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## Energy levels of $F_B(\text{Na})$ -centre in KCl

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**Résumé.** — Nous avons calculé les énergies des bandes d'absorption du centre  $F_B(\text{Na})$  dans KCl par la méthode du réseau statique. On utilise le pseudo-potentiel approximatif de Bartram *et al.* avec le facteur semi-empirique  $\alpha$  pour les effets de la grosseur des ions. En utilisant les valeurs  $\alpha = 1$  pour tous les cations et  $\alpha = 0,53$  pour tous les anions, on obtient un bon accord avec l'expérience pour la séparation en énergie des bandes d'absorption, mais l'énergie de la bande  $F_{B2}$  est 0,8 eV plus élevée que celle trouvée expérimentalement. La distorsion de l'état fondamental et les effets de la grosseur des ions sont importants pour la détermination de la séparation des bandes d'absorption.

**Abstract.** — We have performed the calculation for the absorption energies of  $F_B(\text{Na})$ -centre in KCl by using the lattice static method. The Bartram *et al.* approximate pseudopotential with semi-empirical factor  $\alpha$  is used for ion size effect. We found that  $\alpha = 1$  for all cations and  $\alpha = 0.53$  for all anions give the absorption splitting agrees well with experiments but the  $F_{B2}$ -absorption energy is about 0.8 eV higher than the experimental value. We found that both the ground state distortion and ion size effect are important in determining the absorption splitting.

**1. Introduction.** — The  $F_B$ -centre is an F-centre adjacent to two substitutional impurity cations in the alkali halide crystal. The  $F_B$  band with two peaks appears when a moderately sodium — doped KCl crystal is exposed to F light at room temperature [1, 2, 3]. A model for the lattice configuration of  $F_B$ -centre responsible for the observed  $F_B$  band has been proposed by Schneider [2]. The F-centre lies between the two substitutional impurity cations (Fig. 1).

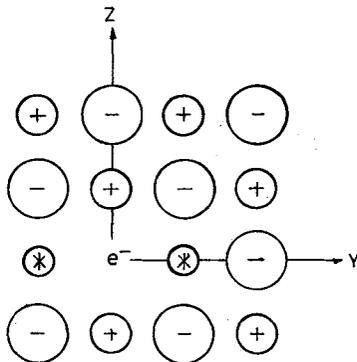


FIG. 1.

The  $F_{B1}$  band involves the transition from 1S to the 2P — like unrelaxed state along the  $y$  — axis, overlapping with two impurity cations. The  $F_{B2}$  band arises from the transition from 1S to the two — fold degenerate 2P — like unrelaxed state along the  $Z$ -axis. Schneider [2] also discussed the other probable lattice configuration for the  $F_B(\text{Na})$ -centre in KCl, where the F-centre lies next to the two nearest neighbour  $\text{Na}^+$  cations.

The absorption processes of  $F_B(\text{Na})$  in KCl have been studied theoretically by Wong and Wang [4] and Evarestov [5]. Wong and Wang used the tight binding calculation method of Kojima, Nishimaka and Kojima [6]. Evarestov used the pseudopotential approach through the model potential form of Abarenkov and Antonova [7]. Both calculations confirmed the lattice configuration for  $F_B$ -centre as shown in figure 1. Calculated  $F_{B1}$  and  $F_{B2}$ -absorption energies agree with experimental results.

We shall use the pseudopotential approach to take care of the ion — size effect through the form of Bartram *et al.* [8]. The weakness of the Bartram *et al.* approximate pseudopotential is that a semi-empirical factor  $\alpha$  has to apply to the pseudopotential coefficients. For appropriate  $\alpha$ , the method could account for the ion size effect and give absorption energies for F-centres [8] and  $F_A$ -centres [9] agreeing fairly well with experiments. The lattice statics method [10, 11] is used to include the detailed distortion field around the defect.

**2. Theory.** — We follow the theoretical model, approximation and methods developed by Ong and Vail [9] for the calculation of the  $F_A$ -centre in alkali halides with NaCl structure. The basic theory is pseudopotential and the variational procedure is used to minimize the estimated energy with respect to the pseudo-trial wave function parameter  $\lambda$  and the distortion field  $\xi$  self-consistently. We include the vacancy and two substitutional impurity cations as region I. The displacement of the ions in region I is

denoted as  $\mathbf{u}$ , and the rest of the lattice as region II. Their displacement is described by  $\xi$ .

Details of the distortion field near the  $F_B$ -centre is calculated by using the lattice static method in which the displacement  $\xi$  is expressed as

$$\xi = \mathbf{A}^{-1} \cdot \mathbf{F}(\lambda_0, \xi, \mathbf{u}) \quad (1)$$

where  $\mathbf{A}$  is the force — constant matrix;  $\mathbf{F}$  is the force due to the defect and  $\lambda_0$  is a variational parameter describing the excess electron. The distortion field is therefore made self-consistent with the parameter of the variational wave function.

We use a simple variational wave function with Gaussian localization for the excess electron. We have used the following trial wave functions :

Vacancy ground state

$$\varphi_1 \sim e^{-\lambda_1^2 r^2} \quad (2)$$

$F_{A1}$ -absorption

$$\varphi_2 \sim r e^{-\lambda_2 r^2} \cos \theta_y = y e^{-\lambda_2^2 r^2} \quad (3)$$

$F_{A2}$ -absorption

$$\varphi_3 \sim r e^{-\lambda_3^2 r^2} \cos \theta_z = z e^{-\lambda_3^2 r^2} \quad (4)$$

The estimated energy of the  $F_B$ -centre in a state  $\varphi$  can be written as

$$E = \langle \varphi | T + V_{\text{pl}} + V_{\text{is}} | \varphi \rangle + V_L(\xi, \mathbf{u}) + (d.e) \quad (5)$$

where  $T$  is the excess electron's kinetic energy operator;  $V_{\text{pl}}$  is the Coulomb potential energy of the excess electron with the point ion lattice;  $V_{\text{is}}$  is the ion size correction of Bartram *et al.*;  $V_L$  is the energy to create the lattice defect from the perfect lattice and  $(d.e)$  is the distortion energy contributed by region II ions.

**3. Results.** — In using Bartram *et al.*'s approximate pseudopotential for ion size correction, one has to choose a suitable value of the semi-empirical factor  $\alpha$  to be multiplied with the pseudopotential coefficients. We present four sets of results according to  $\alpha = 0.53$ ,  $\alpha = 1$ ,  $\alpha = \alpha^{(\pm)}$  and  $\alpha = \alpha^I$ .  $\alpha = 0.53$  and  $\alpha = 1$  refer to the pseudopotential coefficient of all the ions to be multiplied by 0.53 and 1 respectively.  $\alpha^{(\pm)}$  denotes the calculation that all cations have  $\alpha = 1$  and all anions have  $\alpha = 0.53$ .  $\alpha = 0.53$  has been used successfully in F-absorption calculations [8, 12], but fails to predict the  $F_A$ -absorption splitting [9].  $\alpha^{(\pm)}$  has been found to be able to predict the  $F_A$ -absorption splitting [9]. Since  $\alpha = 0.53$  is appropriate to F-absorption, and the splitting of the absorption energies of the impurity centres is due to the presence of the small impurity cations, we introduce  $\alpha = 0.53$  for all the host ions and  $\alpha = 1$  for the impurity ions, denoted by  $\alpha^I$ . In table I, we note that  $\alpha^{(\pm)}$  gives the  $(F_{B2} - F_{B1})$ -absorption splitting and agrees with experiments very well, but both the  $F_{B1}$ -absorption energy and

Table I. — *The absorption energies (eV)  $F_{B1}$  and  $F_{B2}$  for  $F_B(\text{Na})$ -centres in KCl. The calculated results for different forms of ion size correction are presented in the first four columns. The experimental results are taken from reference [5].*

	$\alpha = 0.53$	$\alpha = 1$	$\alpha = \alpha^{(\pm)}$	$\alpha = \alpha^I$	expt
$F_{B1}$	2.94	2.23	2.72	3.13	1.95
$F_{B2}$	1.56	3.60	3.26	1.09	2.43
$(F_{B2} - F_{B1})$ splitting	- 1.38	1.37	0.54	- 2.04	0.48

$F_{B2}$ -absorption energy are about 0.8 eV higher than from experimental results. All the other three forms of ion size correction give splitting which is much too large compared to the experimental value and is even wrong in sign for the case of  $\alpha = 0.53$  and  $\alpha = \alpha^I$ . From the calculation of  $F_A$ -centre absorption [9] and the present work on  $F_B$ -centre absorption, we conclude that the Bartram *et al.* ion size correction with  $\alpha = \alpha^{(\pm)}$  is useful for analysing the absorption splitting of the impurity centres. The high absorption energies are probably due to the neglect of the ionic polarization and the form of wave function for 2p states.

Table II. — *Contributions (eV) to  $F_{A1}$ ,  $F_{B1}$ ,  $F_{A2}$ ,  $F_{B2}$ -absorption energies and  $(F_{A1} - F_{B1})$ ,  $(F_{A2} - F_{B2})$  from kinetic ( $\bar{T}'$ ), point-ion ( $\bar{V}'_{\text{pl}}$ ) and ion-size ( $\bar{V}'_{\text{is}}$ ) energies for  $\alpha = \alpha^{(\pm)}$ .*

	$\bar{T}'$	$\bar{V}'_{\text{pl}}$	$\bar{V}'_{\text{is}}$	Total	expt
$F_{A1}$	1.76	0.33	0.56	2.65	
$F_{B1}$	1.66	0.56	0.25	2.47	
$(F_{A1} - F_{B1})$	0.10	- 0.23	0.31	0.18	0.17
$F_{A2}$	2.23	- 0.42	1.10	2.91	
$F_{B2}$	2.54	- 0.89	1.36	3.01	
$(F_{A2} - F_{B2})$	- 0.31	0.47	- 0.26	- 0.10	- 0.08

In table II, we analyse the role of impurity cations in  $F_B$ -centres, with respect to  $F_A$ -centres, by comparing the various contributions from the kinetic ( $\bar{T}'$ ), point-ion ( $\bar{V}'_{\text{pl}}$ ) and ion-size ( $\bar{V}'_{\text{is}}$ ) energies to the various absorption energies, for the form of ion size correction with  $\alpha = \alpha^{(\pm)}$ . The result for  $F_A$ -centres comes from the work of reference [9] but was not reported there. The main difference between the methods used in this work and those in reference [9] is that two substitutional cations are included in region I instead of the one cation in reference [9]. For  $(F_{A1} - F_{B1})$  energy differences, we find that the second impurity cation lowers the ion-size energy and increases the point-ion energy, because the impurity cation is small in size and relaxes outward by more than the nearest neighbour cation in the  $F_A$ -centre. Thus the point ion interaction between the excess electron and the nearest neighbour is higher in  $F_{A1}$  than  $F_{B1}$ . For  $(F_{A2} - F_{B2})$ , where the excess electron

is not overlapping with the impurity ions, the major contribution comes from the point-ion energy. We conclude that the effect of the second substitutional impurity cation on the absorption energy comes not only through its ion-size difference but also through the detail of its ground state distortion field. However, we have only included the electron energy of  $F_A$  and  $F_B$ -absorption in table II, and should be able to explain the difference of the observed absorption energies. By including the lattice energy ( $V_L + d.e$ ), the calculated ( $F_{A1} - F_{B1}$ ) becomes  $-0.6$  eV, in contrast to the observed  $0.17$  eV. We feel that this is probably due to the accuracy of calculating  $V_L$  and the neglect of the ionic polarization.

One of the nice features of our calculation is that we are able to give the displacement of the ions near the defect self-consistently to the electronic wave function. Some of the calculated displacements for the

Table III. — Ground state distortion field for  $\alpha = \alpha^{(\pm)}$ . The coordinate axis is shown in figure 1.

Perfect lattice site	Displaced lattice site
(0, 1, 0)	(0.00, 1.04, 0.00)
(1, 0, 0)	(0.93, 0.00, 0.00)
(1, 1, 0)	(0.93, 1.01, 0.00)
(1, 0, 1)	(1.00, 0.00, 1.00)
(1, 1, 1)	(0.99, 1.00, 0.99)
(2, 0, 0)	(1.97, 0.00, 0.00)
(0, 2, 0)	(0.00, 1.98, 0.00)

ions in the coordinate axis, as shown in figure 1, are given in table III for  $\alpha = \alpha^{(\pm)}$ . The two impurity cations relax outward about 4% and the four nearest neighbour host cations squeeze in the vacancy by 7%.

## DISCUSSION

*Question.* — H. J. PAUS.

With your calculation you get an inward relaxation of the host lattice ions around the  $F_B$ -centre and an outward relaxation of the impurity ions. How does this situation compare with the simpler  $F_A$  or the F-centre itself. From simple considerations of the ionic charge arrangement and the binding properties of the electron I would suspect the reverse to be true?

*Reply.* — C. K. ONG.

By using the similar model and methods we have found that the nearest neighbour relaxed inward by 5% in F-centre KCl (*Phys. Rev. B* **15** (1977) 3898) and relaxed inward by 4% in  $F_A(\text{Na})$ -centre in KCl (Ref. [9]). The displacements of the ions are determined by the forces, due to the defect acting on it. Different forms of ion-size correction and interionic potential would give different displacements.

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