

The U center and the point-ion method

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ABSTRACT. Recently we calculated the optical absorption of the U center in mixed alkali halide crystals, and obtained also the optical absorption of U centers in several alkali halides using the point-ion method. This method gives better results than others when a physical consideration proposed by us is used. Here we extend the calculations for the optical absorption of the U center to other alkali halides not considered before. The values thus obtained values are compared with those obtained from the Ivey law.

RESUMEN. Recientemente calculamos la absorción óptica del centro U en cristales halogenuros alcalinos mixtos, y obtuvimos la absorción óptica del centro U para varios halogenuros alcalinos puros, usando el método del ion puntual. Cuando aplicamos este método, pero haciendo una cierta consideración física, propuesta por nosotros [20], encontramos mejores resultados que los obtenidos por otros autores. Aquí extendemos los cálculos anteriores [20] de manera que se incluyen halogenuros alcalinos que no habían sido considerados. Los valores obtenidos se comparan con los que se obtienen de la ley de Ivey [21].

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I. INTRODUCTION

The U center consists of a negative hydrogen ion H^- , located substitutionally at an anion site. The U center changes both the phonon spectrum and the optical properties of its host crystal. Using Raman scattering, uv and infrared absorption, several researchers [1-6] have studied the phonon spectrum and the optical properties of the U center. Several theoretical calculations of the electronic energy levels of the H^- ion in the alkali halides exist. Some theoretical investigations have used the point-ion model of Gourary [7] in which the H^- ion is coupled to the lattice with a Madelung type potential (crystal-field approximation). This approach gives considerable insight into the structure of the U center, but the calculated transition energies are approximately 20% smaller than the observed energies.

Spector *et al.* [8] again use the point-ion model, and confirm Gouray's [7] results over the whole range of alkali halides, including those crystals having CsCl structure. This study [8] also includes investigations involving excited states of the U center. Using a model in which

interactions with the first-nearest neighbors are considered in detail and in which all the other are taken as point charges, Wood and Öpik [9] calculated the electronic structure of the H^- ion in KCl, KBr and KI crystals. As in the case of Gourary [7], Wood and Öpik [9] use trial wave functions containing two variational parameters. They [9] also calculated the low-lying states of the U center in KCl by a more refined model. The U band transition energies predicted by both of their models agree significantly better with the experimental values than the point-ion results [7,8]. But, even though Wood and Öpik use models with some refinements, they also argue that the ability of a model to predict a single transition energy is not necessarily a good test for the validity of the model. Haynes [10], using the semiempirical self-consistent-field procedure (CNDO), found the optical absorption of the U center in LiF.

Bennet [11,12] solved numerically the Hartree-Fock-Slater equations for the two electron orbitals of the U center in NaCl, KCl, CdF_2 , CaF_2 allowing relaxation of its first neighbors. Beaumont *et al.* [13] made calculations for the ground and the first excited states of the U center in CaF_2 , SrF_2 and BaF_2 . Sing *et al.* [14] have used also variational wave functions containing two adjustable parameters in order to obtain the U band in CaF_2 , SrF_2 and BaF_2 . Bennet [11,12] uses a more flexible scheme than that employed by Sing *et al.* [14], but the latter results are in better agreement with experiment. The multiple-scattering method has been applied to the calculation of the U band in KCl, by Yu *et al.* [15]. Using the same method, Oliveira *et al.* [16] calculated the optical absorption of the H^- ion in CaF_2 , SrF_2 and BaF_2 . Güimaraés [17] obtained the electronic structure of the U center using the crystalline-cluster-method in a NaCl crystal. Matos and Maffeo [18,19] made the calculation of the U band in LiF, NaF and LiCl using the INDO method and the molecular cluster (MC) approximation. Their obtained values for the U center absorption are higher than other calculations. Recently R. Hernández-Gómez and C. Ruiz-Mejía [20] have calculated the optical absorption of the U center in mixed alkali halide crystals, using the Gourary [7] method. They have proposed that for the ground state of the U center the electrons are concentrated at the lattice site [20]. The calculated energies are in good agreement with the experimental results for KCl, KBr and NaCl single crystals. In this paper we extend these results in order to include the rest of the alkali halides with structure of NaCl. The results are compared with the optical absorption of the U center obtained from the Ivey [21] law.

2. THEORY

Following Gourary [7], all ions are represented by point charges, and polarization effects are neglected. The Hamiltonian for the U center is given by

$$H = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{1}{r_1} - \frac{1}{r_2} + V_L(r_1) + V_L(r_2) + \frac{1}{r_{12}}, \quad (1)$$

where the first two terms represent the kinetic energy of the two electrons, the third and fourth terms correspond to the Coulomb interaction between the electron and the proton, the fifth and sixth terms arise from the interaction of the electrons with the rest of the ions

in the lattice and the last term is the electron-electron interaction. The Hamiltonian is written in atomic units and the proton is considered the center of our coordinate system.

Following Gourary [7], for the point-ion potential we have

$$V_L(r) = \sum'_{x_i, y_i, z_i = -\infty}^{\infty} (-1)^{x_i + y_i + z_i} [(x - ax_i)^2 + (y - ay_i)^2 + (z - az_i)^2]^{-1/2}, \tag{2}$$

where a is the interatomic distance and the prime on the summation sign means that the point $(0, 0, 0)$ is not considered.

For the ground state the Chandrasekhar function [22] is the simplest wave function which gives a stable state for the U center. This is

$$\psi_g = \frac{N}{4\pi} [\exp(-\alpha r_1) \exp(-\beta r_2) + \exp(-\alpha r_2) \exp(-\beta r_1)], \tag{3}$$

where α and β are variational parameters.

The energy of the ground state obtained using this wave function is 0.0143 a.u. larger than that calculated by using an 11-parameter wave-function [7]. Therefore we make a 0.0143 a.u. correction to the obtained energies. The energy functional given by Gourary [7] is

$$E_g(\mu, \nu) = E_{H^-}(\mu/a, \nu/a) + (\psi_g | V_L(r_1) + V_L(r_2) | \psi_g), \tag{4}$$

where $\mu = \alpha a$, $\nu = \beta a$,

$$\begin{aligned} E_{H^-}(\alpha, \beta) = & - \left[\frac{1}{2} + \frac{1}{2} \left(\frac{2\alpha}{\alpha + \beta} \right)^3 \left(\frac{2\beta}{\alpha + \beta} \right)^3 \right]^{-1} \\ & \times \left[\frac{1}{2}(\alpha + \beta) + \frac{11}{32}(\alpha + \beta) \left(\frac{2\alpha}{\alpha + \beta} \right)^3 \left(\frac{2\beta}{\alpha + \beta} \right)^3 - \frac{1}{4}(\alpha^2 + \beta^2) \right. \\ & \left. - \frac{\alpha\beta}{2} \left(\frac{2\alpha}{\alpha + \beta} \right)^3 \left(\frac{2\beta}{\alpha + \beta} \right)^3 - \frac{\alpha\beta}{2} \left(\frac{\alpha^2 + 3\alpha\beta + \beta^2}{(\alpha + \beta)^3} \right) \right] \end{aligned} \tag{5}$$

and

$$\begin{aligned} (\psi_g | V_L(r_1) + V_L(r_2) | \psi_g) = & -\frac{2\alpha_M}{a} + \frac{1}{a} \left[\frac{1}{2} + \frac{1}{2} \left(\frac{2\mu}{\mu + \nu} \right)^3 \left(\frac{2\nu}{\mu + \nu} \right)^3 \right]^{-1} \\ & \times \left[\frac{\mu}{2} S_2(\mu) + \frac{\nu}{2} S_2(\nu) + 2 \left(\frac{\mu + \nu}{4} \right) \left(\frac{2\mu}{\mu + \nu} \right)^3 \right. \\ & \left. \times \left(\frac{2\nu}{\mu + \nu} \right)^3 S_2 \left(\frac{\mu + \nu}{2} \right) \right], \end{aligned} \tag{6}$$

where α_M is the Madelung constant and $S_n(\mu)$ is defined by the following expression

$$S_n(\mu) = \sum'_{z_i \geq y_i \geq x_i \geq 0} h_i (-1)^{x_i+y_i+z_i+1} (2\mu r_i)^n [A_n(2\mu r_i) - A_{n-1}(2\mu r_i)], \tag{7}$$

where $r_i = (x_i^2 + y_i^2 + z_i^2)^{1/2}$ and $h_i = \left(\frac{3!}{n_i!}\right) 2^{3-0_i}$. Again the prime on the summation implies that the point $(0, 0, 0)$ is omitted; n_i is the number of times any number can occur in the triplet (x_i, y_i, z_i) , 0_i is the number of times a zero occurs in this triplet and $A_n(x)$ is defined by the equation

$$A_n(x) = \int_1^\infty t^n e^{-xt} dt. \tag{8}$$

The wave function for the excited state is given by [7]

$$\psi_e = \left(\frac{1}{2}\right)^{1/2} [\phi_1(r_1)\phi_2(r_2) + \phi_1(r_2)\phi_2(r_1)], \tag{9}$$

where

$$\phi_1(r) = \left(\frac{1}{4\pi}\right)^{1/2} 2\gamma^{3/2} \exp(-\gamma r) \tag{10}$$

and

$$\phi_2(r) = \left(\frac{1}{4\pi}\right)^{1/2} \cos \theta \left(\frac{4}{3}\right)^{1/2} \delta^{5/2} r \exp(-\delta r), \tag{11}$$

where γ and δ are variational parameters. For this wave function the functional energy is given by

$$E_e(\gamma, \delta) = \frac{\gamma^2}{2} - \gamma - \frac{\alpha_M}{a} + \gamma S_2(a\gamma) + \frac{\delta^2}{2} - \frac{\delta}{2} - \frac{\alpha_M}{a} + \left(\frac{\delta}{12}\right) S_4(a\delta) + \frac{1}{2}\delta + g(\gamma, \delta), \tag{12}$$

where

$$g(\gamma, \delta) = \left(\frac{28}{3}\right) \delta \left(\frac{\delta}{\gamma}\right)^4 \left(1 + \frac{\delta}{\gamma}\right)^{-7} - \frac{\delta}{2} \left(\frac{\delta}{\gamma}\right)^4 \left(3 + \frac{\delta}{\gamma}\right) \left(1 + \frac{\delta}{\gamma}\right)^{-5} \tag{13}$$

3. RESULTS AND CONCLUSIONS

In order to determine the variational parameters α and β , Gourary [7] minimizes E_g as given in Eq. (4). According to Yu *et al.* [15], 85% of the electronic charges of the ground

TABLE I. Energies and parameter values for the ground (E_g, α, β) and the excited (E_e, γ, δ) states of the U center. $E_{gc} = E_g - 0.0143$ a.u.

	α	β	$-E_g$	γ	δ	$-E_e$	E_{gc}
LiCl	5.050	1.3764	1.2324	4.9271	2.2141	0.9860	1.2467
LiBr	5.3936	1.4699	1.1867	5.2530	2.2882	0.9623	1.2010
LiI	5.8924	1.6058	1.1297	5.7303	2.3841	0.9320	1.1440
NaF	4.5414	1.2376	1.3131	4.4499	2.0876	1.0265	1.3274
NaI	6.3496	1.7304	1.0853	6.1991	2.4621	0.9077	1.0996
KF	5.2377	1.4274	1.2067	5.1045	2.2555	0.9728	1.2210
KBr	6.4744	1.7644	1.0743	6.2894	2.4821	0.9016	1.0886
RbF	5.5286	1.5066	1.1702	5.3820	2.3155	0.9537	1.1845
RbI	7.1914	1.9599	1.0183	6.9787	2.5873	0.8699	1.0326

TABLE II. The absorption energies of the U center for several alkali halides as function of the interatomic distance a . $\Delta E_U^{S.M.S.}$ corresponds to the Spector *et al.* paper [8]. ΔE_U represents our results and ΔE_U^I that obtained from the Ivey law [21].

	a	$\Delta E_U^{S.M.S.}$	ΔE_U	ΔE_U^I
LiCl	4.82	6.12	7.09	7.15
LiBr	5.19	5.66	6.49	6.63
LiI	5.67	5.11	5.76	6.02
NaF	4.37	6.88	8.18	8.02
NaI	6.11	4.68	5.22	5.54
KF	5.04	5.88	6.75	6.84
KBr	6.23	4.60	5.086	5.43
RbF	5.32	5.52	6.27	6.44
RbI	6.92	4.05	4.42	4.83

TABLE III. Optical absorption of the U center for several alkali halides as function of the interatomic distance a . ΔE_U^I is obtained from the Ivey law [21]. ΔE_U^{exp} represents the experimental values.

	a	ΔE_U^I	ΔE_U^{exp}
NaBr	5.64	6.0640	5.9000
KCl	5.93	5.7280	5.7900
KBr	6.23	5.4342	5.4300
KI	6.67	5.0405	5.0800
RbCl	6.19	5.4762	5.4100
RbBr	6.48	5.2000	5.1200

state orbitals are within the central sphere of the cluster. We modified the expression given by Gourary [7] for E_g in order to take into account that fact [15]. So Table I shows the values of α and β and E_g for the case in which the two electrons are concentrated at the lattice site. In this table E_{gc} represents the energy $E_{gc} = E_g - 0.0143$ in order to take into account the correction when E_g is calculated by using an 11-parameter wave function. Table I shows also the variational parameters γ and δ , corresponding to the excited state of the U center, and the excited state energy E_e . For the excited state we use the same expression of Gourary [7], as given by Eq. (12). For the U_2 center, which consists of a hydrogen atom in the crystal, Mimura and Uemura [23] found that the electron is very concentrated around the proton.

Table II shows the optical absorption of the U center as calculated by Spector *et al.* [8] $\Delta E_U^{S.M.S.}$, the values found by us ΔE_U and that obtained from the Ivey law ΔE_U^I . In order to test the values obtained from the Ivey law [21], we show in Table III the optical

absorption of the U center for ΔE_U^I (obtained from the Ivey law) and ΔE_U^{exp} (obtained experimentally) for all the alkali halides (structure type NaCl) which are known.

Taking into account that the Ivey law [21] gives a very good prediction of the experimental results, we can conclude that our theoretical values for the optical absorption of the U band are in good agreement with the experimental ones.

Because there is no other calculation for these alkali halides we cannot make any further comparison. However for the alkali halides for which the U band has been measured our method was found better than the others [20].

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