HIGHLY EXCITED STATES OF F CENTER

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ABSTRACT

Some concepts related with the optical properties of the F center are reviewed, studying principally the highly excited states. Particularly the 4f state is calculated, which according of Kubler and Friauf[5] may originate the L_1 band. The calculations presented here may serve to exemple the methods used to study the F center in the field of solid state physics in connection with optical properties of insulators and semi-conductors. Basically, semicontinuum and point-ion methods are described briefly.
Calculations were made for alkaly halide crystals.

RESUMEN

Algunos conceptos relacionados con las propiedades ópticas del centro F se discuten, se estudian principalmente los estados altamente excitados. En particular se calcula el estado 4f que de acuerdo a Kubler y Friauf puede dar origen a la banda L₁. Los cálculos aquí presentados pueden servir como ejemplos representativos de los métodos usados para estudiar el centro F en el campo de la física del estado sólido en conexión con las propiedades ópticas de aisladores y semiconductores. Básicamente se discuten brevemente los métodos de semicontinuo y de punto-ion. Se hicieron cálculos para cristales de halogenuros alcalinos.

1. INTRODUCTION

In the solid state the F center which is a defect that consists of a trapped electron inside a vacancy of an ionic crystals, plays an important role in the study of optical properties of solids[1].

Considering that this defect is a Quantum Mechanics System, classical methods of this discipline are applied; particularly, calculations of energy levels of the center with traditional methods allow to explain the bands of the optical spectrum as transitions between these levels. Usually, the F band is considered a transition of the type $1s \to 2p$[2] and the K band as a transition of the type $1s \to 3p$[3]. At higher energies other bands called L bands are detected[4].

The purpose of this study is to review some aspects of the optical absorption properties of the F center and give some insights into the some of the theoretical techniques used to study these optical properties, by calculating the $1s \to 4f$ transition, which according to Kubler & Friauf[5] may be responsable of originating the L_1 band.

The first systematic studies about the electronic and optical properties of the F center in alkali halides were done in the 1930's in Götinger under the direction of R.W. Pohl[6]. As a result, new concepts were developed, such as those related to photoconductivity, which were important for the development of semiconductor technology.

The alkali halides, as is well known are normaly transparent and can be colored after having been exposed to X rays. The absorption spectrum

(Fig. 1) of the colored alkali halides has been studied for more than 40 years[6,7]. Since then a great deal of information about the absorption spectrum has been obtained.
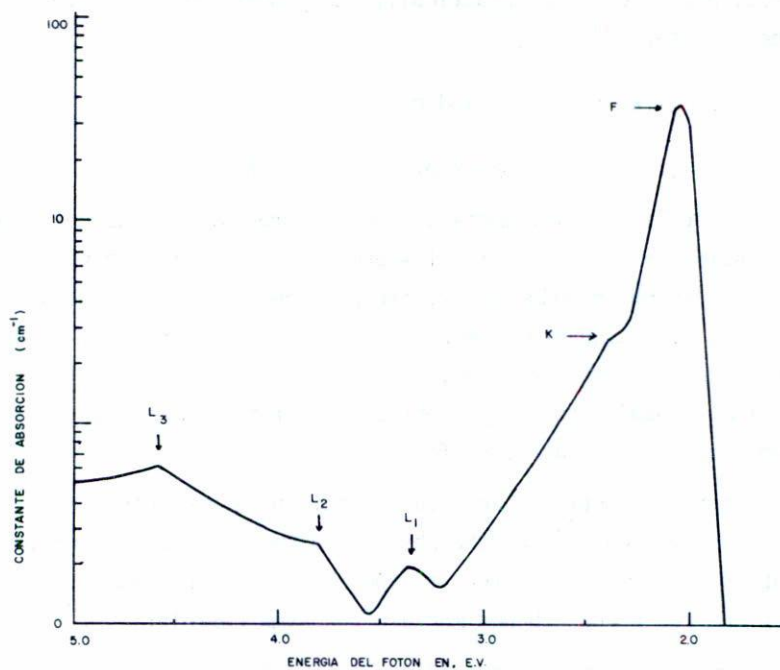

Fig. 1.   Absorption spectrum of KBr at $T = 7.5°K$ [20] $N_F = 4.2 \times 10^{17}/cm^3$ is the density of F centers.

In the present work, we restate some of the results concerning to the properties of this center, as well as the results of the calculations that we have performed of the 4f level and of the transition $1s \rightarrow 4f$, using the ion-point and semicontinuum models for solids.

We are mainly interested in the high energy region, $i.e.$, where the K band and the absorption peaks of the L bands exist. As follows, we present some properties of the L bands.

2. CHARACTERISTICS OF THE L BAND

1) The maximum value of the absorption peak of all the alkali halides shows that the F band is proportional to the K band and the L_i bands, with a proportionality constant practically independent of the concentration of the F centers[4], *i.e.*,

$$\alpha_m(F)/\alpha_m(K-L_i) = \text{cte. indep. of } N$$

with   i = 1,2,3;   N = number of F center per cm^3.

2) Photoconductivity measurements in some colored alkali halides indicate that, while the F band and the low energy side of the K band do not contribute to photoconductivity, the high energy tail of the K and L_i bands, do, with a quantum yield of n = 1 (n is the number of conduction electrons per absorbed photon).

   The L_i bands are independent of temperature even down to liquid helium temperatures, at least for KCl[8].

3) The absorption spectra of colored crystals have been studied by differents methods[9] and the absorption spectra for the complexes of F centers are always different to the absorption spectra of a single F center and the F and L bands mantain the same correlation[10].

4) The absorption spectrum obtained modulating the population of the ground state of the F center in KCl, by optical pumping[10], show that the F, K, and the L_i bands present the same modulation.

5) The positions of the peaks of the F and L_i bands, depend on the lattice parameter a, through the empirical relation of Mollwo-Ivey for the F band, *i.e.*,

$$\nu_a^n = \text{constant} \quad,$$

where ν is the frequency corresponding to the maximum point of the band and n is a constant[11].

6) Apparently there is no relation between the L_i bands and the purity of the crystal[12].

3. THE ORIGIN OF THE L_i BANDS

The foregoing results, seem to give an idea about the origin of the L bands, however these results do not say very much about the nature of the excited states and the transitions responsible of the existance of the L bands. This opens new questions that lead to fundamental problems (in the solid state physics of color centers).

Therefore, from the last section we can conclude the following:

i) From 1 we can say that the K and L bands are associated with the F center. This is so, because the experiments have beem done with high purity samples in which the absorption effects, due to complexes or aggregates of F centers, have been eliminated. In addition the facts in 3, 5 and 6 indicate that the absorption K and L are only due to transitions of the F center and not to aggregates of F centers or impurities.

ii) The result 4 gives experimental evidence that for KC1 the K and L bands originate from the ground state (1s) of the F center; *i.e.*, the same source of the F band.

iii) The results from 2 indicate, that the L_i transitions and part of the K corresponds to cnergies in the conduction bands. A great deal of theoretical investigation has been done, stimulated by the existence of localized states in the conduction band[13].

We can conclude from the foregoing conclusions that the F band is due to a $1s \rightarrow 2p$ transition of a trapped electron; and that the K band is due to a superposition of the 1s - np, for $n \geq 3$, transitions of the F center in agreement with the ideas of Mott and Gurney[14], and also those of Luty, in the sense that the L band is due to higher excited states of the F center.

Based on perturbative calculations of the wave functions of the F center, with Hartree-Fock and pseudopotential theory, Kubler and Friauf[5], suggest the possibility that the L_1 band is related to the 1s (Γ_1^e) - 4f (Γ_4^o) transition of the electron of the F center, where Γ_1, and Γ_4 are the reduced forms of spherical harmonics of the complete cubic group, where the e and o superscripts stand for even and odd parity respec

tively. Their calculation predicts an energy value near the bottom of the conduction band, for the energy of the 4f (Γ_4^0) state.

4. CALCULATION OF THE ENERGY LEVELS OF THE CENTER

In order to investigate the conjeture of Kubler and Friauf, we have computed the 1s → 4f transition energy of the F center using the semicontinuum and point-ion models of the Simpson[15] and Gourary and Adrian[16] respectively. An evaluation of the usefulness of these methods is given later on.

A) *The Semicontinuum model*

In the semicontinuum model the F center is represented by a spherical cavity of radius R embedded in a continuous polarizable medium characterized by a dielectric constant. The effect of a crystalline lattice produced by the atoms is taken into account through the effective mass approximation which correctly take into account the effects of polarization for excited states[17].

The Simpson approach is a self-consistent variational method for the calculation of the wave function and the potential. It has been relatively successful. It has also been used to calculate the transition energies of the F and K bands, as well as absorption and emission of spectra[15,18,19] for different descriptions of the potential of the F center. The results are surpresively in good agreement with those obtained experimentaly and is used to day for different problems[20,21,22].

In the semicontinuum approach recently, there are some new developments. But no there are usefull for high excited states calculations yet[23].

In the Simpson model the electron potential energy for r < R, including the Madelung contribution α_M and the polarization energy, is written (in a u.) as follows:

$$V_0 = -\frac{\alpha_M}{a} + \frac{1}{R}\left(1 - \frac{1}{K_0}\right) \quad ,$$

where a is the lattice constant, R the vacancy radius and K_0 is the high

frequency dielectric constant, this is due to the fact that we are considering optical transitions in which the ions surrounding the F center are stationary.
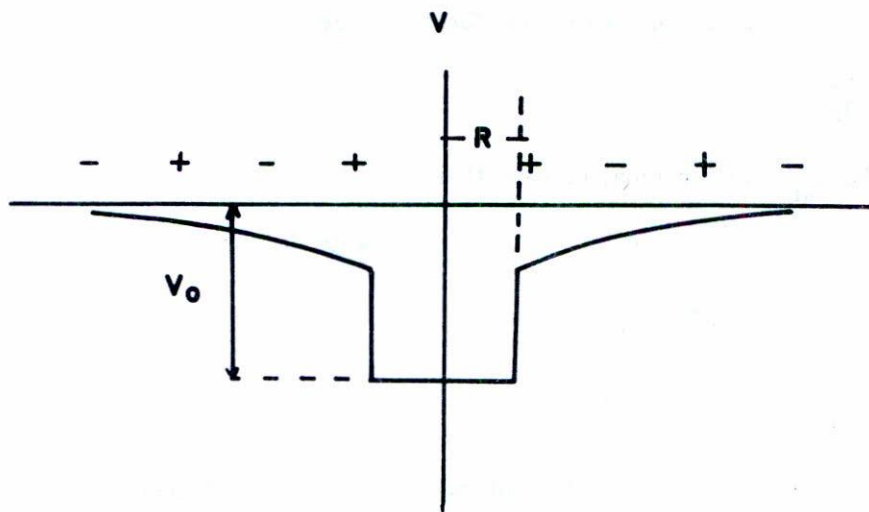

Fig. 2. The potential as function of r, following the Simpson's model.

For $r > R$, the field acting on the electron results in a potential energy given by

$$V_\mu = \int_\infty^r F \, dr \quad ;$$

were

$$F = \frac{1}{Kr^2} [1 - p(r)] + \frac{1}{K_o r^2} p(r); \quad p(r) = \int_0^r |\psi_\mu|^2 d\tau$$

is the fraction of the electronic charge inside a vacancy of radius R and ψ_μ represents the F center electron wave function.

Since the F center resembles the hydrogen atom, the following hydrogen like wave function are used as variational functions:

$$\psi_{1s} = Ae^{-\lambda r}(1 + \lambda r); \quad A = \left(\frac{\lambda^3}{7\pi}\right)^{\frac{1}{2}}$$

and

$$\psi_{4f} = R_{43}(r)\,\Theta_{3\pm3}\,\Phi_{|3|} \qquad ,$$

where ψ_{1s} is the ground state wave function which satisfies

$$\left(\frac{d\psi}{dr}\right)_{r=0} = 0 \quad .$$

For the ψ_{4f} wave function, we have that

$$R_{43}(r) = \frac{\lambda^{3/2}}{96\sqrt{35}}\,\rho^3 e^{-\rho/2} \qquad , \qquad \rho = \frac{1}{2}\lambda r \quad ;$$

$$\Theta_{3\pm3}(\theta) = \frac{\sqrt{70}}{8}\sin^3\theta \quad ;$$

$$\Phi_{|3|}(\varphi) = \frac{1}{\sqrt{2\pi}}\,e^{\pm3i\varphi} \quad .$$

Using ψ_{1s} and ψ_{4f} the following variational integral is solved:

$$W_j = \int_0^\infty \psi_j^* \left(-\frac{1}{2}\nabla^2\psi_j\right)d\tau + \int_0^R \psi_j^* V_0\psi_j\,d\tau + \int_R^\infty \psi_j^* V_4\psi_j\,d\tau \qquad ,$$

where j is 1s or 4f state.

This is minimized through the calculation of the λ parameter letting $\mu = \lambda$ after of to obtain the derivate.

The energy obtained for the 1s state is

$$W_{1s} = \frac{3\lambda^2}{14} + \frac{V_0}{14}\left[G(1,2) + G(1,3) + \frac{1}{4}G(1,4) + 14\right] +$$

$$+ \frac{\lambda^3}{7}\left\{\frac{1}{K_0\lambda^2}\left[G(1,1) + G(1,2) + \frac{G(1,3)}{4}\right] + \frac{4}{7}\mu\left[\frac{1}{K_0} - \frac{i}{K}\right]\right.$$

$$\left[Q(2,2) + Q(3,2) + \frac{Q(4,2)}{4} + 2\lambda\left[Q(2,3) + Q(3,3) + \frac{Q(4,3)}{4}\right]\right. +$$

$$\left.\left. + \lambda^2\left(Q(2,4) + Q(3,4) + Q(4,4)/4\right)\right]\right\} \qquad ,$$

where

$$G(1,n) = \int_{\infty}^{2\lambda r} r^n e^{-r} dr \quad ,$$

$$Q(n,m) = \int_{R}^{\infty} Q(n)\rho^m e^{-\rho} d\rho \quad .$$

The energy for the 4f state is

$$W_{4f} = \frac{\lambda^2}{32} + V_0 \left[\frac{G(1,8)}{8!} + 1 \right] + \frac{1}{2 \times 8!} \left[\frac{\mu \, \mathbb{K}}{8!} \times Q(8,8) + \frac{\lambda \, Q(1,7)}{K_0} \right] \quad ,$$

where

$$\mathbb{K} = \left(\frac{1}{K_0} - \frac{1}{K} \right) \quad ,$$

$$Q(n) = \int_{\infty}^{2\mu r} \frac{G(2,n)}{r^2} dr \quad .$$

B) The Point-Ion Model

The point ion approach consider the crystal as a lattice of point charges (ions) with alternate signs. The F-Center is throught of as a trapped electron in the vacancy of a negative ion. The calculation of the energies and wave functions of the F center are made using a Hartree approximation[16,17], where the following functional is minimized:

$$E_F^H = \int \psi_F^*(r) \left[-\frac{1}{2}\nabla^2 + V_L(r) \right] \psi_F(r) d\tau \Big/ \int |\psi_F(r)|^2 d\tau \quad ,$$

with

$$\int |\psi_F(r)|^2 d\tau = 1.$$

$V_L(r)$ is the potential energy of an electron in the field of a point-ion lattice and is given by

$$V_L(r) = \sum_{X_i, Y_i, Z_i = -\infty}^{\infty} (-)^{X_i + Y_i + Z_i} \left[(X - aX_i)^2 + (Y - aY_i)^2 + (Z - aZ_i)^2 \right]^{-\frac{1}{2}} ,$$

where X_i, Y_i, Z_i are the coordinates of the i-th ion, the sum is performed over all lattice sites except the one at the origin, and a is the lattice

parameter.

Each solution of Eq. (1) belongs to an irreducible representation of the cubic group, because $V_L(r)$ is invariant under this group of transformations.

The potential energy V_L is expanded around the center of the vacancy in terms of cubic harmonics[16] $Q(\Gamma_i^e, \ell, \mu_\ell; \theta, \phi)$

$$V_L(r) = V_{00}(r) \, Q(\Gamma_1^e, 0, 0, \theta, \phi) + V_{40}(r) \times$$

$$Q(\Gamma_1^e, 0, 4; \theta, \phi) + V_{60}(r) \, Q(\Gamma_1^0, 0, 6; \theta, \phi) + \cdots$$

The individual $V_{1, \mu_1}(r)$'s are determined by expanding each term in the potential about the center of the vacancy where 1 and μ_1 are the orbital quantum numbers. The first term of the right-hand side is spherically symmetric. This is the only term in V_L which affects a spherical symmetric wave function.

The reduced form of the spherical harmonics based on the irreducible representation (Γ_i^e) of the complete cubic group is given in Table I.

TABLE I

ORDER (ℓ)	REDUCED FORM
0	Γ_1^e
1	Γ_4^0
2	$\Gamma_3^e + \Gamma_5^e$
3	$\Gamma_2^0 + \Gamma_4^0 + \Gamma_5^0$

Table I. Reduced form of the spherical harmonics

In the rigid-cubic crystal, transitions from a state of Γ_1^e symmetry can go to states of Γ_4^0 symmetry[5]. Observing the Table I, the transitions corresponding to orders $\ell = 0,1$ and $0,3$. This is

$$1s \, (\Gamma_1^e) \rightarrow 2p \, (\Gamma_4^0) \quad ,$$

and if exists state $4f^{(5)}$ to

$$1s \ (\Gamma_1^e) \to 4f \ (\Gamma_4^o) \ .$$

The first of which has been calculated[16] for three different types of test wave functions for the 1s and 2p states, from these only two types will be useful to describe high excited states and those are.

Type I functions.- Hydrogenlike. Here the potential of the vacancy of negative ion is considered as a coulombian potential; where

$$\psi_j Q_j \qquad Q_{1s}(\Gamma_1^e, 0, 0: \theta, \psi) = \left(\frac{1}{4\pi}\right)^{\frac{1}{2}},$$

$$j = 1s \text{ or } 4f \quad R_{1s}(\Gamma_1^e, 0, 0; r) = 2\left(\frac{\xi}{a}\right)^{3/2} e^{-\xi r/\lambda},$$

$$Q_{4f} = \frac{1}{\sqrt{2\pi}} \frac{\sqrt{70}}{80} \sin^3 \theta \, e^{\pm 3i\psi} \qquad ,$$

$$R_{4f} = \frac{2}{3} \frac{(3/a)^{3/2}}{\sqrt{35}} (\xi/a)^3 r^3 \, e^{-\xi r/a} \qquad ,$$

where ξ is a variational parameter.

Type II functions.- These are chosen after examining V_∞ (Fig. 3). V_∞ is constant for $r < a$, so the solution to the wave equation is of the form $j_n\left(\frac{r}{a}\right)$. For $r > a$ the wave function is approximated by a hydrogenic one; $i.e.$, the violent oscillation of V_∞ which deviates it from the coulombian behavior is neglected.

Type II:

$$R_{1s}(\Gamma_1^e, 0, 0; r) = A \, j_o(\xi r/a) \, e^{-\eta_1} , \qquad\qquad r < a;$$

$$R_{4f}(\Gamma_4^o, 3, 0; r) = A \, j_3(\xi) \, e^{-\eta_1 r/a} \qquad , \qquad\qquad r > a;$$

$$R_{1s}(\Gamma_1^e, 0, 0; r) = A \, j_o(\xi) \, e^{-\eta_1 r/a} \qquad , \qquad\qquad r > a;$$

$$R_{4f}(\Gamma_4^o, 3, 0; r) = A \, j_3(\xi r/a) \, e^{-\eta_4} \qquad , \qquad\qquad r > a;$$

$$\eta_1 = 1 - \xi \cot \xi \quad ,$$

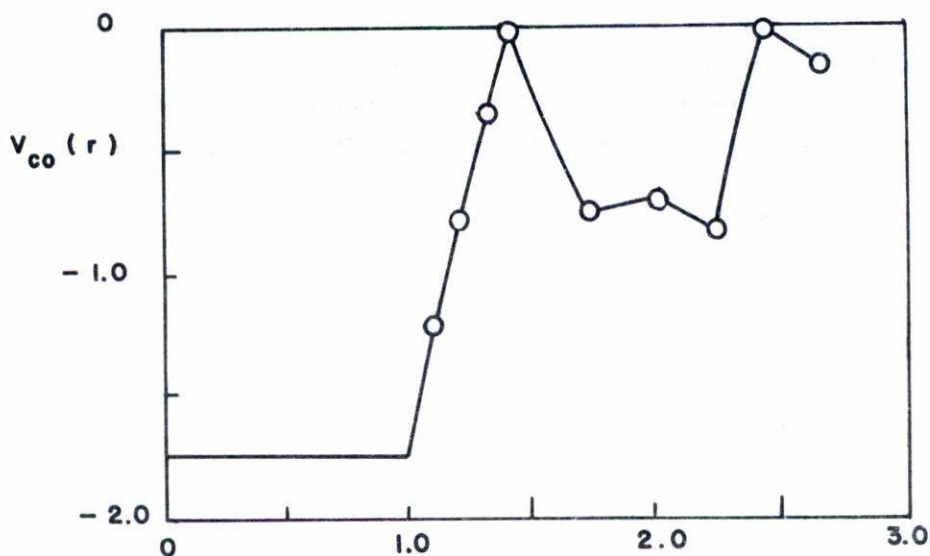$$\eta_4 = 7 - \frac{\xi j_2 (\xi)}{j_3 (\xi)} \quad .$$

Fig. 3. The part of the potential V_{oo} (r), which has spherical symmetry, as function of the distance.

A is a normalization constant and $j_n(x)$ is the spherical Bessel function of order n and ξ the variational parameter. The functionals for the energies of the 1s and 4f states are given by

$$E^I_{1s} = \frac{\xi^2}{2a^2} - \frac{1}{a} \left\{ \alpha_M - e^{-2\xi} \sum_{z_i \geq y_i \geq x_i \geq 0} h_i (-)^{X_i + Y_i + Z_i + 1} \right.$$
$$\left. (1 + \rho_i \xi) \frac{e^{-2\xi} (\rho_i - 1)}{\rho_i} \right\} \quad ,$$

$$E^{II}_{1s} = \frac{1}{2a^2} \left\{ \xi^2 - \frac{G(\xi)}{\eta} \left[\eta^2 - 3\eta - \frac{1}{2} + \xi^2 \left(1 - \frac{1}{\eta} + \frac{1}{2} \eta^{-2} \right) \right] \right\}$$
$$- \frac{1}{a} \left\{ \alpha_M - \frac{1}{2} \eta^{-3} G(\xi) \sum_i h_i (-)^{X_i + Y_i + Z_i + 1} (1 + \eta\rho_i) \frac{e^{-2\eta} (\rho_i - 1)}{\rho_i} \right\} \quad ,$$

where α_M is the Madelung constant

$$h_i = \left(\frac{3!}{n_i!}\right) 2^{3-0_i} \; ; \qquad \rho_i = (X_i^2 + Y_i^2 + Z_i^2)^{\frac{1}{2}}$$

and

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

$$E_{4f}^{I} = \frac{1}{2}\frac{\xi^2}{2} - \frac{1}{a}\left[\alpha_M - \frac{1}{315}\sum_i h_i(-)^{X_i+Y_i+Z_i+1} \times \frac{e^{-2\xi\rho_i}}{\rho_i} \; \mathbb{P}(\xi\rho_i)\right] \; ,$$

$$E_{4f}^{II} = \frac{1}{2a^2}\left\{\xi^2 - 2G(\xi)\left[\frac{\xi^2+\eta^2}{(2\eta)^9}\sum_{k=0}^{8}\frac{8!}{K!}(2\eta)^K - \frac{4}{(2\eta)^7}\sum_{k=0}^{7}\frac{7!}{8!}(2\eta)^k\right]\right\} -$$

$$- \frac{1}{a}\left[\alpha_M - \frac{G(\xi)}{2}\eta^{-9}\sum_i h_i(-)^{X_i+Y_i+Z_i+1}\left(\frac{1}{\rho_i}\right)e^{-2\eta(\rho_i-1)}\mathbb{P}(\xi\rho_i)\right] \; ;$$

$$\mathbb{P}(\xi\rho_i) \equiv 315 + \frac{2205}{4}(\xi\rho_i) + \frac{945}{2}(\xi\rho_i)^2 + \frac{525}{2}(\xi\rho_i)^3 + 105(\xi\rho_i)^4 +$$

$$+ \frac{63}{2}(\xi\rho_i)^5 + 7(\xi\rho_i)^6 + (\xi\rho_i)^7$$

with

$$\eta = \frac{\xi j_4(\xi)}{j_3(\xi)}$$

and

$$[G(\xi)]^{-1} = 1 - j_2(\xi)j_4(\xi)[j_3(\xi)]^{-2} + 2(2\eta)^{-9}\sum_{k=0}^{\infty}\frac{8!}{K!}(2\eta)^k$$

5. RESULTS

The energy values and the variational parameters of the 1s and 4f states for the Simpson method are given in Table II. The optical transition energy, $\Delta E = E_{4f} - E_{1s}$, for those alkali halides in which the

energy of the L_1 band has been reported is also shown.

TABLE II

	E_{1_s}	1_s	E_{4_f}	4_f	$\Delta E(theo)$	$\Delta E(exp)$ L_1 band	% error
NaCl	-3.137	0.511	-0.123	0.211	3.014	4.0	-24.6
KCl	-2.634	0.471	-0.137	0.221	2.497	3.6	-30.6
RbCl	-2.283	0.451	-0.136	0.231	2.147	3.1	-30.3
RbBr	-2.236	0.441	-0.118	0.211	2.118	2.8	-25.7

TABLE II.   Energy values in eV and variational parameters of the 15 and 4f states for the Simpson method.

The values for ν max obtained by the Simpson method are related to a (the lattice parameter) through the Mollwo-Ivey Law. For the F band $E_F = 2.8223\, a^{-1.7316}$ and for the L_1 band $E_{L_1} = 5.56\, a^{-1.928}$. The experimental data for the F band (Lüty) gives $E_F = 3.79\, a^{-1.77}$. Fig. 4 shows the minimun square fitted for the obtain this expressions.

Tables III shown the position of the L_1 band, obtained from theoretical and experimental data; the L_1 band is considered as the energy transition like $1s \rightarrow 4f$, according to the point-ion method.

TABLE III

	Theo (eV)		Exp (e.v.)
	Simpson	G.+A.	
E_{1_s}	-3.20	-6.0135	- - -
E_{4_f}	-0.123	-0.450	- - -
E	3.077	5.563	4.0

Table III.   Position of the L_1 and from theoretical an experimental data.
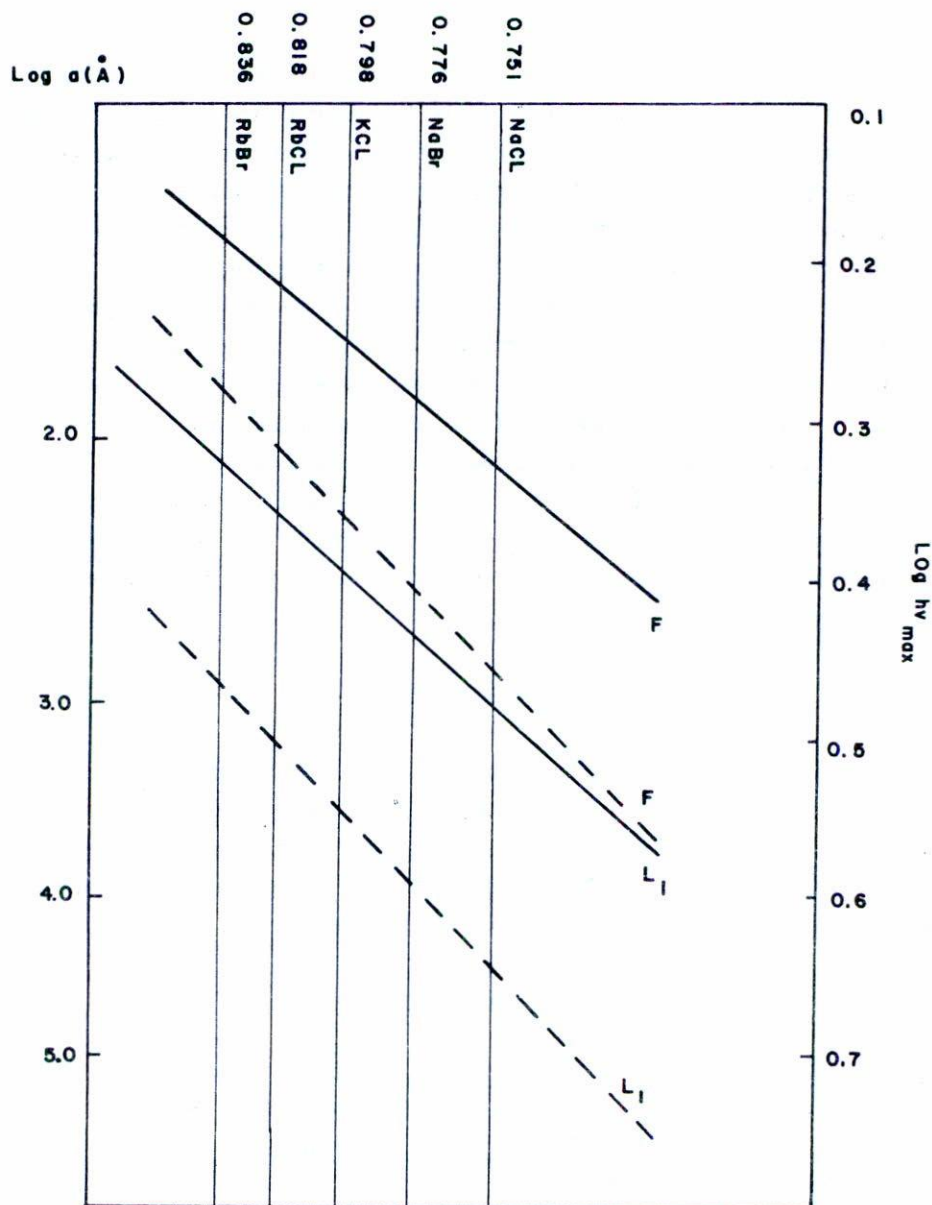
Fig. 4. The F and L_1 bands for several alkali halides; experimental and the theoretical results.

6. CONCLUSIONS

If we accept that the L band is due to transitions from the ground state to localized states of the F center in the conduction band, according to experimental evidence[4], then, we can conclude that the Simpson model is not adecuate to study such transitions; because it gives an infinite number of bound states at the top of forbiden band and a continuum of free particle states in the conduction band.

An the other hand, the point-ion model not include the right form of the polarization effect for the case of high excited states, given instead an over estimation of the transition energies of such states.

So, we can conclude that is necessary a more elaborate treatment, which includes the characteristics of degenerate localized states[24] a charge transfer model[25], or resonant states in the conduction band[26]. Although this last possibility is physically reasonable, recently there are a report[27] questioning the results obtaining by Page *et al.*[26].

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