Z1 band in RbCl crystals with Mg++, Ca++, Sr++ and Ba++ impurities

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ABSTRACT. The optical absorption of the Z1 band in RbCl with Mg++, Ca++, Sr++ and Ba++ impurities is studied, by use of point-ion [1] and ion-size correction [2] models. For the calculations Gaussian wave functions were used. Good agreement with the experimental optical absorption values were found for the xy excited wave function when the point-ion model is used. For the ion-size correction method the excited wave function z is the adequate. For the calculations Gaussian functions were used. According to a recent paper [17] only the Gaussian functions can describe the Z1-center.

RESUMEN. Se calcula la absorción óptica de la banda Z1 en cristales de RbCl con impurezas de Mg++, Ca++, Sr++ y Ba++. Los métodos usados fueron el del ion-puntual [1] y el método de corrección de tamaño [2]. Se usaron funciones Gaussianas que de acuerdo a nuestros resultados son las únicas [17] que reproducen los resultados experimentales. De los cálculos se concluye que para el método de ion puntual conviene usar la función xy para el estado excitado, y para el método de corrección de tamaño la función z.

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1. INTRODUCTION

The Z1-center consists of an F center in [0 0 0] with a [1 0 0] cation vacancy and a [1 1 1] divalent ion near to it [3].

The increasing interest in the study of the Z1-band in alkali halides is due to the important practical applications in recording optical information [4].

Theoretical studies on the Z1-band are scarce. Some models have been proposed for the Z1 center [5-9], but at the present moment there is evidence favoring a model in which the electron responsible for the optical absorption is centered on an anion vacancy. There are some papers [10-13] in which the calculations of the Z1-center has been based on impurity centered models.

Katz et al. [14] conducted an experimental and perturbative theoretical study of the Z1-band in RbCl: Sr++. In this work a phenomenological model was tentatively proposed and worked out to account for the observed transition energies. Dick [15] carried out a simple variational calculation of the ground and excited state energies of a vacancy-centered model for Z1-center in alkali halides. In that paper [15] positive values of the excited state energies are found. Dick's calculations were revised by Weber and Dick [16] using the ion-size correction model of Bartram et al. [2]. They [16] obtained a large splitting of the
three 2p states. Comparison with the experimental values showed good agreement only for the lowest of the three calculated transition energies. Weber and Dick [16] used wave functions type I, II and III of Gourary and Adrian [1]. Recently [17] we revised the Weber and Dick paper [16] in which they used the Gourary and Adrian [1] wave functions type I, II and III. We reproduced their reported results [16], for the ground state of several alkali halides. The more important part of the energy functional is given for the point-ion contribution. For the excited state we reproduce their point-ion contribution, but not their values for the ion-size correction method [2]. As matter of fact we do not found a minimum for the energy functional of the excited state using Gourary and Adrian wave functions type I, II, III and the ion-size correction method [2]. The discrepancy with the Weber and Dick [16] paper was discussed before [11]. Here we present results for the Z_1-center in RbCl and several impurities using Gaussian functions, for which good agreement with experimental results [17] were found.

2. Theory

The energy functional \( E_{1s}^Z \) corresponding to the Gaussian function is of the form

\[
E_{1s}^Z = E_{1s} + Y_{1s}(\sqrt{3} a) - Y_{1s}(a)
\]

where

\[
E_{1s} = \frac{3}{2} \lambda_g^2 - \sum_{z_i \geq y_i \geq x_i \geq 0}^I h_i(-1)^{1+x_i+y_i+z_i}A_g^2 \frac{(\pi/2)^{3/2}}{r_i \lambda_g^3} \text{erf}(\sqrt{2}\lambda_g r_i)
\]

and

\[
Y_{1s}(r) = -A_g^2 \frac{(\pi/2)^{3/2}}{r \lambda_g^3} \text{erf}(\sqrt{2}\lambda_g r)
\]

\( A_g \) is the normalization constant and \( \lambda_g \) the variational parameter.

The energy functional \( E_{2p}^Z \) corresponding to the excited state is

\[
E_{2p}^Z = E_{2p} + Y_{2p}(\sqrt{3} a) - Y_{2p}(a)
\]

where

\[
E_{2p} = \frac{\pi^{3/2} A_c^2}{\lambda_c^3} \sqrt{2} \frac{5}{32} + \sum_{z_i \geq y_i \geq x_i \geq 0}^I h_i(-1)^{1+x_i+y_i+z_i} \left\{ \frac{\pi A_c^2}{3 (\sqrt{2} \lambda_c^3)^4} \exp(-2) \frac{r_i^2}{r_i^2} \right\}
\]

\[
- \frac{\pi A_c^2}{r_i (\sqrt{2} \lambda_c)^5/2} \frac{\sqrt{\pi}}{2} \text{erf}(\sqrt{2}\lambda_c r_i)
\]
and

\[ Y_{2p}(\vec{r}) = \frac{\pi A_e^2 Q}{3(\sqrt{2} \lambda_e)^4} \exp(-2\lambda_e^2 r^2) - \frac{\pi A_e^2 Q}{\sqrt{2}} \frac{\sqrt{\pi}}{2} \exp(\sqrt{2} \lambda_e r) \]

\[ + \frac{8\pi Q P_2(\cos \theta) A_e^2}{15 \pi^2 (\sqrt{2} \lambda_e)^5} \left[ \left( \frac{(\sqrt{2} \lambda_e r)^5}{2} + \frac{5}{4} (2 \lambda_e r)^3 \right) + \frac{15}{8} (\sqrt{2} \lambda_e r) \exp(-2\lambda_e^2 r^2) + \frac{15}{8} \frac{\sqrt{\pi}}{2} \exp(\sqrt{2} \lambda_e r) \right] \]

\[ + \frac{8\pi}{15} A_e^2 P_2(\cos \theta) r^2 \left[ \frac{1}{2} \exp(-2\lambda_e^2 r^2) \right] \]  

(6)

\( A_e \) is the normalization constant and \( \lambda_e \) is the variational parameter, \( Q \) is the charge distribution at a point \( r \), \( P_2(\cos \theta) \) is the Legendre polynomial of order two, where \( \theta \) is the angle between the vector of the point \( r \) and the axis of the \( p \)-function. \( E_{1s} \) and \( E_{2p} \) are the energy functionals corresponding to the \( F \)-center.

In the case of the excited state it is necessary to choose the directions for the \( p \)-function axes according to the symmetry of the impurity and the vacancy (the \( Z_1 \)-center). For our case we used the direction of the axes calculated by Dick [15].

The ground-state energy is obtained by minimizing an energy functional of the form

\[ E^Z = E_g + \sum_s \left[ A_s + (\tilde{V}_p^Z - U_s) B_s \right] |\psi_{1s}(\vec{r}_s)|^2 \]  

(7)

For the first-excited-state the energy is obtained minimizing an energy functional of the form

\[ E^Z = E_{2p} + \sum_s \left[ A_s + (\tilde{V}_p^Z - U_s) B_s \right] |\psi_{2p}(\vec{r}_s)|^2 \]  

(8)

where

\[ \tilde{V}_p^Z = \tilde{V}_p^F - \tilde{V}_{pl} + \left[ A_C + (\tilde{V}_p^F - U_3) B_C \right] \delta(\hat{r} - \hat{r}_C) \]

\[ + \left[ A_D - A_C + (\tilde{V}_p^F - U_3)(B_D - B_C) \right] \delta(\hat{r} - \hat{r}_D) \]  

(9)

where \( U_s \) is the potential of the \( s \)-th ion due to all the other ions, \( A_s \) and \( B_s \) are the characteristic parameters of the ions alone, \( V_{pl} \) is the point ion potential and \( V_p^F \) the pseudopotential corresponding to the \( F \)-center. The indices \( D \) and \( C \) mean divalent impurity and cation respectively.

3. Results and conclusions

In order to study the theoretical optical absorption of the \( Z_1 \)-band in RbCl crystals with \( \text{Mg}^{++}, \text{Ca}^{++}, \text{Sr}^{++} \) and \( \text{Ba}^{++} \) impurities, we made calculations for the ground and
TABLE I. Energy values of the ground and excited states for RbCl crystals using the point-ion and the ion-size-correction methods. The $\lambda_{1s}$ and $\lambda_{2p}$ are the Gaussian wave function parameters and $V_{1s}$ and $V_{2p}$ the value of the pseudopotential in a.u.

<table>
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<th>$\lambda_{1s}$</th>
<th>$-V_{1s}$</th>
<th>$-E_{1s}$</th>
<th>$\lambda_{2p}$</th>
<th>$-V_{2p}$</th>
<th>$-E_{2p}$</th>
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<tbody>
<tr>
<td>RbCl</td>
<td>1.21</td>
<td>0.095</td>
<td>0.1059</td>
<td>0.94</td>
<td>0.127</td>
<td>0.0295</td>
</tr>
<tr>
<td>Mg$^{++}$</td>
<td>1.21</td>
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<td>0.1059</td>
<td>0.95</td>
<td>0.127</td>
<td>0.0287</td>
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<td>Ca$^{++}$</td>
<td>1.21</td>
<td>0.095</td>
<td>0.1059</td>
<td>0.95</td>
<td>0.127</td>
<td>0.0284</td>
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<tr>
<td>Sr$^{++}$</td>
<td>1.21</td>
<td>0.095</td>
<td>0.1059</td>
<td>0.95</td>
<td>0.128</td>
<td>0.0280</td>
</tr>
<tr>
<td>Ba$^{++}$</td>
<td>1.21</td>
<td>0.095</td>
<td>0.1059</td>
<td>0.95</td>
<td>0.128</td>
<td>0.0280</td>
</tr>
</tbody>
</table>

TABLE II. Optical absorption of the $Z_1$-band for RbCl crystals with Mg$^{++}$, Ca$^{++}$, Sr$^{++}$ and Ba$^{++}$ impurities. The experimental values were taken from Refs. [16] and [14]. The energies are in a.u.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta E$</th>
<th>$\Delta E_{\text{exp}}$</th>
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<tbody>
<tr>
<td>RbCl</td>
<td>Mg$^{++}$</td>
<td>0.0764</td>
</tr>
<tr>
<td></td>
<td>Ca$^{++}$</td>
<td>0.0772</td>
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<td></td>
<td>Sr$^{++}$</td>
<td>0.0775</td>
</tr>
<tr>
<td></td>
<td>Ba$^{++}$</td>
<td>0.0779</td>
</tr>
</tbody>
</table>

excited states, using the point-ion and the ion-size correction methods. Table I shows the variational parameters $\lambda_{1s}$ and $\lambda_{2p}$, the pseudopotentials $V_{1s}$ and $V_{2p}$ and the corresponding energies for the Gaussian functions. Table II shows the optical absorption of the $Z_1$-center for RbCl for Mg$^{++}$, Ca$^{++}$, Sr$^{++}$ and Ba$^{++}$ impurities, using the semiempirical parameter $[2,\alpha] = 1$.

For the ground state of the $Z_1$ center the energy functional is minimized using the same ground state wave function than is used for the $F$ center. In the case of the excited state is necessary to choose the direction of the $p$-function axes according to the symmetry of the impurity and the vacancy which together with the $F$ center forms the $Z_1$ center. A suitable choice of the three mutually perpendicular axis will be the three principal axes of the field gradient tensor set up by the $Z_1$ center. Dick [15] calculated these axes. The direction cosines of the principal axes are approximately $(0,0,1)$ (wave function z of the $F$ center), $\left(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0\right)$ ($xy$ wave function; $xy = \frac{1}{\sqrt{2}}(\psi_{ex} + \psi_{ey})$, where $\psi_{ex}$ and $\psi_{ey}$ are excited state wave functions corresponding to $F$ center), and $\left(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0\right)$ ($x\bar{y}$ wave function; $x\bar{y} = \frac{1}{\sqrt{2}}(\psi_{ex} - \psi_{ey})$). We found that is useful to choose the $x\bar{y}$ axis when the point-ion method is used, and $z$ axis when the optical absorption values are obtained using the ion-size correction method. Experimentally [39] there is a very small change in the optical absorption of the $Z_1$ center when the divalent impurity is changed. So, the point-ion method gives useful information.

For the crystal RbCl:Ca$^{++}$ there is a good agreement between theoretical and experimental values [15]. Table II shows the experimental value [14] for RbCl:Sr$^{++}$ which is not close to the experimental value. Because it can not exist so large difference [39] between the experimental value of the optical absorption for RbCl:Ca$^{++}$ and RbCl:Sr$^{++}$, one of the two values must be wrong. The optical absorption of the $Z_1$-center follows the Ivey
law [40]. That means that the optical absorption of the RbCl ($a = 6.19$ a.u.) crystal must be bigger than the $Z_1$-center optical absorption of KBr crystal ($a = 6.23$ a.u.) which is $0.069$ a.u. and smaller than the $Z_1$-center optical absorption of the KCl crystal ($a = 5.93$ a.u.) which is $0.077$ a.u. But the optical absorption value of the $Z_1$-center in RbCl:$Sr^{++}$ given by Katz et al. [14] is $0.065$ a.u.

The Bartram et al. method [2] works reasonably well to describe the color centers [18-27]. There are other methods [27-37] that could be used for the calculation of the $Z_1$ band. Because of the low symmetry of the $Z_1$-center, the Bartram et al. method [2] can be used as a simpler way than others.

References

5. F. Seitz, Phys. Rev. 83 (1951) 134.