

The pseudopotential method and the Z_1 band in KCl:KBr mixed crystals

R. RODRÍGUEZ-MIJANGOS

*Centro de Investigación en Física, Universidad de Sonora
Apartado postal 5-088, 83190 Hermosillo, Sonora, México*

AND

C. RUIZ-MEJÍA

*Instituto de Física
Universidad Nacional Autónoma de México
Apartado postal 20-364, 01000 México, D.F., México*

Recibido el 3 de junio de 1992; aceptado el 22 de septiembre de 1992

ABSTRACT. By taking into account that experimentally the X-ray spectrum of mixed crystals gives a lattice constant a_M which is different from the lattice constant of the two crystals which form the mixed crystal, the optical absorption of the Z_1 -center was calculated in KCl:KBr mixed crystals with Ca^{++} impurities. The pseudopotential method was used. Good agreement with the experimental results is found for pure KCl and KBr.

RESUMEN. Usando el hecho experimental según el cual el espectro de rayos X de cristales mixtos da una constante de la red a_M , la cual es diferente de las dos constantes de la red de los cristales que constituyen el cristal mixto, se calculó la absorción óptica del centro Z_1 en cristales de KCl:KBr con impurezas de Ca^{++} . El método usado fue el de corrección de tamaño. Se encontró buen acuerdo con los resultados experimentales para KCl y KBr puros.

PACS: 61.70.-r; 71.55.-l; 78.50.-w

1. INTRODUCTION

Recently we have studied the behavior of the F and F_A optical absorption in mixed crystals [1-4]. Rodríguez and Ruiz-Mejía [1] conducted a theoretical study of the shift with concentration variation on the optical-absorption F band in KCl:RbCl and KCl:KBr mixed crystals using an F-center semicontinuum model [1]. Logatorov *et al.* [5,6] performed a theoretical calculation employing the ion-point model for a mixed crystal $K_{0.5}Cl:Na_{0.5}Cl$; they consider a statistical distribution of different types of positive ions around the F-center, and assume that the substitution of ions at a lattice place has a perturbative effect on the F-center electron and also produce F_A , F_B and F_C centers, with increased mixed concentration in the colored crystals. The calculations can be done in a systematic way when the concentration of components are the same, such as those by Logatorov *et al.* [6], but for unbalanced concentrations the calculations are more difficult. We have proposed a new point of view [2-4] in order to calculate the optical absorption in mixed crystals. By taking into account that experimentally the X-ray spectrum of mixed crystals [7] gives a lattice constant a_M which is different from the lattice constant of the two crystals

which form the mixed crystal. We have performed calculations for the mixed crystals considering [2-4] that these crystals have an specific physical properties and intrinsic constants, derived from Vegard's rule [8]. For the F and F_A-band in mixed crystals there are good agreement with the Asami and Ishiguro [9] experimental values. The interest in mixed crystals is due [9] to the possibility of using them in IR (infrared regions) laser operation. Also the Z₁-center can be used in laser operation [10], that is why our interest in the study of Z₁-band in mixed crystals. The Z₁ center consists of an F center with a [00 $\bar{1}$] cation vacancy and a [11 $\bar{1}$] divalent ion near to it [10]. The calculations for the optical absorption of the Z₁ center were made for mixed KCl:KBr mixed crystals with divalent impurities of Ca⁺⁺.

2. THEORY

The variational method to obtain the energy levels of the F-center in the point-ion approximation [11] consist of the minimization of the energy functional E_{lm} . That is

$$E_{lm} = \int \psi^* \left[-\frac{1}{2} \nabla^2 + V_{PI}(r) \right] \psi d\tau, \quad (1)$$

where $V_{PI}(r)$ is the point-ion potential and ψ is the trial wave function. For the ground state Gaussian wave function we have

$$\psi_g(r, \lambda_g) = \left[\frac{2\lambda_g^2}{\pi} \right]^{3/4} \exp(-\lambda_g^2 r^2), \quad (2)$$

$$\psi_e(r, \theta, \lambda_e) = \left[\frac{2^7 \lambda_e^{10}}{\pi^3} \right]^{1/4} r \cos \theta \exp(-\lambda_e^2 r^2), \quad (3)$$

for the excited state. The λ_g and λ_e are the corresponding variational parameters. For the F-center the point-ion functional energies are given by

$$E_{1s}^F = \frac{3}{2} \lambda_g^2 + \left(\frac{\pi}{2} \right)^{3/2} \left[\frac{2}{\pi} \lambda_g^2 \right]^{3/2} \sum_i \frac{q_i n_i}{r_i \lambda_g^2} \operatorname{erf}(\sqrt{2} \lambda_g r_i) \quad (4)$$

for the ground state, where n_i is the number of ions with charge q_i .

For the excited state

$$E_{2p}^F = \sum_i \frac{[2^7 \lambda_e^{10} / \pi^3]^{1/2} q_i n_i}{(\sqrt{2} \lambda_e)^2} \exp(-2\lambda_e^2 r_i^2) + \frac{5}{32} \sqrt{2} \frac{\pi^{3/2}}{\lambda_e^3} \left[\frac{2^7 \lambda_e^{10}}{\pi^3} \right]^{1/2}. \quad (5)$$

The energy functional E_{1S}^Z of the Z₁-center corresponding to the ground state is

$$E_{1S}^Z = E_{1S}^F + Y_{1S}(\sqrt{3}a) - Y_{1S}(a), \quad (6)$$

where a is the interatomic distance and

$$Y_{1s}(r) = -A_g^2 \frac{(\pi/2)^{3/2}}{r\lambda_g^3} \operatorname{erf}(\sqrt{2}\lambda_g r); \quad (7)$$

A_g is the wave function normalization constant.

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

$$E_{2p}^Z = E_{2p}^F + Y_{2p}(\sqrt{3}a) - Y_{2p}(a), \quad (8)$$

where

$$\begin{aligned} Y_{2p}(\hat{r}) = & \frac{\pi A_e^2 Q}{3(\sqrt{2}\lambda_e)^4} \exp(-2\lambda_e^2 r^2) - \frac{\pi A_e^2 Q}{r(\sqrt{2}\lambda_e)^5} \frac{\sqrt{\pi}}{2} \operatorname{erf}(\sqrt{2}\lambda_e r) \\ & + \frac{8\pi Q P_2(\cos\theta) A_e^2}{15r^2(\sqrt{2}\lambda_e)^7} \left[\frac{(\sqrt{2}\lambda_e r)^5}{2} + \frac{5}{4}(2\lambda_e r)^3 \right. \\ & \left. + \frac{15}{8}(\sqrt{2}\lambda_e r) \exp(-2\lambda_e^2 r^2) + \frac{15}{8} \frac{\sqrt{\pi}}{2} \operatorname{erf}(\sqrt{2}\lambda_e r) \right] \\ & + \frac{8\pi}{15} A_e^2 \frac{P_2(\cos\theta)}{(\sqrt{2}\lambda_e)^2} r^2 \frac{1}{2} \exp(-2\lambda_e^2 r^2); \end{aligned} \quad (9)$$

A_e is the excited wave function normalization constant, Q is the charge distribution at a point r . $P_2(\cos\theta)$ is the Legendre polynomial of order two, where θ is the angle between the vector at the point r and the axis of the p -function.

For the ground state of the Z_1 -center we can choose the wave function for the F-center $\psi_g(r, \lambda_g)$. In the case of the excited state is necessary to choose the direction for the p -function axes according to the symmetry of the impurity and the vacancy which together with the F-center form 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 [12] calculated the directions of those axes. The direction cosines of the principal axes are approximately $(0, 0, 1)$, $(\frac{1}{\sqrt{2}}, -\frac{1}{\sqrt{2}}, 0)$ and $(\frac{1}{\sqrt{2}}, \frac{1}{\sqrt{2}}, 0)$. That is

$$\psi_{exy} = \frac{1}{\sqrt{2}}(\psi_{ex} + \psi_{ey}) \quad (10)$$

and

$$\psi_{ex\bar{y}} = \frac{1}{\sqrt{2}}(\psi_{ex} - \psi_{ey}), \quad (11)$$

where ψ_{ex} and ψ_{ey} are the wave functions for the F-center. Equation (3) gives the ψ_{ez} for the F-center.

Then for the Z_1 -center we have three wave functions: ψ_{exy} , $\psi_{ex\bar{y}}$ and ψ_{ez} . The point-ion interaction potential is given by

$$\left\langle \psi_e \left| \frac{Q}{|\hat{r} - \hat{r}_i|} \right| \psi_a \right\rangle = A^2 \int \left(\frac{4}{3} \delta_0 + \frac{8}{15} \delta_2 P_2(\cos \theta) \right) \pi f(r) r^2 dr, \quad (12)$$

where $f(r)$ is the part of the wave function ψ_a which depends only on r , and δ_0 and δ_2 are given by

$$\delta_0 = \begin{cases} \frac{1}{r_i}, & r < r_i \\ \frac{1}{r}, & r > r_i \end{cases} \quad (13)$$

and

$$\delta_2 = \begin{cases} \frac{r^2}{r_i^3}, & r < r_i \\ \frac{r_i^2}{r^3}, & r > r_i. \end{cases} \quad (14)$$

In order to obtain Eq. (12) we have used the result given by Coulson [12]:

$$I = \sum_{n,k} \int P_n(\cos \theta_a) P_k(\cos \theta_b) dw = \sum_k \frac{2\pi}{2k+1} P_k(\cos \gamma), \quad (15)$$

where $\theta_a = \gamma - \theta_b$.

The ground-state energy for the Z_1 -center is obtained minimizing an energy functional of the form

$$E_g^z = E_g^F + \sum_s \langle \psi_g(\hat{r}_s) | V_p^z | \psi_g(\hat{r}_s) \rangle. \quad (16)$$

For the first-excited-state the energy is obtained minimizing the energy functional

$$E_C^z = E_C^F + \sum_s \langle \psi_e(\hat{r}_s) | V_p^z | \psi_e(\hat{r}_s) \rangle, \quad (17)$$

where

$$\begin{aligned} V_p^Z &= V_p^F - V_{pl} [A_C + (\bar{V}_p^F - U_1) B_C] \delta(\hat{r} - \hat{r}_c) \\ &\quad + [A_d - A_c + (\bar{V}_p - U_3)(B_d - B_c)] \delta(\hat{r} - \hat{r}_d) \end{aligned} \quad (18)$$

and

$$V_p^F = V_{pl} + \sum_s [A_s + (\bar{V}_p - U_s) B_s] \delta(\hat{r} - \hat{r}_s); \quad (19)$$

TABLE I. Energy values in atomic units for the ground (E_g) and the excited (E_e) states of the Z_1 center in KCl:Br:Ca⁺⁺ for several concentrations c_x .

KCl:BrCa ⁺⁺	λ_g	$-V_g$	$-E_g$	λ_e	$-V_e$	$-E_e$
$c_x = 0$	1.18	0.096	0.1081	0.95	0.130	0.0272
$c_x = .25$	1.17	0.095	0.1088	0.94	0.132	0.0330
$c_x = .50$	1.15	0.094	0.1095	0.93	0.135	0.0390
$c_x = .75$	1.13	0.092	0.1100	0.92	0.136	0.0442
$c_x = 1.00$	1.12	0.092	0.1108	0.92	0.141	0.0505

the U_s is the potential of the 5th ion due to all the all the other ions and A_s and B_s are the characteristic parameters of the ions alone, V_{PI} 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.

E_g^z (or E_e^z) is minimized with respect to λ_g (or λ_e) for a fixed value of \bar{V}_P , then $\langle \psi | V_P^Z | \psi \rangle$ is recomputed from Eq. (18) and the procedure is continued to self-consistency [13].

In order to solve the problem for mixed crystals [2] we take A_γ and B_γ as

$$A_\gamma = A_\gamma^1(1-x) + A_\gamma^2x$$

and

$$B_\gamma = B_\gamma^1(1-x) + B_\gamma^2x,$$

where A_γ^1 and A_γ^2 correspond to one type of crystal and A_γ^2 and B_γ^2 to the other type (which are the components of the mixed crystal), and

$$a_M = a_1(1-x) + a_2x,$$

where a_M is the lattice constant of the mixed crystal; a_1 and a_2 are the lattice constant of the pure crystal, and x the concentration.

3. RESULTS AND CONCLUSIONS

Recently we have found good agreement between theoretical and experimental results for the F [2] and the F_A [3,4] band in mixed crystals. The same idea is used in the study of the Z_1 -band in mixed crystals of KCl:KBr with Ca⁺⁺ impurities. The results are given in Table I and the behavior of the optical absorption of Z_1 -band in Fig. 1. There is not experimental results for these mixed crystals, but the behavior of the Z_1 -band as function of the concentration is similar to that of the F-band.

The calculations were carried on using Gaussian wave functions for the semiempirical parameter $\alpha = 1$. There are other methods in order to calculate the optical absorption of the F-band [14-24] but the Bartram *et al.* method [13] have been [25-30] applied to wide variety of color centers with good results.

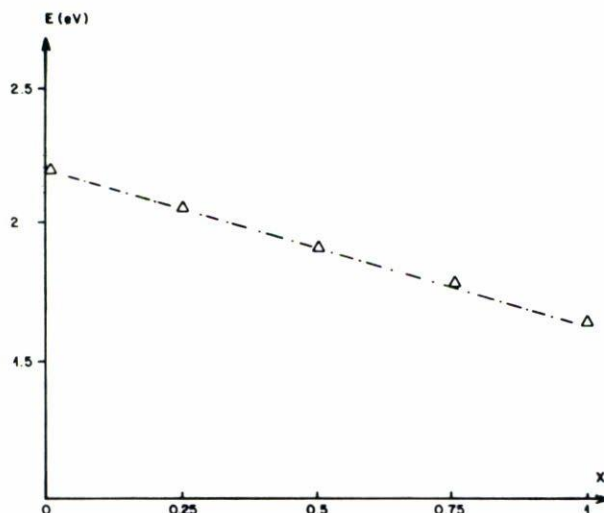


FIGURE 1. Dashed line joints the theoretical values of the absorption energy *vs.* concentration for Z_1 center. Then for energy the following Vegard law type is possible: $\Delta E = \Delta E_1(1 - x) + \Delta E_2X$, and where ΔE is the absorption energy of the mixed crystal; ΔE_1 and ΔE_2 are the absorption energies of the pure crystals, and x the concentration.

REFERENCES

1. R. Rodríguez and C. Ruiz-Mejía, *J. Phys. Chem. Solids* **49** (1988) 505.
2. R. Rodríguez and C. Ruiz-Mejía, *Phys. Rev.* **B39** (1989) 11120.
3. E.R. López-Téllez, D. Cárdenas-García, C. Ruiz-Mejía and R. Rodríguez, *J. Phys. Cond. Matter* **2** (1990) 4513.
4. C. Ruiz-Mejía, *J. Phys. Chem. Solids* **51** (1990) 1151.
5. Y.A. Logatorov and R.A. Evarestov, *Solid State Commun* **8** (1970) 273.
6. Y.A. Logatorov and R.A. Evarestov, *Phys. Stat. Solids* **40** (1970) 413.
7. A. Cordero-Borboa (private communication).
8. L. Vegard and M. Sheljedierup, *Z. Phys.* **18** (1917) 93.
9. K. Asami and M. Ishiguro, *Phys. Rev.* **B34** (1986) 4199.
10. F. Lüty, 'F-Aggregate centers and their application for optical information storage and tuneable IR Lasers', *Solid State Physics Symposium* (México 1979).
11. B.S. Gourary and F.J. Adrian, *Solid State Physics* **Vol. X**, Academic, New York (1960).
12. C.C. Coulson, *Proc. Cambr. Phil. Soc.* **33** (1937) 194.
13. R.H. Bartram, A.M. Stoneham and P. Gash, *Phys. Rev.* **176** (1968) 1014.
14. J. Tennyson and J.N. Murrell, *Mol. Phys.* **42** (1981) 297.
15. A.B. Kunz, *Phys. Stat. Sol.* **36** (1969) 301.
16. A.Y.S. Kung, A.B. Kunz and J.M. Vail, *Phys. Rev.* **B26** (1982) 3352.
17. A.H. Harding and A.H. Harker, *Philos. Mag.* **B51** (1985) 119.
18. P. Soul, J. Kendrick and C.R. Catlow, *Philp. Mag.* **B51** (1985) 107.
19. J.N. Murrell and J. Tennyson, *Chem. Phys. Lett.* **69** (1988) 212.
20. O.E. Taurian, A.H. Tang Kai and V. Lobatch, *J. Phys. Chem. Solids* **47** (1986) 59.
21. T. Takenchi, *Phys. Stat. Sol.* **B140** (1987) 113.
22. Y. Chen, J.L. Kolopus and W.A. Sibley, *Phys. Rev.* **186** (1969) 865.
23. R.F. Wood and H.W. Joy, *Phys. Rev.* **136** (1969) 783.

24. R.F. Wood and Öpik, *Phys. Rev.* **179** (1969) 783.
25. F. Dochy, *Phys. Stat. Solid (b)* **93** (1979) 325.
26. C.K. Ong, *Phys. Lett.* **75A** (1980) 459.
27. A.H. Harker, *J. Phys.* **C9** (1976) 2273.
28. R. Rodríguez, J.L. Marín, A. Navarro, C. Ruiz-Mejía, G. Vázquez and S.A. Cruz, *Cryst. Latt. Defects Amorph. Matter* **10** (1983) 79.
29. C. Ruiz-Mejía, *Cryst. Latt. Defects and Amorph. Matter* **13** (1986) 137.
30. C. Ruiz-Mejía, *Phys. Rev.* **B43** (1991) 2788.