Theoretical Investigations of the Local Structure Distortion and EPR Parameter for Ni\(^{2+}\)-doped Perovskite Fluorides

Xi-min Cao\(^a\), Xiao-yu Kuang\(^a,b,*\), Cheng-gang Li\(^a\), Rui-peng Chai\(^a\)

\(^a\) Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China
\(^b\) International Centre for Materials Physics, Chinese Academy of Sciences, Shenyang 110016, China

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By analyzing the optical spectra and electron paramagnetic resonance parameter \(D\), the local structure distortion of (NiF\(_6\))\(^{4-}\) clusters in AMF\(_3\) (A=K, Rb; M=Zn, Cd, Ca) and K\(_2\)ZnF\(_4\) series are studied using the complete energy matrix based on the double spin-orbit coupling parameter model for configuration ions in a tetragonal ligand field. The results indicate that the contribution of ligand to spin-orbit coupling interaction should be considered for our studied systems. Moreover, the relationships between \(D\) and the spin-orbit coupling coefficients as well as the average parameter and the divergent parameter are discussed.

Key words: Complete energy matrix, Double spin-orbit coupling parameter model, Local structure distortion

I. INTRODUCTION

Because doped materials can display a significant role in the ferroelectric, piezoelectric, photoelectric, and ferromagnetic properties which are absent in pure compounds, impurities in solid materials have been a subject of wide interest in recent years [1−4]. Among these impurities, much attention has been paid to the divalent Ni\(^{2+}\) since the materials doped with Ni\(^{2+}\) always exhibit broad absorption bands in the visible and infrared spectral range [5, 6]. For example, the perovskite fluorides AMF\(_3\) and perovskite-type fluorides K\(_2\)ZnF\(_4\) doped with Ni\(^{2+}\) ions have attracted much attention because of their particular structures, phase transitions, luminescent and ferromagnetic properties and so on [7−9]. In order to gain more insight into the optical and magnetic properties of the Ni\(^{2+}\)-doped perovskite systems, many experimental works have been performed. For instance, the electron paramagnetic resonance (EPR) spectra for the Ni\(^{2+}\)-doped AMF\(_3\) and K\(_2\)ZnF\(_4\) systems have been reported [10−14]. These experimental results have provided important information for studying the interactions between the electronic and molecular structure of the doped systems. From the theoretical point of view, to explain these experimental EPR spectra and determine the local structure distortion for these systems, two theoretical methods have been proposed, namely, the high-order perturbation and the complete energy matrix. It is noted that the method of complete energy matrix is established in the complete d\(^n\) configuration space and all the interactions may be taken into account simultaneously, whereas the high-order perturbation method only considers the partial states. Hence, the approach of complete energy matrix has been widely applied in the studies of EPR parameters \(D\) and the local structure of the Ni\(^{2+}\) doped systems [15−17].

In the framework of complete energy matrix, as a rule, there are two kinds of models to treat the spin-orbit (s.o.) coupling interaction. One is the single s.o. coupling parameter model, in which only the contribution due to the s.o. coupling of the central ion is considered. This model has been widely used in the past several years [15−17]. The other one is the double s.o. coupling parameter model, which not only includes the contribution arising from the s.o. coupling of central ion, but also considers the effect of surrounding ligand. Evidently the latter model is superior to the former in studying EPR parameters. It is well known that the contribution from the ligand should not be neglected in the exact calculation. In fact, many researches have proved that the influence of ligand ions cannot be ignored with respect to the s.o. coupling mechanism [18, 19]. Thus, the method of complete energy matrix based on the double s.o. coupling parameter model is generally regarded as a more effective tool to study the EPR and local structure distortion of the compounds, and the method of complete energy matrix based on the double s.o. coupling parameter model is used less by researchers at home and abroad.

In the present work, by using the complete energy matrix method and based on the double s.o. coupling parameter model, the \(D\) and the local structure distortion parameter \(\Delta R\) for Ni\(^{2+}\) ions doped in AMF\(_3\) and K\(_2\)ZnF\(_4\) systems are studied, and the relationships be-
The dependence of the \( \zeta \) as well as the average parameter \( \zeta_l (\zeta_l = (\zeta + \zeta')/2) \) and the divergent parameter \( \zeta_2 \) \( (\zeta_2 = (\zeta - \zeta')/2) \) are discussed. In addition, the dependence of the \( D \) on \( \Delta R \) is studied together.

II. THEORETICAL ANALYSIS

A. Double s.o. coupling parameter model

Just as remarked by Sugano et al. [20], two s.o. coupling coefficients \( \zeta \) and \( \zeta' \) should be simultaneously introduced to describe the difference in overlap between \( t_{2g} \) and \( e_{g} \) symmetry from the d orbitals of the central ions and to consider the contribution from the p orbitals of the ligands, which are defined as [20]:

\[
\langle t_{2g} | V(1T) | t_{2g} \rangle = 3i\zeta \tag{1}
\]

\[
\langle t_{2g} | V(1T) | e_{g} \rangle = -3\sqrt{2}i\zeta' \tag{2}
\]

where \( \zeta \) and \( \zeta' \) may be expressed as [20–22]:

\[
\zeta = N_f \left( \zeta_0^d + \frac{1}{2} \lambda_2 \zeta_0^p \right) \tag{3}
\]

\[
\zeta' = \sqrt{N_f N_c} \left( \zeta_0^d - \frac{1}{2} \lambda_1 \lambda_2 \zeta_0^p \right) \tag{4}
\]

\( \zeta_0^d \) and \( \zeta_0^p \) represent the s.o. coupling coefficients of the central ion and the ligand ion, respectively. The molecular-orbital wave function can be written as [23]:

\[
|\gamma\rangle = \sqrt{N} \left( |d_{\gamma}^0\rangle - \lambda_\gamma |p_{\gamma}\rangle \right) \tag{5}
\]

\( |d_{\gamma}^0\rangle \) is the basic state of the d orbit for central metal ion; \( |p_{\gamma}\rangle \) is the basic state of the p orbit for ligand ion. The subscripts \( \gamma = t_{2g} \) or \( e_g \) are the irreducible representations of the \( \Omega \) group. The normalization factor \( N_\gamma \) and orbital mixing coefficient \( \lambda_\gamma \) can be obtained from the approximation relation [23]:

\[
f_\gamma = N_\gamma^2 \left[ 1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2 S_{dp}^2(\gamma) \right] \tag{6}
\]

and the normalization correlation [23]:

\[
N_\gamma \left[ 1 - 2\lambda_\gamma S_{dp}(\gamma) + \lambda_\gamma^2 \right] = 1 \tag{7}
\]

\( S_{dp}(\gamma) \) is the group overlap integrals. The covalency factor \( f_\gamma \) are often determined from the ratio of the Racah parameters for the 3d\(^8\) ion in a crystal to those in free state, i.e.,

\[
f_\gamma \approx \frac{1}{2} \left( \frac{B}{B_0} + \frac{C}{C_0} \right) \tag{8}
\]

\( B \) and \( C \) are the Racah parameters of the transition metal ion in the studied crystal and \( B_0 \), \( C_0 \), \( \zeta_0^d \) are the free ion parameters. The values of \( N_\gamma \), \( \lambda_\gamma \), \( \zeta \), and \( \zeta' \) may be obtained from Eqs. (3), (4), (6), and (7).

B. Complete energy matrix for d\(^8\) configuration ions

The perturbation Hamiltonian for a d\(^8\) configuration ion Ni\(^{2+}\) in a tetragonal ligand field can be expressed as [24]:

\[
\hat{H} = \hat{H}_{ee} + \hat{H}_{SO} + \hat{H}_{LF}
\]

\[
\approx \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_i \zeta_0^d(r_i) \hat{t}_i \cdot \hat{s}_i + \sum_j \zeta_0^p(r_j) \hat{t}_j \cdot \hat{s}_j + \sum_i V_i \tag{9}
\]

where \( \hat{H}_{ee}, \hat{H}_{SO}, \) and \( \hat{H}_{LF} \) denote the electron-electron repulsion interaction, the s.o. coupling interaction, and the ligand-field interaction, respectively. The potential function \( V_i \) can be written as:

\[
V_i = \gamma_{00} Z_{00} + \gamma_{20} r_i^2 Z_{20}(\theta_i, \varphi_i) + \gamma_{40} r_i^4 Z_{40}(\theta_i, \varphi_i) + \gamma_{44} r_i^4 Z_{44}(\theta_i, \varphi_i) + \gamma_{48} r_i^4 Z_{48}(\theta_i, \varphi_i) \tag{10}
\]

where \( r_i, \theta_i, \) and \( \varphi_i \) are spherical coordinates of the \( i \)th electron. \( Z_{lm} \) and \( Z_{lm}' \) are defined as:

\[
Z_{00} = Y_{00} \tag{11}
\]

\[
Z_{lm}^c = \frac{1}{\sqrt{2}} Y_{l+1,-m} + (-1)^m Y_{l,m} \tag{12}
\]

\[
Z_{lm}^s = \frac{i}{\sqrt{2}} Y_{l+1,-m} + (-1)^m Y_{l,m} \tag{13}
\]

\( Y_{l,m} \) is the spherical harmonics. \( \gamma_{00} \) and \( \gamma_{lm}' \) are associated with the local lattice structure of the 3d\(^8\) configuration ion by the relations:

\[
\gamma_{00} = - \frac{4\pi}{2l+1} \sum_{\tau=1}^{n} \frac{q_{\tau}}{R_{\tau}^{4\tau}} Z_{00}(\theta_{\tau}, \varphi_{\tau}) \tag{14}
\]

\[
\gamma_{lm}' = - \frac{4\pi}{2l+1} \sum_{\tau=1}^{n} \frac{q_{\tau}}{R_{\tau}^{4\tau}} Z_{lm}'(\theta_{\tau}, \varphi_{\tau}) \tag{15}
\]

\[
\gamma_{lm}^s = - \frac{4\pi}{2l+1} \sum_{\tau=1}^{n} \frac{q_{\tau}}{R_{\tau}^{4\tau}} Z_{lm}^s(\theta_{\tau}, \varphi_{\tau}) \tag{16}
\]

where \( q_{\tau} \) is the effective charge of the \( \tau \)th ligand ion, \( \theta_{\tau} \) and \( \varphi_{\tau} \) are its angle coordinates, \( R_{\tau} \) the impurity-ligand distance. The ligand-field interaction in the tetragonal field is the function of four parameters \( B_{20}, B_{40}, B_{44}^c, \) and \( B_{44}^s \). By choosing the appropriate coordinate system, the ligand-field parameter \( B_{44}^c \) will vanish and \( B_{20}, B_{40}, B_{44}^s \) can be derived as:

\[
B_{20} = 2A_2 \left( \frac{1}{R_1^3} - \frac{1}{R_2^3} \right) \tag{17}
\]

\[
B_{40} = A_4 \left( \frac{4}{R_2^5} + \frac{3}{R_2^5} \right) \tag{18}
\]

\[
B_{44}^s = \frac{35}{8} A_4 R_2^5 \tag{19}
\]
TABLE I The local structure distortion parameter (in Å), group overlap integrals, \( B \) and \( C \), \( f_r \), \( N_r \), \( N_e \), and \( \lambda_r \), \( \lambda_e \), s.o. coupling coefficients \( \zeta \) and \( \zeta' \), average \( \zeta_1 \) and divergent \( \zeta_2 \) parameters (cm\(^{-1}\)) for Ni\(^{2+}\) in crystals.

<table>
<thead>
<tr>
<th>( R )</th>
<th>( S_{\text{dp}} )</th>
<th>( S_{\text{pe}} )</th>
<th>( B^a )</th>
<th>( C^a )</th>
<th>( f_r )</th>
<th>( N_r )</th>
<th>( N_e )</th>
<th>( \lambda_r )</th>
<th>( \lambda_e )</th>
<th>( \zeta )</th>
<th>( \zeta' )</th>
<th>( \zeta_1 )</th>
<th>( \zeta_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>K(_2)ZnF(_3) (4.2 K)</td>
<td>2.0207</td>
<td>0.0244</td>
<td>0.0065</td>
<td>972</td>
<td>3588</td>
<td>0.8047</td>
<td>0.899</td>
<td>0.9048</td>
<td>0.3417</td>
<td>0.3498</td>
<td>583.775</td>
<td>562.191</td>
<td>572.983</td>
</tr>
<tr>
<td>K(_2)ZnF(_3) (78 K)</td>
<td>2.0201</td>
<td>0.0245</td>
<td>0.0065</td>
<td>972</td>
<td>3588</td>
<td>0.8047</td>
<td>0.899</td>
<td>0.9048</td>
<td>0.3417</td>
<td>0.3498</td>
<td>583.779</td>
<td>562.197</td>
<td>572.988</td>
</tr>
<tr>
<td>K(_2)ZnF(_3) (290 K)</td>
<td>2.0168</td>
<td>0.0248</td>
<td>0.0066</td>
<td>972</td>
<td>3588</td>
<td>0.8047</td>
<td>0.899</td>
<td>0.9049</td>
<td>0.3418</td>
<td>0.3498</td>
<td>583.800</td>
<td>562.229</td>
<td>573.015</td>
</tr>
<tr>
<td>KZnF(_4)</td>
<td>2.0607</td>
<td>0.0212</td>
<td>0.0055</td>
<td>972</td>
<td>3588</td>
<td>0.8047</td>
<td>0.899</td>
<td>0.9037</td>
<td>0.3413</td>
<td>0.3483</td>
<td>583.541</td>
<td>561.831</td>
<td>572.686</td>
</tr>
<tr>
<td>RbCaF(_3)</td>
<td>2.0883</td>
<td>0.0192</td>
<td>0.0049</td>
<td>950</td>
<td>4000</td>
<td>0.8147</td>
<td>0.9188</td>
<td>0.923</td>
<td>0.3022</td>
<td>0.3088</td>
<td>594.059</td>
<td>576.690</td>
<td>585.375</td>
</tr>
<tr>
<td>RbCdF(_3)</td>
<td>2.0848</td>
<td>0.0195</td>
<td>0.0050</td>
<td>950</td>
<td>4000</td>
<td>0.8147</td>
<td>0.9189</td>
<td>0.923</td>
<td>0.3022</td>
<td>0.3089</td>
<td>594.074</td>
<td>576.714</td>
<td>585.394</td>
</tr>
</tbody>
</table>

\(^a\) Refs. [30, 31].

where \( R_1 \) and \( R_2 \) stand for the bond lengths in the vertical plane and the horizontal plane in tetragonal D\(_{4h}\) symmetry, respectively. In the previous works, the values of \( A_4 \) and \( A_2 \) have been determined from the optical spectra and local structure of pure NiF\(_2\) [25], i.e., \( A_2 \approx 17.3385 \text{ a.u.} \) and \( A_2 \approx 24.452 \text{ a.u.} \), and these will be employed in the following calculation.

**C. EPR parameters of \( d^8 \) configuration**

EPR spectra of a \( d^8 \) configuration Ni\(^{2+}\) in a tetragonal ligand-field can be analyzed by the spin Hamiltonian [26]:

\[
\hat{H}_S = \mu_B g_{||} H_z S_z + \mu_B g_{\perp} (H_x S_x + H_y S_y) + D \left[ S_z^2 - \frac{1}{3} S(S+1) \right]
\]

(20)

In the absence of the external magnetic field, the ground state \( ^3A_2 \) is split into two spin doublets \( \vert \pm 1 \rangle \) and \( \vert 0 \rangle \). The corresponding ground-state zero-field splitting \( \Delta E \) can be expressed as:

\[
\Delta E = E(\pm 1) - E(0) = D
\]

(21)

**III. CALCULATIONS AND DISCUSSION**

**A. Calculation of the local structure for tetragonal Ni\(^{2+}\) centers**

According to the EPR spectra of the Ni\(^{2+}\)-doped AMF\(_3\) and K\(_2\)ZnF\(_3\) series, we can study the local geometric structure by diagonalizing the complete energy matrix. When the Ni\(^{2+}\) is doped into the host crystal, it will substitute for the divalent cation M\(^{2+}\). The local structure belongs to D\(_{4h}\) symmetry and displays a tetragonal distortion along fourfold axis, and it can be described by use of \( R_1 \) and \( R_2 \) as shown in Fig. 1. \( R_1 \) is the distance between Ni\(^{2+}\) and the two axial F\(^-\) ligands in the vertical plane, \( R_2 \) is the distance between Ni\(^{2+}\) and the four equatorial F\(^-\) ligands in the horizontal plane, and the \( \Delta R \) and \( \bar{R} \) can be expressed as:

\[
\bar{R} = \frac{1}{3} R_1 + \frac{2}{3} R_2, \quad \Delta R = R_1 - R_2
\]

(22)

\( \bar{R} \) may be obtained through simulating the optical spectra of the (NiF\(_6\))\(^4-\) cluster in different perovskite hosts by diagonalizing the complete energy matrix. For the free Ni\(^{2+}\), \( B_0 \approx 1208 \text{ cm}^{-1} \), \( C_0 \approx 4495 \text{ cm}^{-1} \), and \( \zeta_0 \approx 636.5 \text{ cm}^{-1} \), \( \zeta_0' \approx 220 \text{ cm}^{-1} \) for F\(^-\) [23, 27]. The group overlap integrals \( S_{\text{dp}}(\gamma) \), two s.o. coupling coefficients \( \zeta \) and \( \zeta' \) may be calculated from the Slater-type SCF function [28, 29]. The corresponding values are listed in Table I. Then, by diagonalizing the complete energy matrix, the optical spectra and \( D \) for the Ni\(^{2+}\) ions in different crystals are simulated as functions of \( \Delta R \). The calculated results are listed in Table II and III. It is noticeable in Table III that the calculated Stark energy levels are in good agreement with the experimental values. \( D \) can be satisfactorily explained by the obtained \( \Delta R \) as shown in Table II. For the Ni\(^{2+}\)-doped RbCdF\(_3\) and RbCaF\(_3\) systems, the local lattice structures around the octahedral Ni\(^{2+}\) centers display an...
For example, for the KZnF$_3$ systems, the local structure distortion parameters obtained from the double s.o. coupling parameter model differ from those obtained from the single s.o. coupling parameter model. Although the discrepancy of $\Delta R$ based on the two models varies with the different hosts, the difference for all the studied systems is appreciable as shown in Table II. For example, for the K$_2$ZnF$_4$ host the relative error

elongated distortion along the C$_4$ axis; and for the Ni$^{2+}$ doped KZnF$_3$ and K$_2$ZnF$_4$ systems, the local structures display a compressed distortion along the C$_4$-axis.

In order to study the difference between the double s.o. coupling coefficient model and the single s.o. coupling coefficient model, we simulate $D$ at the same $\Delta R$ using the two models, the calculated results are presented in Table II. By comparison, we found that the local structure distortion parameters obtained from the double s.o. coupling parameter model differ from those obtained from the single s.o. coupling parameter model. Although the discrepancy of $\Delta R$ based on the two models varies with the different hosts, the difference for all the studied systems is appreciable as shown in Table II. For example, for the K$_2$ZnF$_4$ host the relative error

\[ r_{\Delta R} = \frac{|\Delta R_a - \Delta R_b|}{|\Delta R_{\text{max}}|} \times 100\% \]

which accounts for about 23%, and for the RbCdF$_3$ host the relative error is somewhat large and accounts for about 66%. The reason may be ascribed to the contribution of the s.o. coupling interaction from the ligands. Since the double s.o coupling parameter model is superior to the single s.o. coupling parameter model, the local structure distortion parameters ($\bar{R}$, $\Delta R$) based on the double s.o. coupling parameter model can be regarded as more accurate and reliable. Simultaneously, the difference of $\Delta R$ also indicates that the contribution of the s.o. coupling interaction of F$^-$ ligands on the local structure distortion of the central ions in the perovskite fluorides is not negligible.

Figure 2 shows the relationship between $D$ and $\Delta R$ for the K$_2$ZnF$_4$:Ni$^{2+}$ system with $\zeta_2=0$, $\zeta_2>0$, and $\zeta_2<0$, based on both of the double and single s.o. coupling parameter models. It indicates that there is an approximate linear relation between $\Delta R$ and $D$, and the values of $D$ will increase with the increase of $\Delta R$. Simultaneously, it is found that for $\zeta_2=0$ (namely, the

\[ r_{\Delta R} = \frac{|\Delta R_a - \Delta R_b|}{|\Delta R_{\text{max}}|} \times 100\% \]

TABLE II The local distortion parameter $\Delta R$ and EPR parameter $D$ for K$_2$ZnF$_4$:Ni$^{2+}$, KZnF$_3$:Ni$^{2+}$, RbCaF$_3$:Ni$^{2+}$, and RbCdF$_3$:Ni$^{2+}$ systems which are calculated from different models.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta R/\text{Å}$</th>
<th>$r_{\Delta R}$</th>
<th>$D/\text{cm}^{-1}$</th>
<th>Expt. [10–14]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cal.$^a$</td>
<td>Cal.$^b$</td>
<td>Cal.$^a$</td>
<td>Cal.$^b$</td>
</tr>
<tr>
<td>K$_2$ZnF$_4$:Ni$^{2+}$ (4.2 K)</td>
<td>$-0.0414$</td>
<td>$-0.0314$</td>
<td>24%</td>
<td>$-1.2399$</td>
</tr>
<tr>
<td>K$_2$ZnF$_4$:Ni$^{2+}$ (78 K)</td>
<td>$-0.0433(2)$</td>
<td>$-0.0329$</td>
<td>24%</td>
<td>$-1.31$</td>
</tr>
<tr>
<td>K$_2$ZnF$_4$:Ni$^{2+}$ (290 K)</td>
<td>$-0.0532$</td>
<td>$-0.0408$</td>
<td>23%</td>
<td>$-1.6701$</td>
</tr>
<tr>
<td>KZnF$_3$:Ni$^{2+}$</td>
<td>$-0.0144(4)$</td>
<td>$-0.0065$</td>
<td>55%</td>
<td>$-0.2501$</td>
</tr>
<tr>
<td>RbCaF$_3$:Ni$^{2+}$</td>
<td>0.0136(2)</td>
<td>0.0193</td>
<td>30%</td>
<td>0.8441</td>
</tr>
<tr>
<td>RbCdF$_3$:Ni$^{2+}$</td>
<td>0.0032(4)</td>
<td>0.0093</td>
<td>66%</td>
<td>0.4078</td>
</tr>
</tbody>
</table>

TABLE III Comparison of optical spectra between the theoretical and experimental values for Ni$^{2+}$ ions in K$_2$ZnF$_4$ (4.2 K), KZnF$_3$, and RbCaF$_3$ crystals, respectively.

<table>
<thead>
<tr>
<th></th>
<th>K$_2$ZnF$_4$(4.2 K)</th>
<th>KZnF$_3$</th>
<th>RbCaF$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{3}$A(F)</td>
<td>0 0 0 0 0 0 0</td>
<td>0 0 0 0 0 0 0</td>
<td>0 0 0 0 0 0 0</td>
</tr>
<tr>
<td>$^{3}$T$_2$(F)</td>
<td>7550 7550 7000 7000</td>
<td>6590</td>
<td>7942</td>
</tr>
<tr>
<td>$^{3}$T$_1$(F)</td>
<td>12965 13091 11999 11243</td>
<td>11243</td>
<td>13347</td>
</tr>
<tr>
<td>$^{1}$E(D)</td>
<td>15313 14327 14289</td>
<td>14867</td>
<td>14900</td>
</tr>
<tr>
<td>$^{1}$T$_2$(F)</td>
<td>21050 21373 20733</td>
<td>20961</td>
<td>21737</td>
</tr>
<tr>
<td>$^{1}$A$_1$(G)</td>
<td>24360 23349 23006</td>
<td>23443</td>
<td>24000</td>
</tr>
<tr>
<td>$^{3}$T$_1$(P)</td>
<td>24760 23892 22886</td>
<td>22500</td>
<td>25130</td>
</tr>
<tr>
<td>$^{1}$T$_1$(G)</td>
<td>26394 25832 25861</td>
<td>25681</td>
<td>28748</td>
</tr>
<tr>
<td>$^{1}$E(G)</td>
<td>30675 32075 30756</td>
<td>30486</td>
<td>32382</td>
</tr>
</tbody>
</table>

FIG. 2 The influence of $\Delta R$ on $D$ with different $\zeta_2$ for K$_2$ZnF$_4$:Ni$^{2+}$ system.
FIG. 3 Dependence of $D$ on $\zeta$ (a) and $\zeta'$ (b) for Ni$^{2+}$-doped AMF$_3$ (A=K, Rb; M=Zn, Cd, Ca) and K$_2$ZnF$_4$, respectively. Variation of $\zeta_1$ (c) and $\zeta_2$ (d) versus $D$ for the Ni$^{2+}$-doped AMF$_3$ (A=K, Rb; M=Zn, Cd, Ca) and K$_2$ZnF$_4$ series.

B. The effects of $\zeta$ or $\zeta'$, $\zeta_1$, and $\zeta_2$ on $D$

As mentioned above, the s.o. coupling coefficients $\zeta$ and $\zeta'$ are introduced by Sugano et al. [20]. For our studied systems, the relationships of $D$ vs. $\zeta$ and $D$ vs. $\zeta'$ are shown in Fig.3 (a) and (b). It should be remarked that $D$ is directly linear relation to $\zeta$ and proportional to the square of $\zeta'$ based on the method of high order perturbation. However, our calculated results show that the curve of $D$ vs. $\zeta$ is not strictly linear relation (see Fig.3(a)), as well as $D$ vs. $\zeta'$ is not strictly quadratic relation (see Fig.3(b)). This difference may be due to the fact that the complete energy matrix method involves all microstates of the $d^8$ configuration, whereas only the part microstates of the $d^8$ configuration are considered in the high order perturbation method.

The relationships of $D$ vs. $\zeta_1$ and $D$ vs. $\zeta_2$ have been plotted in Fig.3 (c) and (d) with the different hosts. From Fig.3(c), it can be seen that the curve of $D$ vs. $\zeta_1$ is approximately quadratic. Meanwhile, all the relative curves pass the same point (0, 0), because $\zeta_1=0$ is related to $D=0$ with the cubic symmetric structure. Moreover, it can be seen that from Fig.3(c), when $D>0$, and the direction of the $D(\zeta_1)$ is upward, when $D<0$, and the direction of $D(\zeta_1)$ is downward. These trends may be ascribed to the fact that there is a corresponding relationship between the direction of $D(\zeta_1)$ and the local structure distortion for the (NiF$_6$)$_{4-}$ clusters. At last, the relation of $D$ vs. $\zeta_2$ has been plotted in Fig.3(d). It is noticeable that there exists an approximately linear relation between the $D$ and $\zeta_2$ in the range of $\zeta_2$ from $-40$ cm$^{-1}$ to 40 cm$^{-1}$, and the value of $D$ will increase with the increase of $\zeta_2$ for all curves.

IV. CONCLUSION

Using the complete energy matrix method and taking into account the contributions from the s.o. coupling of the central ions as well as that of the ligand ions, the optical spectra, the EPR parameter $D$ and the local structure distortion for the AMF$_3$ (A=K, Rb; M=Zn, Cd, Ca) and K$_2$ZnF$_4$ doped with Ni$^{2+}$ ions have been studied. The results indicate that the contribution of
the s.o. coupling interaction for F\(^{-}\) ligands on the local structure distortion of the central ions in the perovskite fluorides is not negligible. Moreover, the relationship between \(D\) and \(\Delta R\) and the dependences of \(D\) on the s.o coupling coefficients \(\zeta\) (\(\zeta', \zeta_1\), and \(\zeta_2\)) have been demonstrated.