

Optimal theoretical values of absorption energies for F-center in alkali halides using ion-size correction

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ABSTRACT. The optimal values of absorption energy of F-center for all alkali halides are calculated by using Bartram *et al.* method. We give the relations between the optical absorption energies and the α parameter for wave functions of type II and type III. These relations are valid only for compounds with larger cations.

RESUMEN. Calculamos los valores óptimos para las energías de absorción de centros F para todos los halogenuros alcalinos utilizando el método de Bartram *et al.* Proporcionamos las relaciones entre las energías de absorción óptica y el parámetro α para las funciones de onda tipo II y tipo III. Estas relaciones sólo son válidas para compuestos con cationes grandes.

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1. INTRODUCTION

Theoretical calculations on electron excess color centers, including ion-size effects using Bartram, Stoneham and Gash method [1], and Gourary and Adrian [2] trial wave functions, have been made by many authors. Based in that method [2], we have studied the optical absorption of F and F_A -centers in CsF [3] and in KCl:KBr [4], as well as the optical absorption of F-centers in mixed crystals [5].

Recently, we presented the correct expression of the energy functional for the Gourary and Adrian [2] wave function of type II and the calculations for all alkali halides [6] with $\alpha = 0.53$. Further, not only we have calculated the Z_1 band in RbCl crystals with Mg^{++} , Ca^{++} , Sr^{++} and Ba^{++} impurities [7] and in other alkali halides [8], but also the F_d -center in KCl:Ca²⁺ [9], using Gourary and Adrian [2] trial wave functions and Gaussian function that proposed by Ong and Vail [10]. Bartram *et al.* [1] found that good agreement with experimental F-center transition energies could be obtained if all calculated parameter A_γ were reduced in magnitude by a factor $\alpha = 0.53$. In the case of the F_A -center Weber and Dick [11] found that the factor $\alpha = 0.53$ gave absorption splitting in the wrong direction. When they set $\alpha = 1$, qualitative agreement with experiment was obtained. Gash [12] showed that α parameter described the variation in the F-center (or another color center) wave functions across the ion cores. In this way, α should be close to unity for very compact core functions. A factor $\alpha = 0.53$ would be appropriate for diffuse ions. E.R. López-Téllez *et al.* [5] have calculated A_γ and B_γ for mixed crystals. The parameter A_γ , which is multiplied by α , is function of the ion radii which form the crystal. Since the α parameter is different for compact and diffusive wave functions, α can be a function

of the interionic distance. Furthermore, from the Mollow-Ivey experimental relation, we know that the optical absorption energy is a function of the interionic distance.

The purpose of the present work is to show the relation between the optical absorption energy and the α parameter which influences in the ion-size correction, and which of Gourary and Adrian's functions [2] describes with more precision the behavior of F-center in alkali halides crystals using the Bartram *et al.* method [1].

2. THEORY

Only the trial wave functions corresponding to Gourary and Adrian [2] of types II and III are reported here, since we did not obtain good results for function type I.

Following Gourary and Adrian [2] the point-ion potential is

$$V_{PI}(r) = \sum'_{x_i, y_i, z_i = -\infty}^{\infty} (-1)^{x_i + y_i + z_i} ((x - ax_i)^2 + (y - ay_i)^2 + (z - az_i)^2)^{-1/2}; \quad (1)$$

the prime on the summation sign means that the point (0,0,0) is not considered, a is the interionic distance.

In order to solve the problem of the F-center, we must determine the orbital Ψ_n which minimizes the functional

$$E = \int \{ \Psi^*(r) [\frac{1}{2}\nabla^2 + V_{PI}(r)] \Psi(r) \} d\tau \quad (2)$$

subject to

$$\int |\Psi(r)|^2 d\tau = 1. \quad (3)$$

For the ground state (g) and excited state (e) wave functions are

$$\Psi_g^{II} = \begin{cases} A j_0(\xi r/a) \exp(-\eta), & r < a, \\ A j_0(\xi) \exp(-\eta r/a), & r > a, \end{cases} \quad (4)$$

where

$$\eta = 1 - \xi \cot \xi; \quad (5)$$

$$\Psi_e^{II} = \begin{cases} A' j_1(\xi' r/a) \exp(-\eta'), & r < a, \\ A' j_1(\xi')(r/a) \exp(-\eta' r/a), & r > a; \end{cases} \quad (6)$$

where

$$\eta' = 3 - \xi'^2(1 - \xi' \cot \xi')^{-1}; \quad (7)$$

$$\Psi_g^{III} = \begin{cases} A j_0(\xi r/a) k_0(\eta), & r < a, \\ A j_0(\xi) k_0(\eta r/a), & r > a, \end{cases} \tag{8}$$

where

$$\eta = -\xi \cot \xi \tag{9}$$

and

$$k_0(x) = \frac{1}{x} \exp(-x); \tag{10}$$

$$\Psi_e^{III} = \begin{cases} A' j_1(\xi' r/a) k_1(\eta'), & r < a, \\ A' j_1(\xi') k_1(\eta' r/a), & r > a, \end{cases} \tag{11}$$

where

$$\eta' = f(\xi') + \{ [f(\xi')]^2 + 2f(\xi') \}^{1/2} \tag{12}$$

and

$$f(\xi') = \frac{1}{2} \xi'^2 (\xi' \cot \xi' - 1)^{-1}, \tag{13}$$

$$k_1(x) = \left(\frac{1}{x} + \frac{1}{x^2} \right) \exp(-x). \tag{14}$$

Here A and A' are the normalizing constants, ξ and ξ' are the variational parameters, $j_n(x)$ and $k_n(x)$ are the spherical Bessel function and the modified spherical Hankel function of order n respectively.

For Bartram *et al.* model [1], the pseudopotential V_P is

$$V_P = V_{PI} + \sum_i (A_i + (\bar{V}_P - U_i) B_i) |\Psi(r_i)|^2, \tag{15}$$

where U_i is the potential of the i -th ion due to all other ions, \bar{V}_P is the expectation value of V_P , and A_i and B_i are the characteristics parameters of the ions alone.

Finally, including kinetic energy T , the functional for F-center energy has the form

$$E = \bar{T} + \bar{V}_{PI} + \sum_i (A_i + (\bar{V}_P - U_i) B_i) |\Psi(r_i)|^2. \tag{17}$$

Then, the corresponding energy functional are for ground state

$$E_g^{II} = \frac{1}{2a^2} \left\{ \xi^2 - \frac{G(\xi)}{\eta} \left[\eta^2 - 3\eta - \frac{1}{2} + \xi^2 \left(1 - \frac{1}{\eta} + \frac{1}{2\eta^2} \right) \right] \right\} - \frac{1}{a} \left\{ \alpha_M - \frac{1}{2} \frac{G(\xi)}{\eta^3} \sum_{z_i \geq y_i \geq x_i \geq 0}^{\infty} h_i (-1)^{x_i + y_i + z_i} (1 + \rho_i \xi) \frac{1}{\rho_i} \exp(-2\eta(\rho_i - 1)) \right\}, \tag{18}$$

where

$$[G(\xi)]^{-1} = \left[1 - \frac{1}{2\xi} \operatorname{sen} 2\xi \right] (\operatorname{sen} \xi)^{-2} + \frac{1}{\eta} \left(1 + \frac{1}{\eta} + \frac{1}{2\eta^2} \right), \quad (19)$$

α_M is the Madelung constant; the prime on the summation sign means that the point $(0, 0, 0)$ is omitted and

$$h_i = \left(\frac{3!}{n_i!} \right) 2^{3-0_i}, \quad (20)$$

where n_i is the number of times any given number occurs in the triplet (x_i, y_i, z_i) , and 0_i is the number of times that zero occurs in this triplet,

$$\rho_i = (x_i + y_i + z_i)^{1/2} \quad (21)$$

$$E_g^{\text{III}} = \frac{1}{2a^2} \frac{\xi^2 \eta}{1 + \eta} - \frac{1}{a} \left\{ \alpha_M + \left[\frac{2\eta\xi^2}{(1 + \eta)(\xi^2 + \eta^2)} \right] \left[\sum'_{z_i \geq y_i \geq x_i \geq 0} h_i (-1)^{x_i + y_i + z_i} \left(\frac{1}{2\eta\rho_i} \exp[-2\eta(\rho_i - 1)] + \exp(2\eta) E_i(-2\eta\rho_i) \right) \right] \right\}. \quad (22)$$

For the excited state,

$$E_e^{\text{II}} = \frac{1}{2a^2} \left\{ \xi'^2 - 2G'(\xi') \left[\frac{\xi'^2 + \eta'^2}{(2\eta')^5} [(2\eta')^4 + 4(2\eta')^3 + 12(2\eta')^2 + 24(2\eta') + 24] - \frac{1}{2(2\eta')^3} [(2\eta')^3 + 3(2\eta')^2 + 6(2\eta') + 6] \right] \right. \\ \left. - \frac{1}{a} \left\{ \alpha_M - \frac{G'(\xi')}{2\eta'^5} \sum_{z_i \geq y_i \geq x_i \geq 0} h_i (-1)^{x_i + y_i + z_i} \frac{1}{\rho_i} \exp[-2\eta'(\rho_i - 1)] [3 + \frac{9}{2}\eta'\rho + 3(\eta'\rho)^2 + (\eta'\rho_i)^3] \right\} \right\}, \quad (23)$$

where

$$[G'(\xi')]^{-1} = 1 - \frac{j_0(\xi')j_2(\xi')}{j_1(\xi')^2} + \frac{1}{2(2\eta')^5} [(2\eta')^4 + 4(2\eta')^3 + 12(2\eta')^2 + 24(2\eta') + 24], \quad (24)$$

$$\begin{aligned}
 E_e^{\text{III}} = & \frac{1}{2a^2} \left[\xi'^2 - \frac{G'(\xi')}{\eta'^2} (1 + \eta'/2)(\xi'^2 + \eta'^2) \right] \\
 & - \frac{1}{a} \left\{ \alpha_M - G'(\xi') \sum_{z_i \geq y_i \geq x_i \geq 0}^{\infty} h_i (-1)^{x_i + y_i + z_i} \right. \\
 & \left. \times \left[\exp(2\eta') [E_i(-2\eta' \rho_i)] - \frac{1}{2(\eta' \rho_i)^2} (\eta' \rho_i - 1) \exp[-2\eta'(\rho_i - 1)] \right] \right\}, \quad (25)
 \end{aligned}$$

where

$$\begin{aligned}
 [G'(\xi')]^{-1} = & \frac{1}{\eta'^2} [1 + (\eta'/2)] \\
 & + \left(1 + \frac{1}{\eta'} \right)^2 \left\{ \frac{1}{[\xi' j_1(\xi')]^2} \left[\frac{1}{2} \left(1 + \frac{\text{sen } 2\xi'}{2\xi'} \right) - [j_0(\xi')]^2 \right] \right\}. \quad (26)
 \end{aligned}$$

3. OPTIMAL α PARAMETER

Bartram *et al.* [1] introduced a factor α in Eq. (17), so the expression with that correction is

$$E = \bar{T} + \bar{V}_{\text{PI}} + \sum_{\gamma} (\alpha A_{\gamma} + (\bar{V}_{\text{P}} - U_{\gamma}) B_{\gamma}) |\Psi(r_{\gamma})|^2. \quad (27)$$

We found the value of α that gives the optimal absorption energy for F-center.

Tables I and II show the optimal values of α for which the theoretical absorption energy is closer to the experimental energy of F-center for all alkali halides. In Table III we can observe the error between the theoretical energy and experimental energy functions type II and III functions. The highest error from experimental values is 1.32% for LiCl using function type II and 3.54% for function type III.

4. RELATION BETWEEN ABSORPTION ENERGY OF F-CENTER AND α PARAMETER

The ion size correction takes into account characteristic parameters of the ions, the parameter A_{γ} is reduced in magnitude by a α factor, we found [6] that $\alpha = 0.53$ gives a good agreement with experimental results using Gourary and Adrian [2] function type II, and we wondered, what the relation between the interionic distance a and parameter α is, and if has an influence on the theoretical energy.

The results from Tables I and II show that for some alkali halides a relation of the following form exists:

$$\alpha = Ba^m, \quad (28)$$

here a is the interionic distance, B and m are constants.

TABLE I. Optimal parameters α , ξ and ξ' , and values of ground state energy (E_g) and energy from excited state (E_e) for function type II. All energies in u.a.

	α	ξ^{II}	$-E_g^{II}$	ξ'^{II}	$-E_e^{II}$
LiF	0.53	2.32	0.2673	3.28	0.0798
LiCl	0.70	2.33	0.2288	3.24	0.1089
LiBr	0.65	2.30	0.2259	3.20	0.1261
NaF	0.48	2.32	0.2585	3.28	0.1219
NaCl	0.72	2.37	0.2160	3.24	0.1141
NaBr	0.53	2.35	0.2183	3.30	0.1317
NaI	0.50	2.40	0.2072	3.40	0.1302
KF	0.58	2.33	0.2465	3.35	0.1424
KCl	0.66	2.40	0.2072	3.37	0.1222
KBr	0.65	2.39	0.2015	3.32	0.1259
KI	0.67	2.43	0.1901	3.39	0.1211
RbF	0.61	2.31	0.2470	3.35	0.1582
RbCl	0.66	2.39	0.2057	3.38	0.1305
RbBr	0.67	2.38	0.1980	3.30	0.1292
RbI	0.67	2.42	0.1876	3.40	0.1246

TABLE II. Optimal parameters α , ξ and ξ' , and values of ground state energy (E_g) and energy from excited state (E_e) for function type III.

	α	ξ^{II}	$-E_g^{II}$	ξ'^{II}	$-E_e^{II}$
LiF	0.57	2.34	0.2623	3.34	0.0749
LiCl	0.60	2.36	0.2343	3.37	0.1171
LiBr	0.59	2.33	0.2283	3.34	0.1292
NaF	0.50	2.34	0.2564	3.35	0.1196
NaCl	0.70	2.37	0.2176	3.33	0.1183
NaBr	0.50	2.37	0.2196	3.39	0.1338
NaI	0.55	2.40	0.2060	3.43	0.1289
KF	0.59	2.35	0.2449	3.40	0.1401
KCl	0.69	2.42	0.2052	3.41	0.1204
KBr	0.70	2.40	0.1988	3.36	0.1234
KI	0.72	2.44	0.1881	3.42	0.1190
RbF	0.61	2.33	0.2466	3.41	0.1572
RbCl	0.68	2.40	0.2042	3.42	0.1290
RbBr	0.70	2.40	0.1962	3.38	0.1276
RbI	0.70	2.43	0.1863	3.44	0.1233

From Mollow-Ivey experimental relation [11]

$$E_F = Ca^{-n}, \quad (29)$$

where E_F is the absorption energy of F-center; C and n are constants.

TABLE III. Values of absorption energy for F-center using functions type II and III and comparison with experimental results.

	E_F^{exp}	E_F^{II}	Error	E_F^{III}	Error
LiF	0.1875	0.1875	0.00%	0.1881	0.32%
LiCl	0.1215	0.1199	1.32%	0.1172	3.54%
LiBr	0.0990	0.0998	0.81%	0.0991	3.54%
NaF	0.1365	0.1366	0.07%	0.1368	0.22%
NaCl	0.1020	0.1019	0.10%	0.0993	2.65%
NaBr	0.0865	0.0866	0.12%	0.0858	0.81%
NaI	0.0770	0.0770	0.00%	0.0771	0.13%
KF	0.1045	0.1040	0.48%	0.1048	0.29%
KCl	0.0850	0.0850	0.00%	0.0848	0.24%
KBr	0.0755	0.0756	0.13%	0.0754	0.13%
KI	0.0690	0.0690	0.00%	0.0691	0.14%
RbF	0.0895	0.0888	0.78%	0.0894	0.11%
RbCl	0.0755	0.0752	0.40%	0.0752	0.40%
RbBr	0.0685	0.0688	0.44%	0.0686	0.15%
RbI	0.0630	0.0630	0.00%	0.0630	0.00%

From Eq. (28) we have

$$a = \left(\frac{\alpha}{B}\right)^{1/m}; \quad (30)$$

replacing Eq. (30) in Eq. (29):

$$E_F = C \left(\frac{\alpha}{B}\right)^{-n/m}. \quad (31)$$

Now

$$E_F = D\alpha^x, \quad (32)$$

where

$$D = C \left(\frac{1}{B}\right)^x \quad (33)$$

and

$$x = -\frac{n}{m}. \quad (34)$$

Then, Eq. (32) shows the relation between the absorption energy of F-center and α parameter.

TABLE IV. Ratio of ionic radii (R), interionic distance (a) and optimal values of parameter α for both functions.

	a	r_+	r_-	R	α^{II}	α^{III}
RbF	5.32	2.80	2.57	0.9179	0.61	0.61
KF	5.05	2.51	2.57	1.0239	0.58	0.59
RbCl	6.23	2.80	3.42	1.2214	0.66	0.68
RbBr	6.48	2.80	3.68	1.3143	0.67	0.70
KCl	5.95	2.51	3.42	1.3625	0.66	0.69
NaF	4.39	1.80	2.57	1.4278	0.48	0.50
RbI	6.95	2.80	4.08	1.4571	0.67	0.70
KBr	6.52	2.51	3.68	1.4661	0.65	0.70
KI	6.69	2.51	4.08	1.6255	0.67	0.72

By using a linear regression only with alkali halides in Table IV it is found the values of C and x . The correlation for function type II is greater than 0.94, and the mathematical expression is

$$E_{\text{F}} = .0361 \alpha^{-1.927}; \quad (35)$$

and for function type III the correlation is greater than 0.95, and

$$E_{\text{F}} = .03561 \alpha^{-1.927}. \quad (36)$$

In Figs. 1 and 2 we represented the values obtained for both expressions [Eqs. (35) and (36)].

5. CONCLUSIONS

The parameters A_{γ} and B_{γ} are of opposite sign for both types of ion. Furthermore, B_{γ} increases more rapidly than A_{γ} with increasing ionic radius. In compounds with relatively large cations, the ion-size correction adds a net attractive potential to the cations with a consequent reduction of the F-band energy from the point-ion value [2]. In compounds with relatively large anions, the added attractive potential at the anions is much reduced and no longer significantly depresses the F-band energy. In order to improve the agreement with experiment like Bartram *et al.* [1], we have diminished all of the A_{γ} 's by an adjustable parameter α . For each value of α , the parameters ξ and ξ' were optimized for 15 alkali halides. Then if we considered the relation $R = (r_-/r_+)$, the expressions (35) and (36) that we obtained for all alkali halides in Table IV are just for small R . It means, that relation between the absorption energy of F-center (E_{F}) and parameter α is so good for larger cations and the parameter A_{γ} is reduced more than 57%, except for NaF. It can be seen from Table IV, that the α 's increase if the interionic distance a increase too.

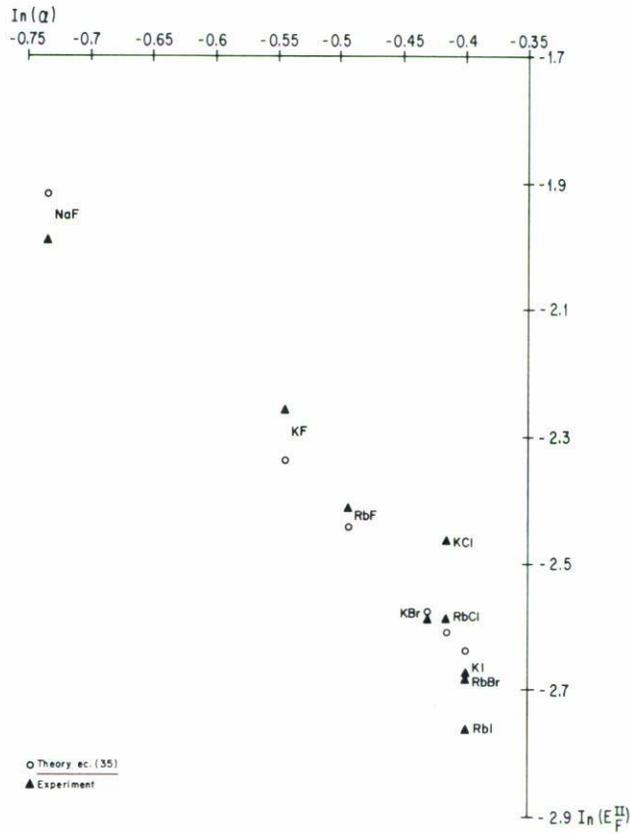


FIGURE 1. Absorption energies of F-center as a function of the α parameter in logarithmic scale for function type II.

It is important to mention that the values of absorption energies from function type I can not be optimized and we do not include the results in this paper. Function of type III gives a better approximation to the ground state than to the excited states and function of type II is better for excited states, however function of type III is better to calculate the absorption energy of F-center. Function of type I describes qualitatively a Coulomb potential that is similar to the potential of the negative ion vacancy of F-center, but it does not consider the oscillations of potential like functions of type II and type III.

Other trial wave functions have been used. Ong and Vail [10] used a Gaussian localized spherically symmetry wave function and considered the lattice distortion. Dochy [13] included in his work a wave function that is an exact solution for a cusplless hydrogenic potential for the ground state, and for the excited state a type I function with $\alpha = 1$. Renn [14] took Dochy's functions and the theory developed by Stumpf [15], Brown and Vail [16,17] considered a saddle-point configuration of the F-center using a gaussian-localized wave function. Vail and Harker [18] considered flexible, symmetry-adapted trial pseudowave functions. In recent years there have been major developments in the field, namely, the computer analysis of the electronic state from first principles, the applica-

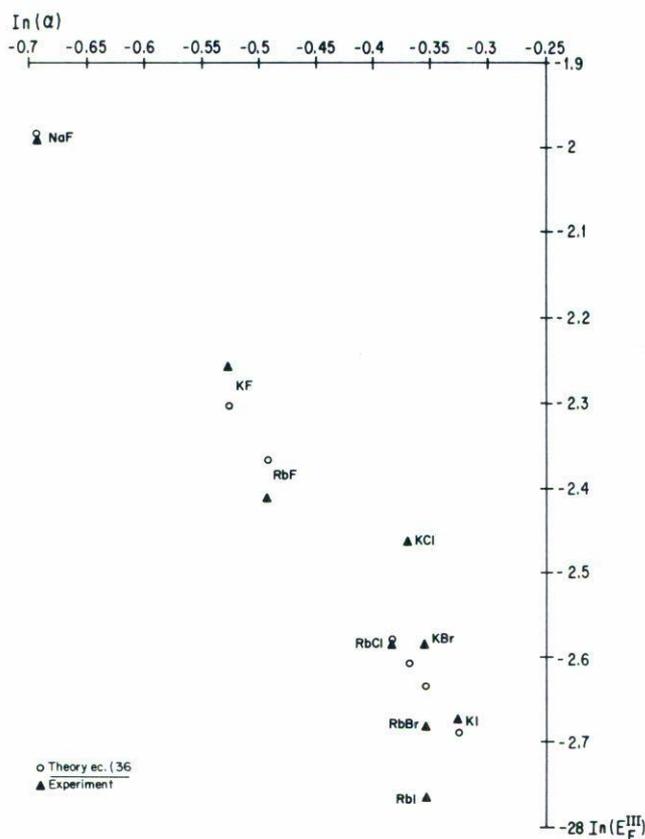


FIGURE 2. Absorption energies of F-center as a function of the α parameter in logarithmic scale for function type III.

tion of the method of lattice statics and new methods for taking into account the ionic polarization [19,20,21].

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