The F_H center in CsF

C. Ruiz-Mejía

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

Abstract. The possibility of the existence of F_H centers in CsF is investigated, using the Bartram *et al.* method.

Several types of wave functions for the F_H-center electron were tested. The optimal value for the semiempirical parameter α was founded about $\alpha = 0.70$. There is not convergence for some wave functions using $\alpha > 0.70$, and for $\alpha < 0.70$ the ion-size correction is smaller than that obtained for $\alpha = 0.70$. Even for this case the change of the F_H optical absorption with respect to the F center is small.

In this paper the correct expression for the ground state energy functional of the Gourary-Adrian wave function type II is given.

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I. Introduction

Some time ago Rodríguez *et al.* [1] investigated the possibility of the existence of F_H centers in alkali halides with NaCl structure. In that work the possibility of the absence of F_H center formation in NaCl-type alkali halides is concluded. Experimentally the F_H center has not been observed and, as was pointed by Pan and Luty [2] this could be due to the fact that either the halogen impurities are not efficient tramps for migratory halogen vacancies, and hence no F_H center would be formed, or the perturbation introduced by the halogen impurity on the F-band is too weak. In the case of cesium halides containing halogen impurities, such as CsBr:Cl, the optical band shows a structure [3] in the F-band, in addition to the observed shift.

Recently Ruiz-Mejía [4] has found that the pseudopotential method of Bartram *et al.* [5] can not be consistently used for alkali halides with CsCl structure at least for the Gourary-Adrian [6] wave functions, but the energy levels of the F_A band in CsF, which have NaCl structure, have been calculated recently by E.R. López-Tellez *et al.* [7]. Even experimentally the F_H center in CsF have not been studied, this material could have similar properties as the CsCl. This is the reason why the F_H center was studied in the CsF crystal.

The aim of this paper is to obtain the optical absorption energy of F_H center in CsF with Cl, Br and I impurities.

II. Theory

Following to Gourary and Adrian [6] we can write for the F_H electron potential energy

$$V_{PI}(r) = \sum_{x_i, y_i, z_i = -\infty}^{\infty} [-1]^{x_i + y_i + z_i} \left[(x - ax_i)^2 + (y - ay_i)^2 + (z - az_i)^2 \right]^{-\frac{1}{2}}, \quad (1)$$

where $V_{PI}(r)$ is called the point-ion potential.

In Eq. (1) a is the nearest neighbor distance, (ax_i, ay_i, az_i) are the coordinates of the i-th nucleus, and the prime on the summation sign means that the point $(0,0,0)$ is omitted.

For the Bartram *et al.* model [5] the pseudopotential V_P has the form

$$V_P = V_{PI} + \sum_\gamma \left[A_\gamma + (\bar{V}_P - U_\gamma) B_\gamma \right] \delta(r - r_\gamma), \quad (2)$$

where U_γ is the potential at the γ-th ion due to all the other ions. $\bar{V}_P$ is the expectation value of V_P and A_γ and B_γ are the characteristic parameters [5] of the ions above, which are given approximately by

$$A_\gamma = 4\pi Q_\gamma \left(r_{\text{ion}\gamma} \right)^2, \quad (3)$$

$$B_\gamma = \tfrac{4}{3} \pi \left(r_{\text{ion}\gamma} \right)^3, \quad (4)$$

where Q_γ is the net charge of the ion γ, and $r_{\text{ion}\gamma}$ the radius of the γ-ion.

Bartram *et al.* [5] found that good agreement with experimental F-center transition energies could be obtained if all calculated parameters A_γ were reduced in magnitude by a factor $\alpha = 0.53$. Gash [9] showed that α described the variation of the F-center wave functions across the ion cores.

Within the framework of the pseudopotential method, the point-ion model is a prerequisite to calculate the ion-size effects.

The variational method to obtain the energy levels of F-center in the pseudopotential approximation consists of the minimization of the energy functional E_{lm}, that is:

$$E_{lm} = \int \Phi_{lm}^* \left[-\tfrac{1}{2} \nabla^2 + V_P(r) \right] \Phi_{lm} \, d\tau. \quad (5)$$

The Φ_{lm} are replaced by the wave functions types I, II and III of Gourary and Adrian [6].

The ground and first excited state energies are obtained minimizing an energy

functional of the form

$$E(\xi) = \bar{T} + \bar{V}_{\mathrm{PI}} + \sum_{\gamma}\left[A_{\gamma} + (\bar{V}_{\mathrm{P}} - U_{\gamma})B_{\gamma}\right]\left|\Phi_{lm}(r_{\gamma})\right|^{2}, \tag{6}$$

where ξ is the variational parameter which is varied to minimize the right side of Eq. (4), with $\bar{V}_{\mathrm{P}}$ fixed.

In the case of the F_{H}-center Eq. (2) is changed to

$$V_{\mathrm{P}}^{\mathrm{F_H}} = V_{\mathrm{P}} - V_{\mathrm{PI}} + \left[A_{\mathrm{I}} - A_{\mathrm{C}} + (\bar{V}_{\mathrm{P}} - U_{2})(B_{\mathrm{I}} - B_{\mathrm{C}})\right]\delta(r - r_{2}) \tag{7}$$

where the indices I and C denote impurity and cation respectively. The A_{γ} and B_{γ} used in this calculation were taken of Table I in Bartram $et\ al.$ [5]. In particular U_{2} represents the potential at the place of the impurity.

Finally, using Eqs. (6) and (7) the expectation value of the Hamiltonian

$$\left\langle\Phi_{lm}\left|T + V_{\mathrm{PI}} + V_{\mathrm{P}}^{\mathrm{F_H}}\right|\Phi_{lm}\right\rangle = \left\langle\Phi_{lm}\left|H_{\mathrm{P}}\right|\Phi_{lm}\right\rangle \tag{8}$$

is minimized with respect to the parameter ξ for a fixed value of $\bar{V}_{\mathrm{P}}$. Then $\bar{V}_{\mathrm{P}}$ is recomputed (not $V_{\mathrm{P}}^{\mathrm{F_H}}$), and the procedure is continued to self-consistency. The energy functional for the point-ion model are given in Ref. [6]. Weber and Dick [9] reported an error in the expression for the energy functional corresponding to the ground function state type II. We have obtained the correct expression, which is given by the next equation:

$$E_{\mathrm{F}}^{\mathrm{II}} = \frac{1}{(2a^{2})}\left(\xi^{2} - \frac{G(\xi)}{\eta}\left[\eta^{2} - \eta - \frac{1}{2} + \xi^{2}\left(1 + \frac{1}{\eta} + \frac{1}{2}\eta^{-2}\right)\right]\right)$$

$$- \frac{1}{a}\left\{\alpha_{m} - \frac{1}{2}\eta^{-3}G(\xi)\sum_{z_{i}\geq y_{i}\geq x_{i}\geq 0}h_{i}(-1)^{x+y_{i}+z_{i}+1}(1 + \eta\rho_{i})\right. \tag{9}$$

$$\times \frac{1}{\rho_{i}}\exp[-2\eta(\rho_{i} - 1)]\Bigg\},$$

where

$$\rho_{i} = (x_{i}^{2} + y_{i}^{2} + z_{i}^{2})^{1/2}, \qquad \eta = 1 - \xi\cot(\xi), \qquad h_{i} = \left(\frac{3!}{n_{i}!}\right)2^{3-o_{i}},$$

and

$$G(\xi) = \left[1 - \left(\frac{1}{2\xi}\right)(\sin 2\xi)(\sin\xi)^{-2} + \frac{1}{\eta}\left(1 + \frac{1}{\eta} + \frac{1}{2}\eta^{-2}\right)\right]^{-1}, \tag{10}$$

$\alpha = 0.70$	$-E^{g1}$	$-E^{g2}$	$-E^{g3}$	$-E^{e1}$	$-E^{e2}$	$-E^{e3}$	ΔE^1	ΔE^2	ΔE^3
CsF(Cl)	0.2072	0.2175	0.2214	0.0943	0.1056	0.1020	3.0703	3.0414	3.2479
CsF(Br)	0.2076	0.2176	0.2221	0.0949	0.1049	0.1041	3.0651	3.0635	3.2106
CsF(I)	0.2073	0.2176	0.2232	0.0936	0.1041	0.1039	3.0934	3.0866	3.2452

TABLE I. The energies (in at units) for the ground (E^{gi}) and the excited state (E^{ei}) for the F_H center in CsF. ΔE^{ei} represents the calculated absorption energy (in eV) for wave functions type I, II and III of Gourary and Adrian.

	CsF(Cl)	CsF(Br)	CsF(I)
λ_{1s}^I	1.74	1.73	1.73
$-V_{1s}^I$	0.254	0.254	0.254
λ_{2p}^I	2.30	2.29	2.32
$-V_{2p}^I$	0.176	0.176	0.177
λ_{1s}^{II}	2.39	2.39	2.39
$-V_{1s}^{II}$	0.287	0.287	0.287
λ_{2p}^{II}	3.17	3.15	3.17
$-V_{2p}^{II}$	0.202	0.199	0.199
λ_{1s}^{III}	2.20	2.29	2.25
$-V_{1s}^{III}$	0.276	2.76	0.274
λ_{2p}^{III}	3.24	3.24	3.25
$-V_{2p}^{III}$	0.187	0.190	0.195

TABLE II. Values of the variational parameter λ and the pseudopotential V_P for the ground and excited states corresponding to the energies of Table I.

where n_i is the number of times any given number occurs in the triplet (x_i, y_i, z_i), and i is the number of times that zero occurs in this triplet.

III. Results and Conclusions

Table I shows the results obtained for the ground and the excited state of the F_H center in CsF using the Bartram *et al.* method [5].

The energies for the ground (E^{gi}) and the excited state (E^{ei}) of the F_H center in CsF are in at units, and the calculated F_H-center absorption energies (ΔE^i) are in eV.

Table II presents the values of the variational parameter ξ for the ground and excited states (λ^{g^i}, λ^{e^i}) corresponding to the energies of Table I. The $V^{g^i}_p$ and $V^{e^i}_p$ are the values of the pseudopotential obtained by using the Bartram *et al.* method [5]. The change in ΔE^i for CsF is of the order of a hundredth of eV, when we consider Cl, Br and I impurities.

The optimal value for the semiempirical parameter α was found about $\alpha = 0.70$. There is not convergence for some wave functions using $\alpha > 0.70$, and for $\alpha < 0.70$ the ion size correction is smaller than that obtained for $\alpha = 0.70$. In the case of F_A center [10] is founded that $\alpha = 1$ is the optimal value of α. Here α is considered as a semiempirical parameter.

Ruiz-Mejía [4] founded that the pseudopotential method of Bartram *et al.* [5] can not be consistently applied to the alkali halides with CsCl structure. In the paper by Rodríguez *et al.* [1] the calculated shifts in the F band due to the halogen impurities were small, but large enough to be observable experimentally. Since for alkali halides with NaCl structure the F_H center has not been observed, in that paper [1] was concluded that the F_H center is not formed in this type of crystals.

In conclusion: a) the optical absorption of F_H center energies were calculated for CsF crystals containing Cl, Br and I impurities. At the present the F_H band in CsF has not been observed. From this and the present calculation, it is possible to conclude that the impurities of Cl, Br and I do not perturb the F band, b) the correct expression for the ground state energy functional of the Gourary-Adrian wave function type II is given.

Now we shall make some comments about the method employed in this paper. Although it has been pointed out by Wood and Joy [10] that the Bartram *et al.* approach [5] has several deficiencies, that method is computationally simple and has been used, successfully, in a large diversity of problems [11,12,13,14].

There are new developments in the field, namely, the method of lattice statics and other methods for taking into account the ionic polarization [15,16,17]. Anyway, the Bartram *et al.* method is good enough in order to investigate the band absorption of the F_H center in CsF.

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Resumen. Se investiga la posible existencia de centros F_H en CsF usando el método de Bartram *et al.*

Se estudian varias funciones de onda para el electrón del centro F_H. El valor óptimo encontrado para el parámetro semiempírico α fue $\alpha = 0.70$. No hay convergencia para algunas funciones de onda usando $\alpha > 0.70$ y para $\alpha < 0.70$ la corrección de tamaño es más pequeña que para $\alpha = 0.70$. Incluso para este óptimo valor ($\alpha = 0.70$), la absorción óptica del centro F_H con respecto a la del centro F es pequeña. En este trabajo se da la expresión correcta para la funcional de energía de la función base tipo II de Gourary y Adrian.