PHYSICAL REVIEW B VOLUME 18, NUMBER 12 15 DECEMBER 1978

Theory of F_A-center optical absorption in alkali halides: Lattice statics analysis

Chong Kim Ong
Department of Physics, Ahmadu Bello University, Zaria, Nigeria

John M. Vail
Department of Physics, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada

(Received 19 June 1978)

F_A-center optical absorption is analyzed theoretically for 12 doped alkali halides, including two with heavy impurities. The ground state is estimated variationally, including static-lattice distortion. A form of the ion-size correction of Bartram, Stoneham, and Gash is found to give good qualitative, and some quantitative, agreement with experimental values of absorption energies and splittings. Details are given of lattice distortion in the ground state and of the contributions from kinetic, point-ion, and ion-size energies to the absorption splitting.

I. INTRODUCTION

The F_A center that we shall discuss is an F center (electron trapped at an anion vacancy) adjacent to a substitutional impurity cation in an alkali halide of the NaCl structure. The review by Lüty[1] remains the definitive work on the experimental properties of these F_A centers. With respect to optical absorption (Ref. 1, Sec. III A), the role of the impurity in shifting and splitting the transition energy relative to that of the ordinary F center in the same host crystal is of primary interest. There have been previous theoretical analyses by several authors,[2-6] as well as by the present authors.[7] This work extends the previous ones in three respects: (i) by examining a wider variety of crystals; (ii) by further assessing the ion-size correction used in describing the electron-ion interaction; and (iii) by including lattice relaxation fully.

In Sec. II, the previous theoretical work is briefly reviewed. In Sec. III, our model and procedure are outlined and compared with the earlier work. In Sec. IV, our results are presented, in comparison with experiment. It is found that the "standard" form of ion-size correction, namely, that which has been highly successful for the F-center absorption process,[8,9] fails entirely for F_A-center absorption, and that two other simple forms provide qualitative, and some quantitative, agreement with experiment. In Sec. V our procedure is discussed critically, and our conclusions are presented.

II. REVIEW OF EARLIER WORK

The earliest theoretical work on F_A-center absorption, done in 1961 by Kojima *et al.*[2] for KCl:Na, was based on a simplified molecular orbital approach, and demonstrated the credibility of the now-accepted model of this defect. Later, Smith[3] performed a pseudopotential analysis for KCl:Na and KCl:Li, including ion-size effects for nearest neighbors only, and obtained results which were in qualitative agreement with experiment. In 1969 Evarestov,[4] using a model potential out to third neighbors, obtained similar results for KCl:Na. There followed three works based on the ion-size correction of Bartram *et al*,[8] which is a pseudopotential method with simplifications. (i) Weber and Dick[5] found, using the self-consistent method of Ref. 8, that the empirical factor $\alpha = 0.53$ gave absorption splitting in the wrong direction (Ref. 5, Table IV, δE_2 for the F_A center in KCl:Na) and that setting $\alpha = 1$ tended to give qualitative agreement with experiment (Ref. 5, Table IX), while at the same time leading to extensive disagreement with the Mollwo-Ivey relation for ordinary F-center absorption (Ref. 5, Fig. 6), a conclusion borne out in Ref. 8 and later by our work,[9] which, unlike Refs. 5 and 8, included lattice relaxation. Weber and Dick also found (Ref. 5, Table X) that an *ad hoc* modification of the scheme of Bartram *et al.*[8] led to more uniform agreement with experiment for F- and F_A-center absorption in KCl. (ii) Alig[6] used an ion-size correction very similar to, and partly derived from, that of Ref. 8, with a variety of pseudo wave functions, and including lattice relaxation for the F_A center's six nearest neighbors, one of which is the impurity cation. His conclusions were very similar to those of Weber and Dick, namely, that $\alpha = 0.53$ was inappropriate for F_A absorption and that $\alpha = 1$ gave qualitative agreement with experiment. (iii) Finally, in 1973 the present authors[7] attempted to analyze F_A absorption and type-I and type-II emission in KCl:Na and KCl:Li. In that work the ion-size correction of Ref. 8 with $\alpha = 0.53$ was combined with the lattice-static method for color centers,[10,11] in which lattice relaxation and variational treatment of the psuedo wave function are incorporated self-consistently. Unfortunately, an error described in Sec. III was made in evaluating the ion-size correction. The result was that, contrary to Refs. 5, 6, and the present work, $\alpha = 0.53$ gave absorption splitting in the correct direction.

III. MODEL AND PROCEDURE

Our model has been extensively discussed in Sec. II of Ref 7, and should be reviewed by the reader, ignoring the very brief references to saddle-point and relaxed excited states. Section II of Ref. 7 is complete and correct: the error in Ref. 7 was in neglecting the dependence of $\overline{V}$ [Ref. 8, Eq. (2.12b)] on lattice distortion $(\underline{\xi}, \underline{\mu})$ in minimizing E with respect to $(\underline{\xi}, \underline{\mu})$ [Ref. 7, Eq. (14)]. This error has been rectified in the present work.

The two most extensive previous works on this subject were by Weber and Dick[5] and by Alig.[6] Our present treatment goes beyond both of these in determining the ground-state lattice relaxation fully self-consistently with the variational pseudo wave function. Weber and Dick apparently did not include any lattice relaxation, and Alig allowed for displacements of the six nearest-neighbor ions only, that for the impurity cation being distinct from the other five. However, instead of minimizing the energy with respect to parameters of the variational pseudo wave function, he used values obtained in other works. Note that Alig's treatment does not allow for the host cation that is diametrically opposite to the impurity to be displaced by an amount different from the four other host nearest neighbors, as it would be, and as in our treatment it is.

At this point it is worthwhile to summarize the deficiencies of our model and procedure. First, lattice-dynamic effects are entirely ignored, as is the electronic polarizability of the ions. Second, there are the approximations used in the ion-size correction: free-ion wave functions, and the ignoring of the variation of the pseudo wave function over the ionic diameter. Third, we assumed instantaneous C_{4v} symmetry of the defect, ignoring the tunneling motion of the impurity that is detected in KCl:Li,[12] but that apparently does not occur in KBr:Li.[13] Fourth, there is the simplicity and symmetry of the form of trial pseudo wave functions, taken spherically symmetric in the ground state and antisymmetric in the excited states, in spite of the average C_{4v} symmetry of the surrounding lattice, and in all cases containing only a single variational (localization) parameter. We shall return to the second and fourth of these points in Sec. V.

IV. RESULTS

A. Absorption energies

Tables I and II summarize our principal results on F_A-center absorption energies, and include the available experimental data. Table I gives the F_{A2}-absorption energies, arising from the excited state that overlaps a pair of host alkali ions, and Table II gives the F_{A2}-F_{A1} splitting, i.e., the energy difference between F_{A2} absorption and F_{A1} absorption (where in the latter, the excited state overlaps the impurity ion). Thus the F_{A1} absorption is obtained by subtracting the splitting from the F_{A2}-absorption energy. Certain features of the experimental data are worth noting, namely, that (i) the F_{A2} absorption is close to the F-center absorption (shown in Table I), following the Mollwo-Ivey relation, and closer for the larger impurity, with the exception of KF; (ii) the F_{A2}-absorption energy increases with impurity cation size for a given host crystal; (iii) the splittings are all positive (and all the observed cases have impurity cations smaller than host cations); and (iv) the splittings diminish with increasing impurity cation size (except in RbCl).

In the theoretical results, three sets of data are given, according to the value of the parameter α of Ref. 8, $\alpha = 0.53$ and $\alpha = 1$ being applied to *all* ions of the crystal in the two cases, respectively, and $\alpha^{(\pm)}$ signifying a calculation in which all cations (including the impurity) have $\alpha = 1$ and all anions have $\alpha = 0.53$. Note in Table II that the case $\alpha = 0.53$, which is highly successful for F-center absorption,[8,9] gives splittings that are very large compared to experiment, but, worse still, are of the wrong sign, making F_{A2} absorption, which should be comparable to ordinary F absorption, much too small. This is unpleasant, because, following the success of $\alpha = 0.53$ for F centers,[8] is was hoped that it would be useful in analyzing other similar defects, and nothing is closer to F-center absorption than F_{A2} absorption. If one falls back on the original form of the theory in Ref. 8, namely, no empirical correction, then although $\alpha = 1$ is unsuccessful in F-center absorption, we see from Tables I and II that the sign of the splitting is rectified (as found by Weber and Dick[5]) in cases that can be compared with experiment, namely, in KCl:Na, KCl:Li, RbCl:Li, and RbBr:K, and that experimental properties (ii) and (iv) above are reproduced as well. However, three of the four splittings are much too large, and all four

TABLE I. F_{A2}-absorption energies (eV) of F_A-centers and F-center absorption energies (experiment, eV) in alkali halides. The first three columns are present theoretical results based on different forms of the ion-size correction of Ref. 8 (see text, Sec. IV A).

Crystal	$\alpha = 0.53$	$\alpha = 1$	$\alpha^{(\pm)}$	Expt.	F center
KF:Na	•••	•••	•••	2.96 [a]	2.80
KF:Li	•••	•••	•••	2.89 [a]	
KCl:Rb	2.87	3.63	3.19	•••	2.34
KCl:Na	1.90	3.28	2.93	2.35 [b]	
KCl:Li	1.42	3.05	2.76	2.25 [b]	
KBr:Rb	•••	2.53	3.46	•••	2.08
KBr:Na	•••	•••	2.68	2.07 [b]	
KBr:Li	1.40	[c]	2.50	2.00 [b]	
RbCl:K	•••	3.40	3.47	•••	2.03
RbCl:Na	1.15	•••	2.58	2.09 [b]	
RbCl:Li	0.73	2.46	1.91	1.95 [b]	
RbBr:K	1.69	2.42	2.53	1.85 [b]	1.85
RbBr:Na	1.16	2.20	2.03	•••	
RbBr:Li	•••	•••	2.09	1.78 [b]	
RbI:Li	•••	•••	•••	1.62 [d]	1.71

[a] L. F. Mollenauer, B. A. Hatch, D. H. Olson, and H. J. Guggenheim, Phys. Rev. B 12, 731 (1975).

[b] F. Lüty, Ref. 1.

[c] No convergence.

[d] H. Ohkura, Prog. Theor. Phys. (Kyoto) Suppl. 46, 11 (1970).

TABLE II. F_A-center absorption energy splitting (eV) in alkali halides. The first three columns are present theoretical results based on different forms of the ion-size correction of Ref. 8 (see Sec. IV A).

Crystal	$\alpha = 0.53$	$\alpha = 1$	$\alpha^{(\pm)}$	Expt.
KF:Na	•••	•••	•••	0.31 [a]
KF:Li	•••	•••	•••	0.55 [a]
KCl:Rb	0.45	−0.24	−0.11	•••
KCl:Na	−0.65	0.76	0.27	0.23 [b]
KCl:Li	−0.95	0.84	0.29	0.27 [b]
KBr:Rb	•••	−0.16	−0.10	•••
KBr:Na	•••	•••	0.22	0.17 [b]
KBr:Li	−0.76	[c]	0.24	0.18 [b]
RbCl:K	•••	0.25	0.06	•••
RbCl:Na	−1.05	•••	0.22	0.24 [b]
RbCl:Li	−1.26	0.88	0.24	0.23 [b]
RbBr:K	−0.37	0.16	0.05	0.18 [b]
RbBr:Na	−0.87	0.58	0.18	•••
RbBr:Li	•••	•••	0.19	0.21 [b]
RbI:Li	•••	•••	•••	0.14 [d]

[a] L. F. Mollenauer, B. A. Hatch, D. H. Olson, and H. J. Guggenheim, Phys. Rev. B 12, 731 (1975).

[b] F. Lüty, Ref. 1.

[c] No convergence.

[d] H. Ohkura, Prog. Theor. Phys. (Kyoto) Suppl. 46, 11 (1970).

F_{A2}-absorption energies are too high. The final column of theoretical results, $\alpha^{(\pm)}$, is motivated by the idea that $\alpha = 1$ may be appropriate for the highly localized cations, but that $\alpha = 0.53$ (or some similar number < 1) is needed to compensate for the pseudo wave function's variation over the anions, which is otherwise neglected in Ref. 8. The result, (Tables I and II) is that the splittings become quite satisfactory in three out of the four cases and in four others, namely, KBr: Na, KBr: Li, RbCl: Na, and RbBr: Li, remaining correct in sign, and also the F_{A_2} energies are improved over the $\alpha = 1$ case, though they are still high with one exception: RbCl: Li. To summarize at this point, we conclude that the form of ion-size correction identified by $\alpha^{(\pm)}$ provides good qualitative, and some quantitative, agreement with experimental F_A-center absorption. It would be interesting to know how well this applied to F-center absorption, and whether F- and F_A-absorption results collectively would be improved by a similar scheme (i.e., different α's for cations and anions, not necessarily 1 and 0.53, respectively).

Some further details of our results will now be discussed. Note that in Tables I and II results are given for two F_A centers with impurities *larger* than the host cations, namely, KCl:Rb and KBr:Rb. In these two cases the predicted splittings (with $\alpha = 1$ or $\alpha^{(\pm)}$) are *negative*, which is plausible, and the F_{A2} absorption follows the trend established by Li and Na impurities. Experimental evidence for one of these centers is found in a paper by Ohkura and Mori,[14] where they identify the F_A center in KCl:Rb, but do not give its absorption spectrum.

As in our previous work (Ref. 7, Sec. III E), wherever an entry appears in Tables I and II, there is available not only the data given, but the various contributions to the ground-state energy from kinetic ($\overline{T}$), point-ion ($\overline{V}_{\text{PI}}$), ion size ($\overline{V}_{\text{IS}}$), and lattice defect [$V_L(\underline{0})$] energies ignoring harmonic lattice distortion, plus the total energy E_d associated with harmonic lattice distortion and self-consistent readjustment of the trial pseudo wave function. Also the kinetic ($\overline{T}^1$), point-ion ($\overline{V}^1_{\text{PI}}$), ion-size ($\overline{V}^1_{\text{IS}}$), and lattice defect ($V^1_L$) energies of the excited states (with the lattice in the configuration of the ground state) are available. These data enable us to identify the contributions of $\overline{T}^1$, $\overline{V}^1_{\text{PI}}$, and $\overline{V}^1_{\text{IS}}$ to the absorption splitting. This is done in Table III for the seven crystals for which the $\alpha^{(\pm)}$ form of ion-size correction is most successful in comparison with experiment. Qualitatively, one finds that the ion-size and kinetic energies are both lower for the F_{A1} state than for the F_{A2} state by about 0.7 and 0.5 eV, respectively, because the impurity is small and relaxes outward by more than the other nearest neighbors, while the point-ion interaction with the excess electron is higher in the F_{A1} than in the F_{A2} state, coming to within 0.2–0.3 eV of canceling the other two terms. We conclude that the lattice distortion plays a large role, along with the ion-size effect, in determining the F_A absorption splitting.

In addition to the above data, values of the wave-function parameters, denoted α_j ($j = 1, 2, 3$) in Eqs. (5)–(7) of Ref. 7, are available, as well as self-consistent nearest-neighbor displacements in the ground state, to be discussed below.

The situation, which is evident in Table II, that the F_A-absorption splitting changes sign somewhere between $\alpha = 0.53$ and $\alpha = 1$ has been examined in some detail. It is found that there is a region, which for KCl:Na includes $\alpha = 0.75$, 0.80, and 0.85, where self-consistency in determining $\overline{V}$ [Ref. 8, Eq. (2.12b)] in the ion-size correction is not obtainable for the F_{A1} state, which overlaps the impurity. This suggests a complicated analytical dependence of energy on α that we shall not follow up because we believe that *ad hoc* assignment of various values for α is of limited value.

TABLE III. Contributions (eV) to F_A-center absorption splitting from kinetic ($\overline{T}^1$), point-ion ($\overline{V}^1_{\text{PI}}$), and ion-size ($\overline{V}^1_{\text{IS}}$) energies.

Crystal	$\overline{T}^1$	$\overline{V}^1_{\text{PI}}$	$\overline{V}^1_{\text{IS}}$	Total
KCl:Li	0.62	− 1.10	0.78	0.29
KCl:Na	0.47	− 0.75	0.54	0.27
KBr:Li	0.57	− 1.01	0.68	0.24
KBr:Na	0.41	− 0.64	0.45	0.22
RbCl:Li	0.60	− 1.10	0.75	0.24
RbCl:Na	0.49	− 0.88	0.61	0.22
RbBr:Li	0.59	− 1.14	0.74	0.19

B. Ground-state lattice distortion

The displacements as calculated in units of nearest-neighbor spacing for the F_A center's six nearest neighbors in the $\alpha^{(\pm)}$ form of ion-size correction are given in Table IV. The coordinate axes are those shown in Fig. 1(a) of Ref. 7, where the impurity cation lies on the positive y axis at 010. Of the five nearest-neighbor host cations, four are equivalent to 100 and the fifth is $0\overline{1}0$. The components of a displacement $\vec{u}$ are denoted (u_x, u_y, u_z). The qualitative features of Table IV are essentially what one might expect: (i) that small impurities relax outward along the y axis, $u_y(010) > 0$, by amounts that decrease as their sizes increase, and that large impurities (Rb in KCl and KBr) relax inward; (ii) that with the smallest impurity, Li, the diametrically opposite host cations shifts outward in the negative y direction, $u_y(0\overline{1}0) < 0$, but with heavier impurities it shifts inward by larger amounts for larger impurities (note, however, that this effect may be a response to the spherical symmetry adopted for the ground-state trial pseudo wave function); (iii) that the nearest neighbors equivalent to 100 in the plane perpendicular to the defect's y axis

TABLE IV. Calculated nearest-neighbor displacements $\vec{u}$ in the F_A-center ground state (units: host-nearest-neighbor spacing). Impurity cation is at 010 before relaxation.

Crystal	u_y (010)	u_y ($0\overline{1}0$)	u_x (100)	u_y (100)
KCl:Li	0.08	− 0.008	− 0.05	0.009
KCl:Na	0.05	0.001	− 0.04	0.009
KCl:Rb	− 0.04	0.02	− 0.004	0.002
KBr:Li	0.07	− 0.007	− 0.005	0.008
KBr:Na	0.04	0.003	− 0.04	0.007
KBr:Rb	− 0.04	0.03	− 0.005	0.003
RbCl:Li	0.11	− 0.02	− 0.04	− 0.01
RbCl:Na	0.07	0.003	− 0.05	0.01
RbCl:K	0.02	0.02	− 0.03	0.01
RbBr:Li	0.10	− 0.01	− 0.06	0.003
RbBr:Na	0.06	0.005	− 0.05	0.01
RbBr:K	0.02	0.02	− 0.03	0.01

relax inward, $u_x(100) < 0$, by amounts comparable to those of nearest neighbors in a similar model of the F center (Ref. 9, Table IV), and also, with one exception, shift slightly in the positive y direction, $u_y(100) > 0$, toward the impurity; and (iv) that the relaxation of the impurity is generally greater than that of the other nearest neighbors. Alig's results for lattice distortion (Ref. 6, Table II) were obtained on the basis of a much-less-thorough treatment, and are considerably different, showing F-center and F_A-center host nearest-neighbor cations relaxing outward, $\sigma_0 < 0$ (note that his sign convention is different from ours), and with outward shifts, $\delta_0 < 0$, of the impurity larger than we obtain, no doubt partly because his procedure ignores relaxation of more distant ions, which is included in our lattice-statics treatment. Although our procedure is much more thorough and consistent that Alig's, it is known that the calculated small distortions around F-type center ground states are very sensitive to details of the model, and so we would not assume all qualitative details of Table IV to be valid predictions for as-yet unmeasured real distortions.

V. DISCUSSION AND CONCLUSION

At the end of Sec. III we listed some deficiencies of our model and procedure. One of these had to do with the form of the ion-size correction. We have seen that $\alpha^{(\pm)}$ ($\alpha = 0.53$ for anions, $\alpha = 1$ for cations) is a form that gives moderately good agreement with experiment, except that F_{A2} energies are about 0.5 eV too high. It is not known whether such a prescription can unify F- and F_A-center absorption results to provide good agreement with experiment, but it is known that Bartram *et al.*[8] tried a number of alternatives before determining that $\alpha = 0.53$ was best for the F-center, and that subsequent work of Gash[15] failed to produce any superior simple alternative. Thus it appears that a form of ion-size correction as simple as that of Ref. 8 cannot be relied upon to apply to a variety of states in a variety of color centers. An alternative form of ion-size procedure is required. Another deficiency of our method is the use of trial pseudo wave functions of symmetry higher than that of the surrounding lattice defect. This is a deficiency that could be removed, narrowing the range of model features responsible for the remaining discrepancy between theory and experiment. Some work has been done on this problem,[16] and will be submitted for publication.

In conclusion, we have carried out extensive calculations of F_A-center absorption energies, using a well-defined consistent model, which has reproduced the main qualitative features of the experimental results, as well as giving quantitative agreement on absorption splitting. The work enables one to clearly assess the ion-size correction used, and provides plausible details of ground-state lattice distortion, illustrating its role along with the ion-size effect in determining the splitting.

ACKNOWLEDGMENT

This work was supported in part by a research grant from the National Research Council of Canada.

---

[1] F. Lüty, in *Physics of Color Centers*, edited by W. B. Fowler (Academic, New York, 1968), Chap. 3.

[2] K. Kojima, N. Nishimaki, and T. Kojima, J. Phys. Soc. Jpn. 16, 2033 (1961).

[3] D. Y. Smith (unpublished), reported in Ref. 1, pp. 192–193.

[4] R. A. Evarestov, Phys. Status Solidi 35, K157 (1969).

[5] W. Weber and B. G. Dick, Phys. Status Solidi 36, 723 (1969).

[6] R. C. Alig, Phys. Rev. B 2, 2108 (1970).

[7] C. K. Ong and J. M. Vail, Phys. Rev. B 8, 1636 (1973).

[8] R. H. Bartram, A. M. Stoneham, and P. Gash, Phys. Rev. 176, 1014 (1968).

[9] C. K. Ong and J. M. Vail, Phys. Rev. B 15, 3898 (1977).

[10] A. M. Stoneham and R. H. Bartram, Phys. Rev. B 2, 3403 (1970).

[11] J. M. Vail, Phys. Status Solidi B 44, 443 (1971).

[12] F. Rosenberger and F. Lüty, Solid State Commun. 7, 983 (1969).

[13] T. Watanabe, Y. Mori, and H. Ohkura, J. Phys. Soc. Jpn. 42, 1787 (1977).

[14] H. Ohkura and Y. Mori, J. Phys. Soc. Jpn. 21, 817 (1966).

[15] P. W. Gash, Ph.D. thesis (University of Connecticut, 1970) (unpublished).

[16] J. M. Vail and A. H. Harker (unpublished).