5] where V_{Cd} denotes Cd^{2+} vacancy. Each RE^{3+} ion of the pair has a C_{3v} site symmetry and the interionic separation, R, is around 6.0 Å. A minority RE^{3+}-(C_S^+ vacancy) complex of lower symmetry (C_S) was also identified by EPR [6]. Subsequent laser-spectroscopic studies on $CsCdBr_3$ doped with Nd^{3+} [7], Er^{3+} [8] and Pr^{3+} [9] have reported the presence of a minority asymmetric in chain RE^{3+}–RE^{3+}–V_{Cd} complex, with R around 3.4 Å.

2. Experimental details

$CsCdBr_3$ single crystals with 1.3% ytterbium concentration were grown by Bridgman method. EPR spectra were recorded on a Bruker ESP 300e spectrometer equipped with a variable temperature accessory from

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Oxford Instrument. The microwave frequency was measured with a Systron Donner frequency-counter. Typical measurements were made at 7 K with a microwave power of 20 mW and a frequency of approximately 9.5 GHz.

3. Results and discussion

Free Yb^{3+} has a $4f^{13}$ configuration. The ground state is $^2F_{7/2}$ and the $^2F_{5/2}$ excited state is around 10 000 cm^{-1}. In the trigonal field of the D_{3d} symmetry, $J=7/2$ level splits into four Kramers doublets. At liquid helium temperature, only the lowest doublet is populated and thus the EPR spectrum can be treated by a Hamiltonian with an effective spin $S=1/2$. In addition to even isotopes (nuclear spin $I=0$), ytterbium has two odd isotopes which give rise to hyperfine structure, ^{171}Yb with nuclear spin $I=1/2$ (natural abundance 14.4%) and ^{173}Yb with nuclear spin $I=5/2$ (natural abundance 16.6%).

Fig. 1 shows the principal EPR signal of Yb^{3+} in $CsCdBr_3$ recorded with external magnetic field B parallel to the crystallographic c-axis. The angular dependence of this signal in the ac (or bc) and ab crystallographic planes shows that the resonance lines have axial symmetry about the trigonal c-axis. As will be shown below, all the important features of the spectrum can be accurately described by assigning the resonance lines to the weakly antiferromagnetically coupled pairs of Yb^{3+} ions of the type $^{even}Yb–V_{Cd}–^{even}Yb$, $^{171}Yb–V_{Cd}–^{even}Yb$ and $^{173}Yb–V_{Cd}–^{even}Yb$ in identical crystallographic sites.

The spin Hamiltonian for a pair of identical interacting ions 1 and 2 can be written as:

$$H = H_1 + H_2 + H_{int} \tag{1}$$

where H_1 and H_2 take the form of a spin Hamiltonian, relevant to an isolated ion and the interaction term H_{int} is [10]:

$$H_{int} = -2J\,\vec{S}_1 \cdot \vec{S}_2 + \frac{\beta^2}{R^3}\left[-2g_{\parallel}^2(S_{1z}S_{2z}) + \frac{g_{\perp}^2}{2}(S_{1+}S_{2-}+S_{1-}S_{2+})\right] \tag{2}$$

The first and the second terms in the above expression are the isotropic exchange and anisotropic dipolar contributions respectively, J is a scalar exchange interaction, R is the RE—RE distance and S_1 and S_2 are the effective spins of the lowest ground state Kramers doublet of the two ions. The pure magnetic dipole–dipole expression has been used for the dipolar interaction because the distances between the two ions of a pair are much larger than the ion size. The z-axis (RE—RE axis) is parallel to the crystal symmetry axis in expression (2).

For similar ions without hyperfine structure, when B is parallel to z, total spin Hamiltonian in Eq. (1) becomes

$$H = g_{\parallel}\beta\, B(S_{1z}+S_{2z}) + (4D_1 - 2J)(S_{1z}S_{2z}) + (D_2 - J)(S_{1+}S_{2-} + S_{1-}S_{2+}) \tag{3}$$

where $D_1 = \beta^2(-g_{\parallel}^2)/2R^3$ and $D_2 = \beta^2(g_{\perp}^2)/2R^3$

From the eigen states of this Hamiltonian, we expect two $\Delta M_S = \pm 1$ transitions at magnetic fields

$$B_{\pm} = B_o\left[1 \pm \frac{(-2D_1 + D_2)}{g_{\parallel}\beta\, B_o}\right] \tag{4}$$

where B_o is the center field of resonance.

When ion 1 has a hyperfine structure (for example for the pairs of the type $^{171}Yb–V_{Cd}–^{even}Yb$ or $^{173}Yb–V_{Cd}–^{even}Yb$), the terms $A_{\parallel}(S_{1z}I_{1z}) + 1/2A_{\perp}(S_{1+}I_{1-} + S_{1-}I_{1+})$ are added to Eq (3).

For a particular $m_1 = \langle I_z \rangle$ state, $\Delta M_S = \pm 1$ transitions can now be shown to occur at fields (theoretical treatment is similar to that outlined by Smith and Pilbrow [11]):

$$B_{1,2} = B_o\left[1 \mp \frac{2D_1'}{g_{\parallel}\beta\, B_o} - \frac{\left(\frac{1}{2}A_{\parallel}m_1 \mp \varphi\right)}{g_{\parallel}\beta\, B_o} - \frac{1}{2}\frac{A_{\perp}^2\left[I(I+1) - m_1^2\right]\left(b_1^2 + a_2^2\right)}{(g_{\parallel}\beta\, B_o)^2}\right]$$

$$B_{3,4} = B_o\left[1 \mp \frac{2D_1'}{g_{\parallel}\beta\, B_o} - \frac{\left(\frac{1}{2}A_{\parallel}m_1 \pm \varphi\right)}{g_{\parallel}\beta\, B_o} - \frac{1}{2}\frac{A_{\perp}^2\left[I(I+1) - m_1^2\right]\left(a_3^2 + b_4^2\right)}{(g_{\parallel}\beta\, B_o)^2}\right] \tag{5}$$

with corresponding relative intensities, to first order, being

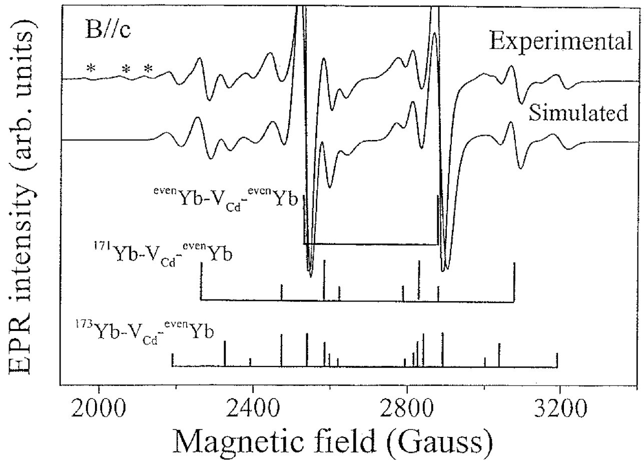

Fig. 1. Experimental and simulated EPR spectrum of $CsCdBr_3$:1.3% Yb^{3+} at 7 K with the external magnetic field B parallel to the crystallographic c-axis. The stars indicate very weak EPR lines due to single ion Yb^{3+} centers in perturbed sites of lower symmetry.

$$\frac{1}{4}(a+b)^2 \text{ and } \frac{1}{4}(a-b)^2 \tag{6}$$

respectively. The parameters D_1' and $D_2'$are defined as $D_1' = D_1 - J/2$ and $D_2' = D_2 - J$ and the other parameters ε, a and b are given as:

$$\varphi = \left(D_2'^2 + \frac{1}{4} A_\parallel^2 m_1^2 \right)^{1/2};$$

$$a = \frac{D_2'}{\left[D_2'^2 + \left(\varphi - \frac{1}{2} A_\parallel m_1 \right)^2 \right]^{1/2}} = \frac{D_2'}{f_1} \text{ and}$$

$$b = \frac{\varphi - \frac{1}{2} A_\parallel m_1}{f_1}$$

We expect $4(2I+1)$ allowed $\Delta M_S = \pm 1$ transitions when one of the ytterbium isotopes of a pair has a nuclear magnetic moment. Thus for ^{171}Yb–V_{Cd}–^{even}Yb pairs there will be eight allowed transitions while for ^{173}Yb–V_{Cd}–^{even}Yb pairs there will be 24 allowed transitions.

The spin Hamiltonian parameters, listed in Table 1, are determined by fitting the experimental spectrum with its computer simulation. Simulated spectrum, shown in Fig. 1, is obtained by assuming the resonance lines to be the derivative of Gaussian curves with a peak to peak line width of ~20 Gauss. The line positions and intensities are calculated from Eqs. (4), (5) and (6) and are depicted by a stick diagram in Fig. 1. In the case of ^{173}Yb–V_{Cd}–^{even}Yb pairs, eight very weak resonance lines in the field range 2520–2840 Gauss are not shown in the stick diagram. The $g_\perp$ and $A_\perp$ parameters, given in Table 1, are obtained by a similar analysis of the main EPR signal recorded with external magnetic field B perpendicular to the c-axis.

The distance between the two Yb^{3+} ions in a pair can be directly computed from the experimentally determined values of the dipolar parameters D_1 and D_2. From their measured values, an interionic separation, R, of 5.88 Å is calculated. This distance is in good agreement with the value of 5.93 Å for the Gd^{3+}–V_{Cd}–Gd^{3+} complexes in $CsCdBr_3$ at 77 K obtained by McPherson et al. [4,5]. It is, however, much smaller than the distance of 6.72 Å between two Cd^{2+} ions in second neighbour positions in the host lattice. This shows that there is a significant relaxation (about 12%) of Yb^{3+} ions towards the Cd^{2+} vacancy along the Yb^{3+}–V_{Cd}–Yb^{3+} axis (c-axis). According to the sign of the J parameter in Table 1, the exchange coupling between the two Yb^{3+} ions of a pair is antiferromagnetic but extremely weak. The small value of J is not surprising as the two Yb^{3+} ions in a pair are fairly far apart.

Table 1
Spin Hamiltonian parameters of the Yb^{3+}–V_{Cd}–Yb^{3+} complexes in $CsCdBr_3$:1.3% Yb

Parameter		
$g_\parallel$		2.503±0.001
$g_\perp$		2.619±0.001
$A_\parallel$ (10^{-4} cm^{-1})	^{171}Yb	666±5
	^{173}Yb	182.0±0.5
$A_\perp$ (10^{-4} cm^{-1})	^{171}Yb	708±4
	^{173}Yb	193.2±0.5
D_1 (10^{-4} cm^{-1})		−66.5±0.3
D_2 (10^{-4} cm^{-1})		72.8±0.3
J (10^{-4} cm^{-1})		−16±2

Besides the main EPR signals discussed so far, several very weak EPR lines are also observed (few of these are indicated by stars in Fig. 1). From their angular-dependence, it is concluded that these weaker lines are due to non-axial Yb^{3+} centers.

The present EPR studies show that more than 95% of the Yb^{3+} ions in $CsCdBr_3$:1.3% Yb sample form symmetric Yb^{3+}–V_{Cd}–Yb^{3+} pair complexes, the rest of the single Yb^{3+} ions being in perturbed sites of lower symmetry. It may thus be easy to distinguish the observed lines in the optical spectra of this compound by their relative intensities. All the lines in the luminescence excitation spectra in the narrow frequency region of the $^2F_{7/2}(0) \rightarrow {}^2F_{5/2}(2')$ transition in Ref. [3] should thus be assigned to symmetric ion pairs. No line is due to asymmetric complexes of the type Yb^{3+}–Yb^{3+}–V_{Cd}. The hysteresis of near-infrared and cooperative up-conversion luminescence as a function of incident laser intensity was observed exclusively for excitation of the optical line about 2 cm^{-1} above the main absorption line of Yb^{3+}–V_{Cd}–Yb^{3+} centers [3]. This relatively intense transition was attributed to asymmetric pairs Yb^{3+}–Yb^{3+}–V_{Cd}, which now appears unlikely on the basis of the present EPR experiments.

4. Conclusion

From the present EPR studies on $CsCdBr_3$:Yb^{3+}, it has been possible to identify weakly antiferromagnetically coupled symmetric Yb^{3+}–V_{Cd}–Yb^{3+} ion pairs. Excellent agreement is achieved between experimental spectra and those obtained by computer simulations, assuming complexes of the type ^{even}Yb–V_{Cd}–^{even}Yb, ^{171}Yb–V_{Cd}–^{even}Yb, ^{173}Yb–V_{Cd}–^{even}Yb. These studies have also shown the existence of single ion Yb^{3+} centers of lower symmetry in very small proportions. It is important to note that there are no asymmetric pair complexes of the type Yb^{3+}–Yb^{3+}–V_{Cd}. This implies that observed bistable luminescence in $CsCdBr_3$:1% Yb [3] should be interpreted in terms of symmetric pair complexes.

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