Explanation of the Optical Spectra and Spin-Hamiltonian Parameters for Nickel(II) in Cadmium Bromide Crystal

J.T. GONG\textsuperscript{a,*}, L.J. WANG\textsuperscript{b}, W.L. FENG\textsuperscript{c,d}, X.Z. YANG\textsuperscript{c} and F. ZHANG\textsuperscript{c}

\textsuperscript{a}School of Physics and Electron, Mianyang Normal University, Mianyang, 621000, China
\textsuperscript{b}Department of Physics and Electronic Engineering, Neijiang Normal College, Neijiang, 641112, China
\textsuperscript{c}Department of Applied Physics, Chongqing University of Technology, Chongqing, 400054, P.R. China
\textsuperscript{d}International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang, 110016, P.R. China

(Received June 28, 2010)

Based on crystal- and ligand-field theory, double-spin–orbital coupling approach was used to analyze the crystal-field energy levels and spin-Hamiltonian parameters of Ni\textsuperscript{2+} ion at trigonal site in CdBr\textsubscript{2}. The local lattice distortion (\(\Delta R\) and \(\tau_{Ni^{2+}}\)) is estimated from the crystal field parameters; the crystal field energy Hamiltonian was diagonalized in the full basis consisting of 45 wave functions of the Ni\textsuperscript{2+} ion. Results of calculations are in good agreement with experimental data. The reasonableness of the theoretical results is discussed.

PACS: 71.70.Ch, 75.10.Dg, 61.72.Bb, 76.30.Fc

1. Introduction

CdBr\textsubscript{2} is an important metal dihalide compound in which the Cd\textsuperscript{2+} plane is sandwiched between two Br\textsuperscript{−} anions planes (see Fig. 1) \cite{1, 2}. Its crystal structure is rhombohedral and it belongs to the space group \(D_{5h}^3\) \cite{1, 2}. Because there are good transparent and dielectric characteristics of CdBr\textsubscript{2} crystal, various theoretical and experimental methods were used to study its physical and chemical properties and microstructure \cite{3-5}. The optical and electron paramagnetic resonance (EPR) spectra [i.e., the spin-Hamiltonian (SH) parameters including the anisotropic \(g\) factors and zero-field splitting \(D\)] of CdBr\textsubscript{2}:Ni\textsuperscript{2+} was measured for the substitutional Ni\textsuperscript{2+} center \cite{4, 5}. Since the SH parameters of paramagnetic ions depend sensitively on the structural parameters \(R\) and \(\theta\), it will be useful to determine these parameters with a transition-metal ion as the probe. The EPR study of Ni\textsuperscript{2+} ions in CdBr\textsubscript{2} has been done by Fang et al. \cite{6}. They calculated the EPR parameters with the high-order perturbation formulae. As much as we know, however, there is no unified theoretical analysis for both optical and EPR spectra of these experimental data of CdBr\textsubscript{2}:Ni\textsuperscript{2+} crystal. The lattice structure data of these impurity centers have not been acquired yet by the unified calculation method. In fact, since the spin–orbit coupling coefficient of the ligand Br\textsuperscript{−} (e.g., \(\zeta_p^0 = 2460\) cm\textsuperscript{-1} \cite{7}) is bigger than that of the central Ni\textsuperscript{2+} (e.g., \(\zeta_d^0 = 640\) cm\textsuperscript{-1} \cite{8}), the ligand influence should be included in the analysis of the optical and EPR spectra data. In this work, the full energy matrix based on the basis consisting of 45 wave functions of the Ni\textsuperscript{2+} ion are established and then applied to Ni\textsuperscript{2+} center in CdBr\textsubscript{2} crystal. In the calculations, the contributions from the ligands \(p\) orbitals and the local angle distortions due to the mismatch of ionic radius between the host and impurity are taken into account with the double-spin–orbit coupling approach.

Fig. 1. The local structure around Ni\textsuperscript{2+} centers in CdBr\textsubscript{2}:Ni\textsuperscript{2+} crystals, including the angle \(\theta\) used in the calculation.
2. Calculations

2.1. Double-spin–orbital coupling approach model

According to the molecular orbital (MO) theory, the single electron wave function can be reasonably well described by the following form:

\[ |\gamma\rangle = N_\gamma(|d_\gamma\rangle - \lambda_\gamma|p_\gamma\rangle), \]

where \( \gamma = t_{2g} \) or \( e_g \) is the irreducible representation of the O\(_h\) group, \( |d_\gamma\rangle \) is a metal orbital and \( |p_\gamma\rangle \) is a symmetry-adapted linear combination of valence orbital of the involved ligand. \( N_\gamma \) and \( \lambda_\gamma \) are, respectively, the normalization coefficients and the mixing coefficients of the atomic orbits.

Using the double-spin–orbit coupling approach, the spin–orbit coupling operator for two-electron Hamiltonian \( H_{\text{SO}} \) is taken as

\[ H_{\text{SO}} = \sum_i \zeta_d(r_d) l_i s_i + \sum_i \zeta_p(r_p) l_i s_i. \]

Here the first term corresponds to spin–orbit coupling effect of the central ion while the second term refers to that of the ligand.

The MO coefficients \( N_\gamma \) and \( \lambda_\gamma \) can be estimated by a semi-empirical method [9]. According to this method, the approximation relation and the normalization correlation can be given as

\[ \bar{B}/B_0 \approx N_\gamma^2 \left[ 1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2 S_{dp}^2(\gamma) \right], \]

\[ N_\gamma \approx \sqrt{1 - \lambda_\gamma^2 S_{dp}(\gamma)} \approx 1, \]

where \( B/B_0 \) is the rate between the electrostatic Coulomb energy of the transition-metal ions in the crystal and of the free ions. \( S_{dp}(\gamma) \) is the group overlap integral of \( d_\gamma \) and \( p_\gamma \) orbitals.

2.2. The full energy matrix and EPR (SH parameters) formulae

For a 3d\(^8\) ion in a trigonal crystal field, the full energy Hamiltonian can be written as

\[ H = H_{\text{ec}}(B, C) + H_{\text{CF}}(D_q, D_\tau, D_\sigma) + H_{\text{SO}}(\zeta_+, \zeta_-), \]

where \( H_{\text{ec}}(B, C) \), \( H_{\text{CF}}(D_q, D_\tau, D_\sigma) \) and \( H_{\text{SO}}(\zeta_+, \zeta_-) \) are the electrostatic interaction, \( B \) and \( C \) \((\approx BC_0/B_0, B_0 \approx 1084 \text{ cm}^{-1} \text{ and } C_0 \approx 4831 \text{ cm}^{-1} \) [8]) are the Racah electrostatic parameters characterized with the electrostatic Coulomb interaction as mentioned above, the crystal field and the spin–orbit Hamiltonian of the central-metal ion (3d) and the ligand ion (4p) interactions, respectively.

Based on the double-spin–orbit coupling approach, the two spin–orbit parameters \( \zeta_+ \), \( \zeta_- \) and two orbital reduction factors \( k_+ \), \( k_- \) can be written as [10, 11]:

\[ k_+ = N_\gamma \left[ 1 - 2\lambda_\gamma S_{dp}(t_{2g}) + \lambda_\gamma^2 / 2 \right], \]

\[ k_- = (N_\gamma N_\epsilon)^{1/2} \left( c_0^2 - \lambda_\epsilon c_p^0 / 2 \right), \]

\[ \zeta_+ = N_\gamma \left[ c_0^2 + \lambda_\epsilon c_p^0 / 2 \right], \]

\[ \zeta_- = (N_\gamma N_\epsilon)^{1/2} \left( c_0^2 - \lambda_\epsilon c_p^0 / 2 \right), \]

Considering the equivalence between the SH parameters and the Zeeman terms, we have

\[ D = E \left( |t_{2g}^3 A_2 \pm 1 e_2\rangle^\prime \right) - E \left( |t_{2g}^3 A_2 0 e_2\rangle\right), \]

\[ g_\parallel = \left( |t_{2g}^3 A_2 1 e_2\rangle |k_\parallel L_z + g_s S_{z}\right) \left| t_{2g}^3 A_2 1 e_2\rangle \right), \]

\[ g_\perp = \sqrt{2} \left( |t_{2g}^3 A_2 0 e_2\rangle |k_\perp L_x + g_s S_{x}\right) \left| t_{2g}^3 A_2 1 e_2\rangle \right), \]

where \( |^3A_2(t_{2g}^3 e_2^2), M_s\rangle \) and \( E(^3A_2(t_{2g}^3 e_2^2), M_s) \) are, respectively, the eigenfunction and eigenvalue of the ground state \( ^3A_2 \) with spin \( M_s \) obtained by diagonalizing the above complete energy matrix. \( L_j \) \((j = x, y, z) \) and \( S_j \) represent the operators of orbit and spin angular momenta. \( g_s \approx 2.0023 \) is only the spin value.

The trigonal field parameters \( D_\tau \) and \( D_\sigma \) in the energy matrix are calculated from the Newman superposition model [12]. From the model, for the trigonal \( d^n \) ions in octahedral, we have

\[ D_\tau = \frac{2}{7} \tilde{A}_1(R) \times (35 \cos^2 \theta - 30 \cos^2 \theta + 3 + 7 \sqrt{2} \sin^3 \theta \cos \theta), \]

\[ D_\sigma = -\frac{6}{7} \tilde{A}_1(R) (3 \cos^2 \theta - 1), \]

where in the intrinsic parameters \( \tilde{A}_1(R) \) and \( \tilde{A}_3(R) \) are related to the reference distance \( R \). \( R \) value can be estimated from the empirical formula \( R \approx r_h + (r_c - r_h) / 2 \) \([13, 14]\). From literature [1, 15], we have the bond length of the host crystal \( R_h \approx 2.71 \text{ Å} \), the radius of the impurity \( \text{Ni}^{2+} \) \((r_c) \approx 0.69 \text{ Å} \), the radius of the host ion \( \text{Cd}^{2+} \) \((r_h) \approx 0.97 \text{ Å} \), thus, \( R \approx 2.57 \text{ Å} \) can be obtained. For a \( d^n \) ion in octahedral complex, \( \tilde{A}_1(R) \approx (3/4)D_0 \) \([16–19]\), where \( D_0 \) is the cubic field parameter which is often obtained from the optical spectra of the studied system. \( D_0 \approx 640 \div 720 \text{ cm}^{-1} \) is found for \( \text{NiBr}_6^{2-} \) octahedra in crystals, we take \( D_0 \approx 660 \text{ cm}^{-1} \) here. By studying the optical and EPR spectra for \( 3d^n \) ions in many crystals, the ratio \( A_2(R)/A_3(R) \) is found to be in the range of \( 8\div12 \) \([16–21]\), we take \( A_2(R)/A_3(R) = 9 \). The group overlap integrals \( S_{dp}(\epsilon_0) \approx 0.0269332 \) and \( S_{dp}(t_{2g}) \approx 0.0079138 \) are obtained from the Slater-type SCF functions \([22, 23]\) and the metal–ligand distance \( R \).

Thus, in the full energy matrix of the \( 3d^8 \) electronic configurations, there are only two unknown or adjustable parameters \( \theta \) and \( B \). They can be obtained by matching the calculated optical spectra and SH parameters \( (g_\parallel, g_\perp, D) \) to the experimental values. From the calculations using the full energy matrix with the double-spin–orbit coupling approach, we obtain for \( \text{NiBr}_6^{2-} \) cluster in \( \text{CdBr}_2: \text{Ni}^{2+} \) crystal.
The coefficient $N_\gamma$ and the parameters in Eq. (3) calculated from the above $\lambda_\gamma$ are collected in Table I. The comparison between the calculated and experimental optical spectra and SH parameters are shown in Table II and Table III.

### 3. Discussions and results

(a) If we assume that the $S_{dp}(\gamma) = 0, \lambda_\gamma = 0$ and $\zeta_p = 0$, which the case is for the single-spin–orbit coupling, from Table II, the calculation $^a$ shows that the theoretical results are in poor agreement with the experimental values if without regard to the effect of the ligand. In fact, the mixing parameter $\lambda_{teg}$ (about 0.38) in $\gamma = \theta_5 \approx 54.81^\circ$, $B \approx 832 \text{ cm}^{-1}$.

(b) From Table II and III, the sign of zero-field splitting $D$ is suggested as negative. According to the approximate relation $D = -\zeta_\delta (g_\parallel - g_\perp)$ for $3d^9$ electron configurations in trigonal symmetry [24], the $\zeta_\delta > 0$ and $g$-shift $\Delta g = g_\parallel - g_\perp > 0$, thus, the negative sign of $D$ can be regarded as reasonable.

(c) Because the ionic radius and electronegative property of Ni$^{2+}$ are different from those of the Cd$^{2+}$, therefore the Ni$^{2+}$ in the bromine octahedral has a small change of the lattice structure. The shift of bond length $\Delta R (\approx R - R_h) \approx -0.14 \text{ A}$, and bond angle distortion $\gamma_{Ni^2+} (\approx \theta - \theta_h = 54.814 - 57.30^\circ[1]) \approx -2.486^\circ$ can be obtained from the investigation. This case shows that the CdBr$_2$:Ni$^{2+}$ crystal possesses a compressed distortion comparing with the host CdBr$_2$.

### Table I

The group overlap integral, the molecular orbital coefficients and orbital reduction factors for CdBr$_2$:Ni$^{2+}$ crystal.

<table>
<thead>
<tr>
<th>$S_{dp}(t_{2g})$</th>
<th>$S_{dp}(t_{2e})$</th>
<th>$N_t$</th>
<th>$N_e$</th>
<th>$\lambda_{teg}$</th>
<th>$\lambda_{te}$</th>
<th>$k_+$</th>
<th>$k_-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0269332</td>
<td>0.0079138</td>
<td>0.8787</td>
<td>0.8853</td>
<td>0.3795</td>
<td>0.3878</td>
<td>0.9367</td>
<td>0.8053</td>
</tr>
</tbody>
</table>

### Table II

The SH parameters of CdBr$_2$:Ni$^{2+}$ crystal.

<table>
<thead>
<tr>
<th></th>
<th>$g_\parallel$</th>
<th>$g_\perp$</th>
<th>$D$ [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cal.$^a$</td>
<td>2.2797</td>
<td>2.2773</td>
<td>-0.3246</td>
</tr>
<tr>
<td>Cal.$^b$</td>
<td>2.1900</td>
<td>2.1881</td>
<td>-0.2200</td>
</tr>
<tr>
<td>Expt. [5]</td>
<td>2.19(2)</td>
<td>2.18(2)</td>
<td>0.220(5)</td>
</tr>
</tbody>
</table>

$^a$ Taking no account of the effect of the ligand.

$^b$ Taking account of the effect of the ligand.

### Table III

The energy levels (or optical spectra) of CdBr$_2$:Ni$^{2+}$ crystal.

<table>
<thead>
<tr>
<th>Levels</th>
<th>Energy [cm$^{-1}$]</th>
<th>Levels</th>
<th>Energy [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t^6e^13^1A_2$</td>
<td>$E$ 0 0</td>
<td>$t^6e^13^1T_2$</td>
<td>$A$ 19342 19200</td>
</tr>
<tr>
<td>$t^6e^13^3T_2$</td>
<td>$E$ 6312</td>
<td>$t^6e^13^3T_1$</td>
<td>$E$ 21051 21081</td>
</tr>
<tr>
<td>$t^6e^13^1T_1$</td>
<td>$A$ 10478</td>
<td>$t^6e^13^1T_1$</td>
<td>$A$ 21476</td>
</tr>
<tr>
<td>$t^6e^21^1E$</td>
<td>$E$ 13716 11820–13210</td>
<td>$t^6e^21^1A_1$</td>
<td>$A$ 53630</td>
</tr>
</tbody>
</table>
References