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Theory of F_A-center optical absorption in alkali halides: Symmetry-adapted wave functions

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Flexible symmetry-adapted trial pseudowave functions are used to estimate variationally the optical-absorption energies of F_A centers in KCl:Na, KCl:Li, RbCl:Na, and KF:Li and of F centers in KCl, RbCl, and KF. The results are compared with previous work in which simple 1*s* and 2*p* functions were used. In the present work a form of the ion-size correction of Bartram, Stoneham, and Gash is used and lattice distortion is ignored except for a static displacement of the impurity cation. Contributions to the absorption splitting from kinetic, point-ion, and ion-size energies are obtained, and the effect of wave-function flexibility is analyzed.

I. INTRODUCTION

The present work is complementary to a recent paper by Ong and Vail[1] on the theory of F_A-center optical absorption. The reader may consult Ref. 1 for a review of earlier work, with references. It was found that the static point-ion model with the ion-size correction of Bartram *et al.*[2] could account qualitatively, and to some extent quantitatively, for experimental absorption data, provided the empirical factor $\alpha = 0.53$ was applied only to the anions. While Ref. 1 treated ground-state lattice distortion accurately by the method of lattice statics, very simple one-parameter Gaussian localized 1*s* and 2*p* trial pseudo wave functions were used, and these did not conform to the lowering of the F-center symmetry by the substitutional monovalent cation impurity in the F_A center. In the present work, more flexible wave functions, capable of reflecting the actual symmetry of the defect, are used in exactly the same crystal model, but lattice distortion is ignored except for displacement of the impurity cation along the defect's axis.

In Sec. II, details of the computational procedure are given. Section III begins with a discussion of impurity-cation displacement, followed by an analysis of the role of the empirical factor α of Ref. 2, giving results in agreement with Ref. 1. In Sec. IV detailed results are given in KCl:Na, KCl:Li, RbCl:Na, and KF:Li, including comparison with F-center results computed in the same way, comparisons with experiment, and analysis of the effect of increasing wave-function flexibility and of the contributions of kinetic, point-ion, and ion-size energies to the absorption splitting. In Sec. V we summarize our results and conclusions.

II. COMPUTATIONAL PROCEDURE

Our results have been obtained using a Harwell program written by one of us (A.H.H.), namely PRISM (polarized-relaxed-ion-size model), for the calculation of the electronic structure of one-electron-excess color centers in ionic crystals. PRISM has a variety of convenient features, only a few of which were used in the present work. Thus vacancies and ionic interstitials can be introduced into the lattice, which enabled us to deal with the F_A center, including impurity-cation displacement. Otherwise, lattice distortion and polarization were neglected. Defect electronic energy levels are estimated variationally, and the ion-size correction of Ref. 2 can be included with any desired values of the coefficients, and this enabled us to investigate the effect of empirical modification of the coefficients. In most cases the energy was evaluated to an accuracy of 3×10^{-3} eV.

PRISM applies the variational principle to wave functions of the form

$$\phi(\vec{r}) = \sum_{l,m} X_{l,m}(\theta,\phi) R_{l,m}(r) \quad , \tag{1}$$

where

$$R_{l,m}(r) = \sum_i w_{ilm} R'_{ilm}(r) \quad , \tag{2}$$

$$R'_{ilm}(r) = N_{ilm} r^{n_{ilm}-1} \exp(-K_{ilm} r) \quad , \tag{3}$$

TABLE I. F_A-center ground-state energy (eV) in KCl:Na as a function of impurity-cation displacement y_0 (units of nearest-neighbor distance) away from the vacancy. E_{el} is electron energy and V_L is lattice energy.

y_0	E_{el}	V_L	$(E_{\text{el}}+V_L)$
0.10	−4.59	6.49	1.90
0.20	−4.30	6.17	1.87
0.30	−4.05	6.04	1.99

$$N_{ilm} = \left\{ \frac{(2K_{ilm})^{2n_{ilm}+1}}{(2n_{ilm})!} \right\}^{1/2} , \qquad (4)$$

so that

$$\int_0^\infty dr\, r^2 R_{ilm}'(r) = 1 \quad .$$

In Eq. (1), $X_{l,m}$ are normalized real-spherical harmonics. The user specifies the ranges of l, m, and i in Eqs. (1) and (2), and the integer values of n_{ilm} in Eq. (3). PRISM then minimizes the energy with respect to any unspecified K_{ilm} and w_{ilm} (up to specified limits), maintaining normalization of $R_{l,m}$. In our work we determined preliminary values of K's for simple functions of the form $X_{l,m} r^l \exp(-Kr)$. Multiples and fractions of these K values in conjunction with values of $n_{ilm} \geq 1$, sometimes selected on the basis of further preliminary calculations, were then used to form five R_{ilm}''s as in Eq. (3), whose coefficients w_{ilm} in Eq. (2) were varied in the minimization. This procedure has been found to be quite efficient.

Our final results on F_A-center states used four $X_{l,m}$ in Eq. (1), so most of what follows is based on 20-parameter variational functions. The F_A-center ground state and the F_{A1} excited state that overlaps the impurity cation were represented by (l,m) values (0,0), (1,0), (2,0), (3,0), i.e., with s, p, d, and f components. PRISM provided the two lowest states of this form. The F_{A2} excited state, oriented perpendicular to the defect's axis, was represented by $(l,m)=(1,1)$, (2,1), (3,1), (3,3), i.e., by p, d, and f components. In this way the same maximum l-value and the same number of variational parameters occurred for each of the ground and two excited states. For the F center, the ground state has s and g components $(l,m)=(0,0)$, (4,0), and the excited state had p and f components $(l,m)=(1,0)$, (3,0). Full details of all wave functions used in this work are available.

TABLE II. Splitting $F_{A2}-F_{A1}$ and F_{A2} absorption energies (eV) of the F_A center in KCl:Na versus empirical parameter α of Ref. 2, compared with experiment.

	$\alpha=0.53$	$\alpha=1$	$\alpha^{(\pm)}=(1,0.53)$	expt.
$F_{A2}-F_{A1}$	−0.10	0.28	0.19	0.23
$F_{A2\text{abs.}}$	1.67	2.12	2.63	2.35

III. MODEL PRELIMINARIES

The four F_A centers analyzed in this paper include different impurities in a given host (KCl:Li and KCl:Na), different host cations for given anion and impurity (KCl:Na and RbCl:Na), and different host anions for given host cation and impurity (KCl:Li and KF:Li). All four have been investigated experimentally.[3,4] Two are type I and two are type II with respect to emission, and KF:Li is an extreme case, having much the largest absorption splitting of any known F_A center. The distinction between type-I and type-II F_A centers is described in Ref. 3. Basically, type-I emission is from the vacancy lattice configuration, as for the F center, while type-II emission is from the saddle point, or activated vacancy configura-

TABLE III. Theoretical and experimental F- and F_A-center absorption energies (eV).

	Theory			Experiment		
	F center	$F_{A2\text{abs.}}$	$F_{A2}-F_{A1}$	F center	$F_{A2\text{abs.}}$	$F_{A2}-F_{A1}$
KF	3.44			2.80		
KF:Li		3.58	0.45		2.89	0.55
KCl	2.61			2.34		
KCl:Li		2.63	0.24		2.25	0.27
KCl:Na		2.63	0.19		2.35	0.23
RbCl	2.44			2.03		
RbCl:Na		2.43	0.18		2.09	0.24

TABLE IV. Effect of increasing wave-function flexibility on F- and F_A-center energies (eV) in KCl:Na (see Sec. IV).

F_A center	ground	$F_{A\,2\text{abs.}}$	$F_{A2}-F_{A1}$
$\vert s\rangle, \vert p\rangle$	−4.27	2.82	0.33
$\vert s+p\rangle, \vert p\rangle$	−4.72	2.88	0.29
$\vert s+p+d+f\rangle, \vert p+d+f\rangle$	−4.73	2.63	0.19

F center	ground	$F_{\text{abs.}}$
$\vert s\rangle, \vert p\rangle$	−4.43	2.80
$\vert s\rangle'\rangle, \vert p'\rangle$	−4.96	3.24
$\vert s''\rangle, \vert p''\rangle$	−4.90	2.87
$\vert s+g\rangle, \vert p+f\rangle$	−4.98	2.61

tion.

The results of Ref. 1 (Table IV), based on thorough treatment of lattice relaxation, show outward displacements from the vacancy of 0.08, 0.05, and 0.07 nearest-neighbor distances for the impurity in the ground state of the F_A center in KCl:Li, KCl:Na, and RbCl:Na, respectively, and these are large compared with the displacements of all other ions, except that the four nearest host cations in the plane perpendicular to the defect axis are drawn inward by comparable amounts (0.04–0.05). We have chosen to include only impurity cation displacements of 0.08 for KCl:Li, 0.06 (*sic*) for KCl:Na, 0.07 for RbCl:Na, and 0.10 for KF:Li, for the latter of which no previous calculations have been done. Note that these values are smaller than those obtained by minimizing total energy (electron plus lattice) with respect to impurity-cation displacement alone, plus wave function, because the variational principle favors distribution of the lattice relaxation energy among more ions when the calculation allows it, as in Ref. 1. This is illustrated in Table I for KCl:Na by combining our results for electronic energy E_{el} with the lattice energy V_L,[5] based on charged point ions with Born-Mayer repulsion, for different values of Na^+ displacement, y_0. We see that the energy minimum would occur for $y_0 \gtrsim 0.15$, compared to 0.05 obtained in Ref. 1.

In Ref. 1 it was found that the empirical parameter $\alpha = 0.53$ introduced for all ions by Bartram *et al.*,[2] which provided good agreement with experimental F-center absorption energies, led to splitting in the wrong direction for the F_A-center absorption lines. It was further found, in agreement with previous results of Weber and Dick[6] and of Alig,[7] that $\alpha = 1$ (no empirical correction) led to splittings in the correct direction, but much too large (with one exception), while reintroducing $\alpha = 0.53$ only for the anions gave good quantitative agreement with experiment for the splittings, leaving the absorption energies ~0.5 eV too high. We have re-examined the role of α in the absorption process, Table II, with results that agree qualitatively with Ref. 1. Thus we conclude that these results of Ref. 1 did not arise from neglect of lowered wave-function symmetry. We can also see, by comparing Table II with Ref. 1 (Tables I and II, KCl:Na) that our flexible symmetry-adapted wave

TABLE V. Contributions (eV) to F_A-center absorption splitting from kinetic (T), point-ion (V_{PI}), and ion-size (V_{IS}) energies.

Crystal	T	V_{PI}	V_{IS}	Total
KF:Li	0.258	−0.054	0.250	0.45
KCl:Li	0.245	0.005	−0.004	0.24
KCl:Na	0.173	−0.009	0.029	0.19
RbCl:Na	0.183	−0.015	0.017	0.18

TABLE VI. Contributions (eV) to F_A-center absorption splitting in KCl:Na as a function of impurity-cation outward displacement y_0 (units of nearest-neighbor spacing).

y_0	T	V_{PI}	V_{IS}	Total
0.03	0.150	0.045	+0.000	0.19
0.06	0.173	−0.009	0.029	0.19
0.10	0.218	−0.088	0.056	0.19

functions reduce the variation of the results from one value of α to another. In Sec. IV we restrict attention to calculations in which $\alpha = 0.53$ is used for anions, and $\alpha = 1$ is used for cations, for which we introduce the notation $\alpha^{(\pm)}$.

IV. RESULTS

In this section we begin with our results for F- and F_A-center absorption energies, compared with experiment, and then examine some details of wave-function flexibility and of various contributions to the energy.

As described in Sec. II, we have estimated F_A-center absorption using ground and excited states which include components up to $l = 3$, with 20 variational parameters, and F-center states with l up to 4, and 10 variational parameters. In all cases we have used $\alpha^{(\pm)}$ (see Sec. III), with impurity-cation outward displacements $y_0 = 0.06$, 0.08, 0.07, and 0.10 for KCl:Na, KCl:Li, RbCl:Na, and KF:Li, respectively. Using the same value of y_0 for ground and excited states is consistent with the Franck-Condon principle that no lattice relaxation occurs during absorption, and using $y_0 = 0.08$ for KCl:Li ignores the fact that in this defect the impurity tunnels between four equivalent off-axis sites.[8] Our results are summarized in Table III, along with experimental data. We observe, as expected, that the agreement with experiment for F-center absorption, here based on $\alpha^{(\pm)}$, is inferior to that obtained with $\alpha = 0.53$ for all ions as used by Harker[9] in a similar calculation with somewhat less flexible wave functions. However, the difference between F and F_{A2} absorption energies is fairly consistent with experiment, as is $F_{A2} - F_{A1}$ absorption splitting, with absorption energies 0.3 to 0.7 eV too high, as found in Ref. 1. We conclude from this that the role of the impurity is rather well described by our use of $\alpha^{(\pm)}$.

In Table IV we show the effect of increasing the flexibility of the trial wave function for F and F_A centers in KCl:Na, using $\alpha^{(\pm)}$. For the F_A center, three cases are considered: (i) $|s\rangle$ and $|p\rangle$ ground and excited states, respectively, with one variational parameter each, namely, the K of Eq. (3); (ii) $|s+p\rangle$ ground and F_{A1} excited states, with a $|p\rangle$ F_{A2} excited state, each l component having five variable w's [Eq. (2)]; and (iii) the $|s+p+d+f\rangle$ and $|p+d+f\rangle$ states described in Sec. II, each with 20 parameters. The results show a steadily dropping ground-state energy and $F_{A2} - F_{A1}$ splitting, but irregular F_{A2} absorption energy. These results occur for the other F_A centers as well. For the F center, four cases are considered: (i) the same as for the F_A center; (ii) $|s'\rangle$ and $|p'\rangle$ functions each with two variable K's; (iii) $|s''\rangle$ and $|p''\rangle$ functions each with five variable w's; and (iv) the $|s+g\rangle$ and $|p+f\rangle$ combinations described in Sec. II. We see that (ii) and (iii) are comparable in estimating the ground-state energy, but the former is very poor in estimating the excited-state energy, while the g and f admixtures to the ground and excited states, respectively, have a not quite negligible effect, particularly on the absorption energy, when comparison is made with the experimental values of Table III.

It is of interest to see how kinetic, point-ion, and

TABLE VII. Contributions (eV) to F_A-center absorption splitting in KCl:Na for wave functions of increasing flexibility.

Wave functions	T	V_{PI}	V_{IS}	Total
$\|p\rangle, \|p'\rangle$	0.167	−0.219	0.384	0.33
$\|s+p\rangle, \|p''\rangle$	0.208	−0.214	0.306	0.30
$\|s+p+d+f\rangle, \|p+d+f\rangle$	0.173	−0.009	0.029	0.19

TABLE VIII. Ground-state electronic energy (eV) of the F_A center in KCl:Na.

y_0	Wave function	T	V_{PI}	V_{IS}	Total
0.05	$\exp(-\lambda^2 r^2)$	2.06	−7.58	0.66	−4.86
0.06	$\exp(-Kr)$	1.85	−6.96	0.85	−4.27
0.06	$\lvert s+p+d+f\rangle$	1.94	−7.37	0.72	−4.73
0.03	$\exp(-Kr)$	1.86	−7.07	0.84	−4.37
0.03	$\lvert s+p+d+f\rangle$	1.95	−7.49	0.72	−4.82

ion-size contributions to the electronic energy show up in the F_A-center's absorption splitting. These contributions, representing the difference between the two inequivalent F_{A2} and F_{A1} excited states, are given in Table V. The results are quite different from those obtained in Ref. 1, where T and V_{IS} were found to contribute about equally to the splitting, with strong cancellation from a large negative V_{PI} contribution. Here, most of the splitting comes from the kinetic energy difference, with weak V_{PI} and V_{IS} contributions tending to cancel. The features which distinguish Ref. 1 from the present work are the full lattice relaxation and the simple symmetric Gaussian localized wave functions of the former. The results of Table V are insensitive to impurity-cation displacement y_0, as shown in Table VI for our most flexibie functions, but are quite sensitive to wave-function asymmetry and flexibility, as shown in Table VII for $y_0=0.06$, where the simpler functions [not quite as symmetrical as those of Ref. 1, since here we use $(l,m)=(1,0)$ for the simplest F_{A1} state and $(l,m)=(1,1)$ for the F_{A2} state] behave more like those of Ref. 1.

Finally a comment on the form of trial wave functions used here. We can directly compare (Table VIII) our estimate of the F_A-center's ground-state energy, in KCl:Na for example, with $y_0=0.06$ and 0.03, using a simple 1s-type of function $\phi\sim\exp(-Kr)$ and also using a symmetry-adapted $\lvert s+p+d+f\rangle$ function containing 20 parameters, with Ong's result[10] for the ground-state electronic energy evaluated with $y_0=0.05$ but without any other lattice relaxation, using $\phi\sim\exp(-\lambda^2 r^2)$. The result is that, simply in terms of energy, the one-parameter Gaussian is superior to our most ambitious wave function, and that with increasing flexibility our wave functions move toward the higher kinetic energy and lower potential energy of the Gaussian. This sort of result has also been observed in F^+-center calculations in CaO.[11]

V. CONCLUSION

This work demonstrates that when symmetry-adapted trial wave functions are introduced into F_A-center absorption calculations, certain results of Ref. 1 persist, namely (Table II), that $\alpha^{(\pm)}=(1,0.53)$ for the empirical parameter of Ref. 2 yields quantitatively correct splitting but absorption energies ~0.5 eV higher than experimental values. Since this result is insensitive to impurity cation displacement (Table VI), the splitting depends essentially on the impurity's ion-size effect. Among the results (Table III) is the first theoretical analysis of the F_A center in KF:Li. Generally, we find that to introduce wave-function components up to $l=3$ has a significant effect on the absorption energies (Table IV) and on the relative roles of excited-state kinetic and potential energies in the absorption splitting (Tables V and VII), but it is suggested (Table VIII) that Gaussian rather than Slater-type localization may be more appropriate for F and F_A centers.

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