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THE F BAND OF A SURFACE F CENTER

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ABSTRACT

Perturbation theory of quantum mechanics and the method of images of electrostatics are used in a simple calculation of the F band position in the absorption spectra of a surface F center. The case of alkali-halides with the NaCl structure is considered.

RESUMEN

La teoría de perturbaciones de la mecánica cuántica y el método de imágenes de la electrostática se utilizan en un cálculo sencillo de la posición de la banda F en el espectro de absorción de un centro F superficial. Se considera el caso de halogenuros alcalinos con estructura NaCl.

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I. INTRODUCTION

The F center is the best understood and most typical color center, usually being included in solid state textbooks$^{(1)}$ dealing with the optical properties of point defects.

As is well known, alkali halides, the ionic crystals per excelence, become colored by the effect of ionizing radiation or by a lack of stecheometry, i.e., excess of its metallic component. Electrons trapped in anion vacancies created by those methods yield, when excited, and absorption spectrum characterized mainly by an absorption peak known as the F band, which is due to the transition of the F center electron from its fundamental state to its first excited state.

The energies corresponding to excited states of the F center may be calculated by using a finite spherical potential well$^{(2)}$ as a model of the potential associated with the vacancy. The parameters of this potential may be fitted by an empirical Mollwo-Ivey relation. A better description of the excited states requires the specific form of the potential$^{(3,4)}$.

The semicontinuum model calculations have been shown not to be useful in order to explain the Stokes shift and vibronic coupling of the excited states, but can be used with relative success to obtain the features of the absorption band.

In the semicontinuum approach the polarizable crystalline medium is represented by a continuum characterized by its dielectric constant K. The F center is considered as an electron trapped in a spherical cavity of positive charge, e, representing the vacancy left by a missing anion. The potential energy of the electron is then given basically by both the Madelung and the polarization contributions. In the point ion approximation the crystal is represented by a point ion lattice of alternated signs. The F center is considered as an electron trapped at the field of a missing anion. The potential energy is then calculated as a lattice sum of the Coulomb interaction.

There is little information about surface F center. The energy of the optical excitation corresponding to the F band for an F center near a surface has only just recently been obtained$^{(5)}$. This calculation is based on the point ion approximation and it is of a semiquantitative nature.

We have found that the semicontinuum approach is adequate to illustrate the use of perturbation theory and the method of images of electrostatics. These methods are very useful in the calculation of the effect of the surface on the F center energies and wave functions. These are familiar topics for undergraduate students and may serve as tools for an introduction to the expanding subject of optical properties of point defects and surface effects in solids.

In Sec. II we describe in detail the basics of the semicontinuum approach to the calculation of the bulk F center energies and in Sec. III we introduce the surface F center image potential as a perturbation.

Finally in Sec. IV some results and conclusions are presented.

II. SEMICONTINUUM APPROACH

The potential well used in calculating the energies of the F center electron in the semicontinuum approach is shown in Fig.1. The potential of a test charge —the F center electron itself— is a constant $\phi_\circ$ for $r < R$, where R is the radius of the vacancy. This constant includes the Madelung or electrostatic potential ϕ_M and a contribution ϕ_P resulting from the polarizability of the medium due to the charge of the vacancy, thus

$$\phi_\circ = \alpha_M e/a - e(1-1/K_O)\big/R = \phi_M + \phi_P \quad , \tag{1}$$

where $\alpha_M = 1.7476$ is the Madelung constant for a NaCl-like structure and a stands for the lattice constant. The polarization term ϕ_P is due to the effect of the spherically distributed positive charge e inside the spherical cavity of radius R embedded in the continuum medium. From the classical theory of dielectrics, it is known that for this case the radial components of the dielectric displacement vector $D(r)$ and the electric field vector $E(r)$ are

$$D(r) = e/r^2$$

and

$$E(r) = e/Kr^2$$

where K is the static dielectric constant. These are related to the radial component of the polarization by

$$P(r) = [D(r)-E(r)]/4\pi = e(1-1/K)/4\pi r^2 \quad ;$$

the ϕ_P term in Eq.(1) follows from

$$\phi_P = \int_R^\infty [P(r)/r^2]\, 4\pi r^2 dr \quad .$$

We have used the high frecuency dielectric constant K_e instead of K because during a transition of the F center electron, only the electrons that are in the neighborhood of the cavity follow its motion.

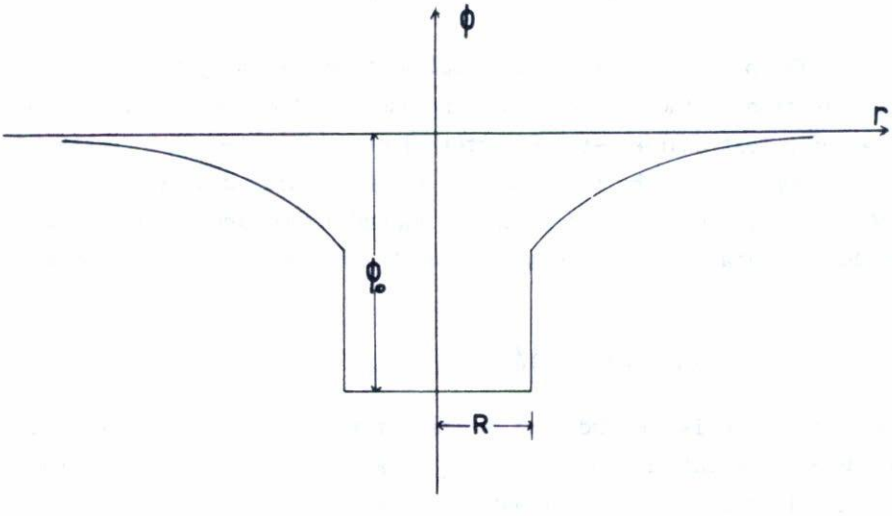

Fig.1 Potential used in calculating the energies of the F center electron in the semicontinuum approach.

For $r > R$ the field consists of two parts:

i) the field $e/K_\circ r^2$ due to the cavity of positive charge e .

ii) the field $-ef/K_\circ r^2$ due to the low frecuency part of the polarization which is produced by the positive charge and the fraction of the electronic charge within a sphere of radius r .

The function $f(r)$, takes the form

$$f(r) = \int_0^r |\psi|^2 4\pi r^2 dr \quad , \tag{2}$$

where ψ represents the F center electron wave function. The infrared polarization P_i corresponds to a displacement of the nuclei and their corresponding electronic clouds and is defined as$^{(6)}$

$$P_i(r) = C\ D(r)/4\pi \quad ,$$

where

$$C = (1/K_o - 1/K)$$

and

$$D(r) = -e\,[\,1-f(r)\,]/r^2 \quad ,$$

Thus the field acting on the electron at a distance $r > R$ is

$$F(r) = e/K_o r^2 - e\,[\,1-f(r)\,]\,(1/K_o - 1/K)/r^2$$

or

$$F(r) = e\,[\,1-f(r)\,]/Kr^2 + ef(r)/K_o r^2 \quad , \tag{3}$$

which depends on ψ as in Eq.(2). The potential $V(r)$ to be used in the Schrödinger equation is the potential of this field, hence, it must be calculated by a self-consistent method. The same holds for ψ.

A self-consistent method has been outlined by Simpson$^{(7)}$ and may be briefly summarized as follows:

i) The hydrogen-like initial wave functions

$$\psi_{1S} = A\ e^{-\alpha r}(1+\alpha r) \quad ,$$

$$\psi_{2P} = Br\ e^{-\beta r}\cos\theta \quad ,$$

are chosen for the fundamental (1S) and first excited (2P) states. This is done assuming that the F center arrangement resembles that of the hydrogen atom. A spherically symmetric electric field is also assumed. The factor $(1 + \alpha r)$ in ψ_{1S} is included to insure that

$$(\partial\psi_{1s}/\partial r)_{r=0} = 0 \quad ,$$

as would be expected of a potential function like the one that has been chosen. A and B are found by the normalization conditions as

$$A = (\alpha^3/7\pi)^{1/2} \quad \text{and} \quad B = (\beta^5/\pi)^{1/2} \quad .$$

ii) It is assumed that the final wave functions which satisfy Schrödinger's equation for both cases – ψ_{1S} and ψ_{2P} – are of the same form as the probe wave functions. These are written as

$$\psi'_{1S} = A'e^{-\alpha' r}(1+\alpha' r) \tag{4}$$

and

$$\psi'_{2P} = B're^{-\beta' r} \cos\theta \tag{5}$$

iii) The best final wave functions are obtained by letting

$$\partial E/\partial\alpha' = 0 \tag{6}$$

and

$$\partial E/\partial\beta' = 0 \tag{7}$$

where E is the variation integral

$$E = \int \psi'^{*} [-\hbar^2\nabla^2/2m + V(r)] \Psi' dt \quad . \tag{8}$$

Clearly, the value of E depends on α –or β– through the relation $V(r) = \int_{\infty}^{r} F(r)dr$. The condition (6) –or (7)– gives α' –or β'–as function of α –or β.

iv) To attain consistency we must have $\alpha = \alpha'$ –or $\beta = \beta'$.

With the proper value of α' we are able to obtain the corresponding wave function and therefore calculate the energy using Eq.(8).

The values for α, β, E_{1S} and E_{2P} obtained for some alkali halides of NaCl-like structure are listed in Table I. Values for the optical transition energy $\Delta E_\circ = E_{2P} - E_{1S}$ and the experimental data for the energies of the F band maxima are also given in the same table.

TABLE I

	E_{1S}	E_{2P}	$\Delta E_\circ$	$E_{F\ BAND}$	α	β
NaCl	-3.137	-1.017	2.120	2.68[b]	0.511	0.361
KCl	-2.634	-0.859	1.775	2.30[a]	0.471	0.351
RbBr	-2.236	-0.703	1.533	1.85[a]	0.441	0.271
NaBr	-2.823	-0.873	1.950	2.30[b]	0.491	0.351

a Ivey, H.F., Phys. Rev. 72, (1947) 341.
b Luty, F., Zeit. F. Phys. 160, (1960) 1.

Table I. Calculated values and position of the F band for some alkali halides (Energy is in eV and the variational parameters in atomic units).

III. THE METHOD OF IMAGES AND THE ENERGIES OF A SURFACE CENTER

In order to calculate the energy shifts of the 1S and 2P states when the F center lies near a surface of a crystal, it is again proposed that the crystal is a continuous dielectric medium of dielectric constant K and that the F center is a point charge q embedded in it. The surface is an infinite plane interface which separates the crystal from a medium with dielectric constant K. The z-axis is chosen in a direction perpendicular to the surface, located at $z = -d$. The solution to this problem has been discussed in detail by several authors$^{(8)}$. Assuming the point charge q to be located at $z = 0$ –at a distance d from the interface as in Fig.2– and using cylindrical coordinates, the potential at point P is given by

$$\phi = (q/R_1 + q'/R_2)/K = \Phi + \Phi' \tag{9}$$

where q' is the image charge located in $z = -2d$ and

$$R_1 = (\rho^2 + z^2)^{1/2} \quad , \quad R_2 = [\,\rho^2 + (z+2d)^2]^{1/2} \quad .$$

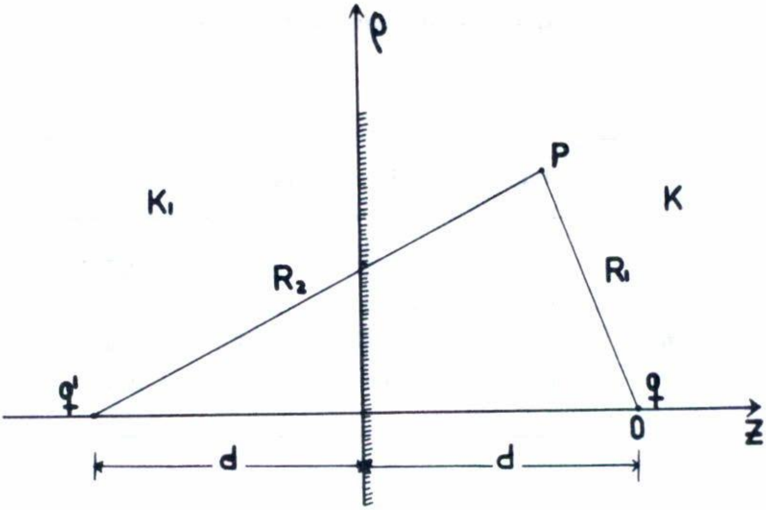

Fig.2 Geometry of the image charge problem. The boundary representing the surface is at $z = -d$, the F center charge q is at $z = 0$ and the image charge at $z = -2d$.

Taking the potential of the image charge as a perturbation in calculating the 1S and 2P states by perturbation theory, it is found that the perturbing term is given by

$$[\,(K-K_1)/K(K+K_1)\,] \int \psi^* \left\{ q/[\,\rho^2 + (z+2d)^2]^{1/2} \right\} \psi d\tau, \qquad (10)$$

where

$$q = (1 - \int_0^R |\psi|^2 \, dt) \qquad (11)$$

and the volume element in cylindrical coordinates is $d\tau = \rho d\rho dz d\phi$.

In the case of absorption it is assumed that q is the same for both states by the Franck-Condon principle. Using Eq. (10) the perturbation can be calculated for each state , resulting in the following equations:

$$E'_{1S} = \langle\psi_{1S}\,|\Phi'|\psi_{1S}\rangle = [\,(K-K_1)/K(K+K_1)\,]\,(\alpha^3/7\pi)\;2\pi q$$

$$\int_{-d}^{\infty}\int_{0}^{\infty}\left\{[\,1+\alpha(\rho^2+z^2)^{1/2}]^2\Big/[\,\rho^2+(z+2d)^2]^{1/2}\right\}e^{-2\alpha(\rho^2+z^2)^{1/2}}\rho\,d\rho\,dz, \qquad (12)$$

$$E'_{2P} = \langle\psi_{2P}\,|\Phi'|\psi_{2P}\rangle = [\,(K-K_1)/K(K+K_1)\,]\,(\beta^5/\pi)\;2\pi q$$

$$\int_{-d}^{\infty}\int_{0}^{\infty}[\,\rho^2+(z+2d)^2]^{-1/2}\,e^{-2\beta(\rho^2+z^2)^{1/2}}\rho^2\,d\rho\,dz \qquad ; \qquad (13)$$

the wave functions are those of Eqs. (4) and (5). They are expressed in cylindrical coordinates as

$$\psi_{1S} = (\alpha^3/7\pi)^{1/2}\,[\,1+\alpha(\rho^2+z^2)^{1/2}\,]\,e^{-\alpha(\rho^2+z^2)^{1/2}}$$

and

$$\psi_{2P} = (\beta^5/\pi)^{1/2}\rho\,e^{-\beta(\rho^2+z^2)^{1/2}} \qquad ,$$

where the prime has been omitted for the sake of simplicity.

TABLE II

	$E_{1S}+E'_{1S}$			$E_{2P}+E'_{2P}$			ΔE
	d_0	d_1	d_2	d_0	d_1	d_2	d_0
NaCl	-2.853	-3.012	-3.081	-0.598	-0,654	-0,806	2.255
KCl	-2.38	-2.5	-2.563	-0.519	-0.553	-0.673	1,861
RbBr	-2.095	-2.162	-2.214	-0.521	-0.538	-0,603	1.574
NaBr	-2.623	-2.713	-2.767	-0.473	-0.513	-0.801	2.150

Tabla II. Ground and first excited state energy shifts and optical transition energy for a surface F center (d is in atomic units).

Numerical evaluation of (12) and (13) gives the results quoted in Table II, where $d_n = na$ with $n = 0,1,2\ldots.$ The energy absorbed in the transition $1S \rightarrow 2P$ is

$$\Delta E = (E_{2P}-E_{1S}) + (E'_{2P}-E'_{1S}) = \Delta E_\circ + \Delta E',$$

where $\Delta E_\circ$ refers to the bulk F center (Table I).

IV. DISCUSSION

There are a few experimental data to compare with the present calculation of ΔE given in Table II. Experimental and theoretical data for NaCl and NaF have been reported by Smart and Jennings(5). The NaF case was not included in our calculations for lack of reliable data for the NaF wave functions. The data obtained for NaCl by the image method and that of Ref. 5 are compared in Table III.

TABLE III

	$\Delta E = \Delta E_\circ + \Delta E'$		
	CALCULATED		EXPERIMENTAL
	REF. 3	PRESENT WORK	REF. 3
NaCl	1.92	2.25	2.23

Table III. Comparison between calculated and experimental values of the F band energy for NaCl.

We conclude that if the surface effect on the F center energies is in fact a perturbation arising from the image charge, then the surface F center has a simple physical interpretation and the problem can be handled by an advanced undergraduate physics student. Furthermore, this simple model yields results comparable to those obtained with much more elaborate methods.

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