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The Electronic Structure of F-Centres in Alkali Halide Crystals

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A method is presented for estimating the number of bound states of different orbital angular momentum quantum number for an F-centre residing in an alkali halide crystal through the introduction of a spherically symmetric potential well of finite depth. The method is illustrated through its application to the F-centre in sodium chloride, and the results for F-centres in various alkali halide lattices are tabulated. The results provide a good account of the experimental features of the F-centre including the K-band which we suggest is due to transitions from the $2p$ to excited levels. Values for the effective range of penetration of the defect electron with the neighbouring cation in different crystals are determined by requiring that the well depth be independent of orbital angular momentum quantum number. The technique is applied to estimate the Madelung constant and Madelung potential for the host crystal.

Apresenta-se um método para estimar o número de estados ligados de diferente momento angular orbital para um F-centro residente em um cristal de haleto alcalino, pela introdução de um polo de potencial esfericamente simétrico de profundidade infinita. O método é ilustrado pela sua aplicação ao F-centro em cloreto de sódio, e os resulta-

dos para F-centros em várias redes de haletos alcalinos são tabulados. Os resultados descrevem bem os dados experimentais do F-centro incluindo a banda K, que sugerimos ser devida a transições do nível $2p$ a níveis excitados. Determinamos valores para o alcance efetivo de penetração do elétron de defeito com o cation vizinho em diversos cristais, impondo que a profundidade do poço seja independente do número quântico de momento angular orbital. A técnica é aplicada para estimar a constante de Madelung e o potencial de Madelung para o cristal hospedeiro.

1. INTRODUCTION

Trapped electrons impart a colour to the crystal inwhich they reside owing to an electronic transition in the ultraviolet-visible region of the spectrum that is characteristic of the particular defect or "colour centre". In this paper a quantum mechanical method is developed to determine the electronic structure of an F-centre in an alkali halide crystal. The central hypothesis of this procedure is that the F-centre lies in a spherically symmetric potential well, while in fact the crystal lattice has cubic symmetry. Using the experimentally measured transition energy of a given F-centre and the ground state energy ofthe centre relative to the conduction band', one can ascertain the number of bound states of different orbital angular momentum quantum number through the solution of the transcendental equations summarized below.

The simplifying assumption of a spherically symmetric effective potential for a colour centre may be *rationalized* in *several* ways. First, we observe that the charge distribution of the alkali halide crystal lattice surrounding the defect centce may be viewed approximately as a spherical shell of charge surrounding the centre. The potential field of a sphere of total charge q and radius "a" is, in *mks* units[2],

$$V(r) = q/(4\pi\varepsilon a) \qquad (r \leq a) \qquad (1)$$

$$V(r) = q/(4\pi\varepsilon r) \qquad (r > a) \qquad (2)$$

where E is the dielectric constant of the medium. Thus the potential of the spherically symmetric charge distribution is constant within the

shell. Second, in their review article, Gourary and Adrian[3] point out that the potential for a colour centre can be written as the sum of two terms; a periodic potential and a spherically symmetric potential. The periodic potential is often eliminated by substituting an effective mass for the actual mass of the colour centre, leaving one with the spherically symmetric attractive potential and the polarizable cores. From a consideration of the radial charge distribution functions, we have found that 80-95% of the electronic charge of the U-centre (normally considered to be a hydride ion) in an alkali halide lattice is enclosed within a sphere of radius equal to the lattice constant[4]. We shall assume in the following that the "a" of equation (1) is equivalent to the nearest-neighbour distance in the host crystal unless otherwise specified.

2. METHOD

We consider the spherically symmetric, three-dimensional square-well potential of depth V, and radius "a" pictured in Figure 1. For a particle of mass m in this well, Schrödinger's equation in spherical coordinates is

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]\Psi+V(r)\Psi=E\Psi \tag{3}$$

where $V(r) = -V$, for $r \leq a$ and $V(r) = 0$ otherwise. Making the substitutions $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ and $\chi(r) = R(r)/r$, we find for the radial part of Schrödinger's equation that

$$-\frac{h^2}{2m}\frac{d^2\chi}{dr^2} - V_0\chi = E\chi \qquad (r < a) \tag{4}$$

$$-\frac{h^2}{2m}\frac{d^2\chi}{dr^2} = E\chi \qquad (r > a) \tag{5}$$

Therefore, the radial motion is similar to the one-dimensional motion of a particle in the potential (5)

$$V(r) = -V_0 + \frac{\ell(\ell+1)\hbar}{2mr^2} \tag{6}$$

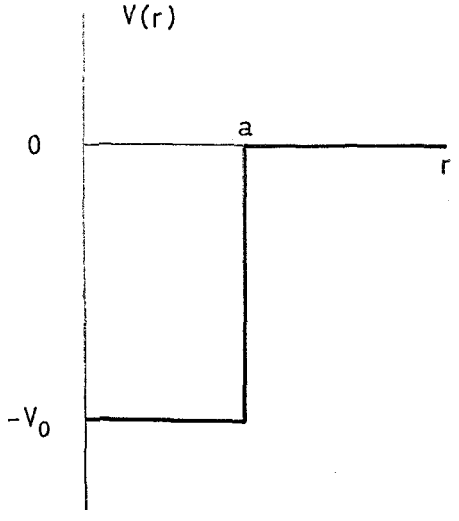

Fig. I - A spherically symmetric, three-dimensionalsquare well potential of Strengtn V_0a^2.

According to Schiff[6], the second term in equation (6) corresponds to an additional centrifugal potential energy for a particle having orbital angular momentum $L = \sqrt{\ell(\ell+1)}\hbar^2$.

In the ensuing discussion of these equations we shall employ the nomenclature from the hydrogen atom solutions. Thus energy levels will be labelled by an integer n and the angular momentum states will be referred to as s-and p-states, although all energy levels appearing here are non-degenerate.

A. Zero Angular Momentum

For the case of s-states the solutions of equatíons of equations (4) and (5) which satisfy the constraints that $R(r)$ is finite at $r=0$ and that $R(r)$ vanishes as $r\to\infty$ have the form

$$\chi = A \sin(\alpha r) \qquad (r < a) \tag{7}$$

$$\chi = B \exp(-\beta r) \qquad (r > a) \tag{8}$$

where

$$\alpha = \left[2m(V_0 - |E|)/\hbar^2\right]^{1/2} \tag{9}$$

and

$$\beta = \left[2m\ |E|/\hbar^2\right]^{1/2} \tag{10}$$

By equating the logarithmic derivative $(1/R)\ \frac{dR}{dr}$ of the two solutions at $r=a$, one can solve numerically or graphically for the s-state energies. A conveniente procedure is to define $\xi = (\alpha a)$ and $\eta = (\beta a)$ and solve the equations

$$\xi \cot \xi = -\eta \tag{11}$$

$$\xi^2 + \eta^2 = mV_0 a^2/\hbar^2 \tag{12}$$

Since ξ and η are required to be positive by definitions, the s-state energy levels may be found from the interaction in the first quandrant of the curves given by equations (11) and (12), provided the weil strength $V_0 a^2$ is known. Such a plot: is given in Figure 2. From this plot it follows that there are

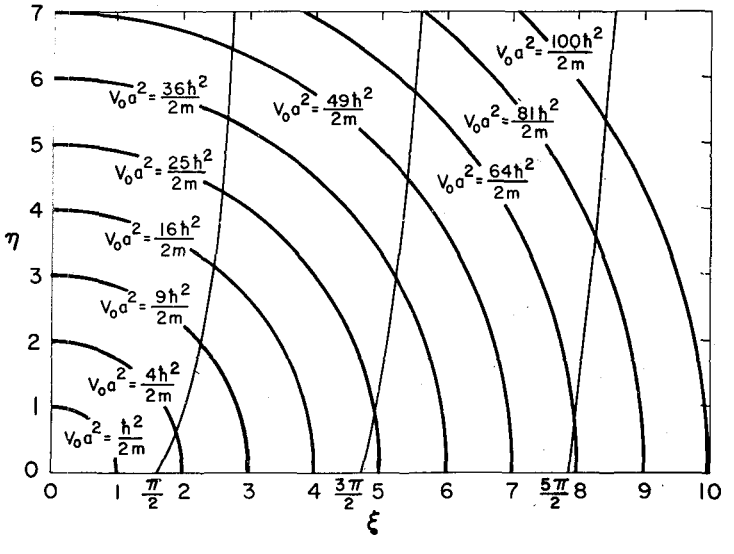

Fig. 2 - Curves of $\eta = -\xi \cot\xi$ and $\xi^2 + \eta^2 = 2mV_0a^2/\hbar^2$.

no bound s-states if $V_0 a^2 \leqslant (\pi^2\hbar^2/8m)$

one bound s-state if $(\pi^2\hbar^2/8m) < V_0 a^2 \leqslant (9\pi^2\hbar^2/8m)$

two bound s-state if $(9\pi^2\hbar^2/8m) < V_0 a^2 \leqslant (25\pi^2\hbar^2/8m)$

etc.

Alternatively, as for the case of the F-centre, if one knows "a" and E_{ns}, the energy of the nth s-state, Figure 2 may be utilired to find a value of V, and the number and energies of the bound s states as well.

B. Arbitrary Angular Momentum

After substituting $\Psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$ into equation (3), one has for the radial part of Schrödinger's equation for a particle with orbital angular momentum **R** that

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} + \left[1 - \frac{\ell(\ell+1)}{\rho^2}\right]R = 0 \tag{13}$$

where $\rho = (\alpha r)$ for $r<a$ and $\rho = (iBr)$ for $r>a$. For the case of orbital angular momentum quantum number $\ell=1$, equating the logarithmic derivatives of the interior and exterior solutions at $r=a$ and setting $\xi = (\alpha a)$ and $\eta = (\beta a)$, as before, leads to

$$\left(\frac{\cot\xi}{\xi} - \frac{1}{\xi^2}\right)\eta^2 - \eta - 1 = 0 \tag{14}$$

$$\xi^2 + \eta^2 = 2mV_0a^2/\hbar^2 \tag{15}$$

Equation (14) is a quadratic equation of the form

$$S\eta^2 + \eta + u = 0$$

and the solutions of interest to it are

$$r, = (1 + \sqrt{1 + 4S})/2S \tag{16}$$

Equations (14) and (15) are displayed in Figure 3. From this graph one finds that there are

no bound p-states if $V_0 a^2 \leqslant (\pi^2\hbar^2/2m)$

one bound p-state if $(\pi^2\hbar^2/2m) < V_0 a^2 \leqslant (2\pi^2\hbar^2/2m)$

two bound p-state if $(2\pi^2\hbar^2/2m) < V_0 a^2 \leqslant (9\pi^2\hbar^2/2m)$

etc.

Schiff[7] rationalizes the fact that the smallest value of the well strength for which there exists a bound state is greater for R = 1 than the corresponding value for R = 0 by referring to the term in the radial wave equation describing the centrifugal potential energy. Physically this suggests that a particle possessing orbital angular momentum requires a stronger attractive potential to bind it than a particle with no orbital angular momentum. It turns out that the minimum strength $V_0 a^2$ required to bind a particle increases monotonically with increasing R.

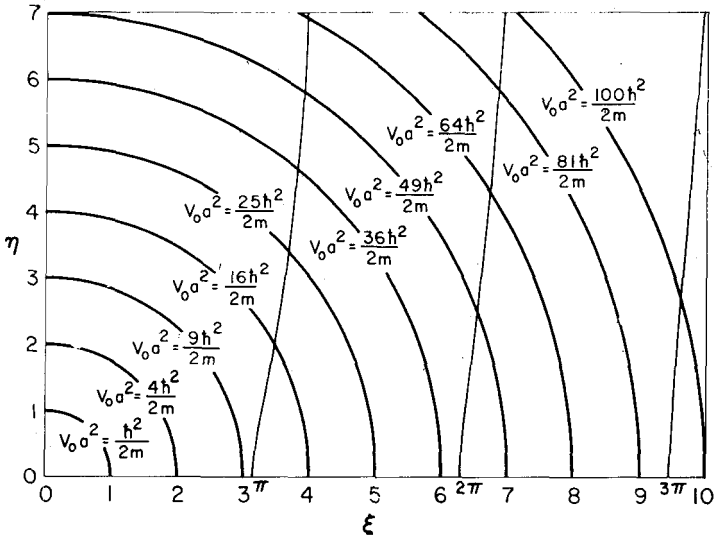

Fig. 3 - Curves of $\frac{\cot \xi}{\xi} - \frac{1}{\xi^2}$ and $\xi^2 + \eta^2 = 2mV_0a^2/\hbar^2$.

Analogous to the case of s-states, one can employ Figure 3 to solve for the energies of the bound p-states. Alternatively if one knows !'a" and the value of the optical transition $\Delta E = E_{2p} - E_{1s}$, Figure 3 may be utilized to find a value of V, and the number and energies ofthe bound p-states as well.

3. APPLICATION TO THE F-CENTRE IN NaCl

For the *F-centre in* NaCl the value of the optical *transition* for the colour centre is (8a)

$$\lambda_F = 4580\ A \quad \text{at } 20\ ^{o}C.$$

(The value of λ_F is 4540 A at -253 ^{o}C (8b)). Therefore, at room temperature

$$\Delta E = E_{2p} - E_{1s} = hc/\lambda_F = 9.9483 \quad 10^{-2} \quad \text{a.u.}\ , \tag{17}$$

where 1 a.u. = 27.207 eV. Gourary and Adrian's point-charge-rnodel calculations on the F-centre in sodium chloride yield that relative to the conduction band[1]

$$E_{1s} = -\ 6.47\ \text{eV} = -\ 2.3778 \times 10^{-1}\ \text{a.u.} \tag{18}$$

Equations (17) and (18) then irnply that

$$E_{2p} = -\ 1.3830 \times 10^{-1}\ \text{a.u.} \tag{19}$$

Rewriting equations (9) and (10) inatoinicunits ($\hbar = e = m_e = 1$) results in

$$\xi = \alpha a = R\sqrt{2(V_0 - |E_{1s}|)}\ ,\ \eta = \beta r = a\sqrt{2|E_{1s}|} \tag{20}$$

As rnentioned previously, "a" is taken as equivalent to the crystal parameter, so that for NaCl, a = 5.31 Bohrs. Thus,

$$\eta = 3{,}6618 \tag{21}$$

From Figure 2 we then find E_{1s} on the first $\eta = -\xi\cot\xi$ curve, or

$$2.53 \simeq \xi = 2.5359 \tag{22}$$

where the latter value is obtained numerically from equation (11) using thevalue for η given inequation (21). Fromequations (12), (21) and (22), one obtains the well strength

$$V_0 a^2 = 9.9199$$

so that

$$V_0 = 0.35818 \text{ a.u.}$$

This implies, according to our previous discussions, that there is only one bound s-state for the F-centre in NaCl; this we shall call the ground state.

Pertaining to the number of bound p-states, we have, in atomic units,

$$\xi = \alpha a = a\sqrt{2(V - |E_{2p}|)} \quad , \quad \eta = \beta r = a\sqrt{2|E_{2p}|} \tag{23}$$

$$\frac{\cot\xi}{\xi} - \frac{1}{\xi^2} = \frac{1}{\eta} + \frac{1}{\eta^2} \ , \quad \xi^2 + \eta^2 = 2V_0 a^2 \tag{24}$$

Since a = 5.31 Bohrs,

$$\eta = 2.7929 \ . \tag{25}$$

Then the first curve of the transcendental equation (24) displayed in Figure 3 yields

$$3.61 \simeq \xi = 3.5994 \quad , \tag{26}$$

where the latter value is obtained from the numerical solution of the transcendental expression ,in equation (24) using equation (25). This gives a well strength of 10.3782 according to equations (24)-(26), and the well depth is

$$V_0 = 0.3681 \text{ a.u.}$$

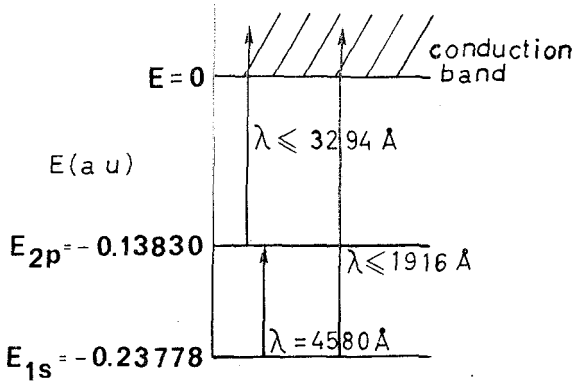

Fig. 4 - Energy level diagram of the F-centre in NaCl

Here, too, we see that there is only one bound state. We also note thst the value of V, obtained for s- and p-states agree reasonably well. Therefore, we are able to draw the energy level diagram for the *F*--centre in sodium chloride as shown in Figure 4. A qualitative representation of the electronic spectrum for the defect centre based on this diagram consists of a rather sharp peak centred at 4540 A for the $1s \rightarrow 2p$ transition, a broad band from 3294 A to higher values for the $2p$ excitation into the conduction band with relatively low intensity and a second broad, low-intensity band originating at 1916 A for the $1s \longrightarrow$ continuum transition. This description may be compared with the experimentally observed spectrum shown in reference (9b); the agreement between the two *is* apparent.

4. APPLICATION TO OTHER ALKALI HALIDE CRYSTALS

The method developed and illustrated above has been applied to the F-centre residing in all the alkali halide lattices for which a ground-state energy of the bound electron has been calculated by Gourary and Adrian[10]. The results are listed in Table 1. The well width "*a*" employed in each case is the nearest-neighbour distance. E_{2p} has been calculated, as before, from the equation

$$E_{2p}^{*} = E_{1s} + hc/\lambda_F$$

where the second term in the sum is an experimental quantity while the first term is calculated via the point-charge model. It would have been preferable to employ experimental values for E_{1s}, of course, had they been available.

Table I. Results of Calculations on the P-centre in Various Alkali Halide Lattices

Lattice	Well Width a (au) (1)	λ_F (A) (2)	E_{1s} (au) (1)	E_{2p} (au) (3)	V_0a^2 for s-states	V_0a^2 for p-states	V_0 for s-states (au)	V_0 for p-states (au)	no. of bound s-states	no. of bound p-states	E_{2s} (au)	E_{3p} (au)
LiF	3.80	2570	-0.297	-0.1197	7.2797	7.6786	0.5041	0.5318	1	1	-	-
NaF	4.37	3410	-0.271	-0.1374	8.2606	8.8295	0.4326	0.4624	1	1	-	-
LiCl	4.86	3850	-0.253	-0.1346	9.1334	9.5156	0.3867	0.4029	1	1	-	-
NaCl	5.31	4580	-0.238	-0.1383	9.9199	10.3790	0.3518	0.3681	1	1	-	-
KCl	5.93	5560	-0.219	-0.1371	10.9857	11.4540	0.3124	0.3257	1	1	-	-
RbBr	6.48	6940	-0.205	-0.1391	11.9479	12.6313	0.2845	0.3008	2	1	-0.0050	-

(1) Gouracy. B.S. and Adrian, F.J., *Solid State Phys.*, *10*, 127 (1960); p.214;
(2) *Ibid*, pp. 135-136
(3) $E_{2p} = \frac{hc}{\lambda_F} + E_{1s}$

From Table 1 it is obvious that, with the exception of the F--centre in RbBr, which has a bound 2s state, the results are qualitatively the same as for NaCl. An energy level diagram for the F-centre in RbBr is shown in Figure 5. A qualitative description of the electronic spectrum of the F-centre in RbBr expected on the basis of this diagram consists of a narrow, intense peak at 6940 A for the $1s \rightarrow 2p$ excitation, a broad, less-intense band starting at 3392 A for the $2p \rightarrow 2s$ excitation and spreading over the $2p \longrightarrow$ continuum transition which starts at 3271 A, a band for the $1s \rightarrow$ continuum from 2222 A plus a possible, though certainly broad and weak, band from the $2p \rightarrow$ continuum at 91120 A.

An additional band, known as the K-band, has been observed on the high-energy side of the main F-band in the high-resolution absorption spectra of coloured potassium and ribidium chloride, bromide and iodide salts[11-15]. Examples of the K-band in RbCl at two different temperatures are shown in the work of Spinolo and Smith[9]. Even at low tem-

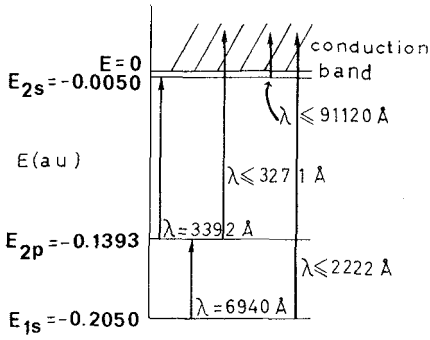

Fig. 5 - Energy level diagram of the F-centre in RbBr

peratures, no resolved K-bands have been observed in the lithium or sodium salts, although in NaCl the experimental F-band has a long, high-energy tail which may be due to the presence of an unresolved K-band. Mott and Gurney have suggested that the additional band is due to the electronic transition of the F-centre to highly excited states[16]. They employed a hydrogenic model for the F-centre and assigned the K-band to the sum of $1s \rightarrow np$, $n \geqslant 3$, transitions. There has been some dispute over this interpretation although it seems to be clearly established now that the K-band absorption is at leat partly due to transitions within the F-centre[3]. On the basis of our calculations, however, it would seem that the K-band is instead due to transition of $2p$ electrons to the conduction band as well as $1s$ and $2p$ electrons to higher excited states, especially $2p \rightarrow 2s$, that exist in the crystal.

Table 2. Variation of Well Width a for the F-centre in NaCl

E_{1s} = -0.238 au
E_{2p} = -0.1383 au

Well Width a (au)	V_0a^2 for s-states	V_0a^2 for p-states	V_0 for s-states (au)	V_0 for p-states (au)	$\Delta V_0 = V_0(s)-V_0(p)$ (au)	no. of bound s-states	no. of bound p states	E_{2s} (au)	E_{3p} (au)
4.0	6.7357	8.3101	0.4210	0.5194	-0.0984	1	1	-	-
5.0	9.0996	9.8506	0.3640	0.3940	-0.0300	1	1	-	-
5.31(1)	9.9199	10.3790	0.3518	0.3681	-0.0063	1	1	-	-
5.7317(2)	11.1035	11.1341	0.3379	0.3389	-0.0010	1	1	0.0000	-
6.0	11.8973	11.6378	0.3305	0.3233	+0.0072	2(barely)	1	-0.0005	-
7.0	15.1388	13.6734	0.3090	0.2790	+0.0300	2	1	-0/0437	-

1. Value of a equal to the crystal parameter in NaCl
2. Value of a for which E_{2s} = 0.0000 au

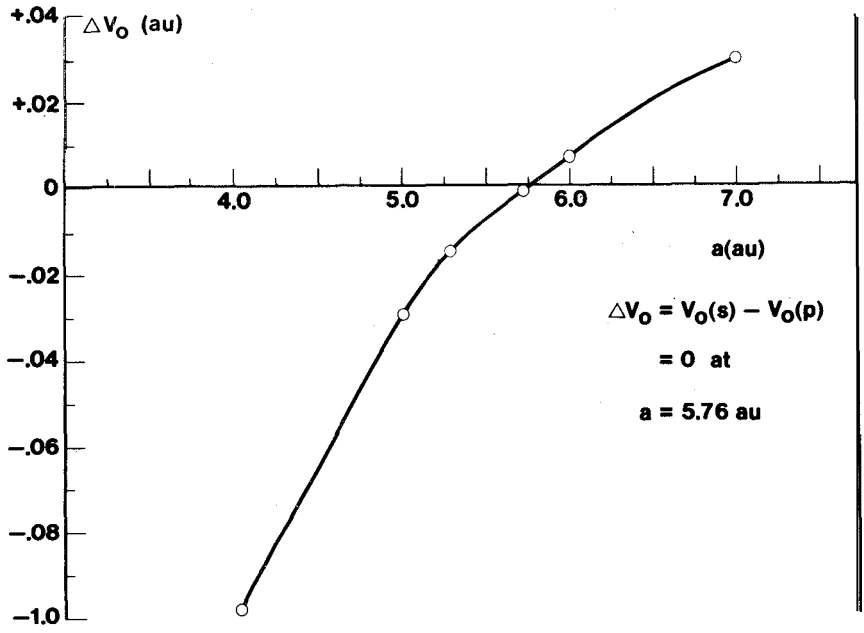

Fig. 6 - $\Delta V_0 = V_0(s\text{-states}) - V_0(p\text{-states})$ **as a function of the well width a for the F-centre in NaCl.**

5. F-CENTRE PROPERTIES AS A FUNCTION OF THE WELL STRENGTH

Calculations have been carried out on the F-centre in NaCl to determine the effect of the well width "a" on the well strength $V_0 a^2$, and consequently, on the number of bound states. The results are reported in Table 2. It is interestina to observe the change in the difference V_0 of the potential for s- and p-states. This quantity is defined as

$$\Delta V_0 \equiv V_0 \text{ (s-state)} - V_0 \text{ (p-state)}$$

and is plotted as a function of the well width "a" in Figure 6. The spherically symmetric square-well potential defined in Figure 1 is independent of the value of the orbital angular momentum quantum number; thus the value of V_0 should be exactly the same for s- and p- states. Although this is approximately true for all the F-centres treated in Table 1, where the value of "a" equal to the crystal parameter of the host

Table 3. Calculations on the F-centre Ernploying a Value of the Well Width a Equal to the Sum of the Nearest-Neighbour Distance Plus the Radius of the Neighbouring Cation.

Lattice	Well Width a (au) (1)	V_0a^2 for, s-states	V_0a^2 for p-states	V_0 for s-states (au)	V_0 for p-states (au)	no.of bound s-states	no. of bound p-states	E_{2s} (au)	E_{3p} (au)
LiF	5.29	11.6338	9.7210	0.4157	0.3474	2(barely)	1	-0.0035	-
NaF	6.22	13.9210	12.0237	0.3598	0.3108	2	1	-0.0337	-
LiCl	6.15	12.9610	11.7691	0.3427	0.3112	2	1	-0.0189	-
NaCl	7.16	15.6991	14.0223	0.3062	0.2735	2	1	-0.0498	-
KCl	8.44	19.2247	16.9500	0.2699	0.2380	2	1	-0.0751	-
RbBr	9.28	21.3351	19.3495	0.2477	0.2247	2	1	-0.0829	-

(1) a is equal to the sum of the nearest-neighbour distance given in Table I plus the ionic radius of the neigbouring cation listed in Table 9, p.129 of Kittel, C., *Introduction to Solid State Physics*, 4th ed., John Wiley, N.Y., c 1971. The values of E_{1s} and E_{2p} employed in these calculations are those appearing in Table I.

lattice was employed, it can be seen from Figure 4 that in NaCl, $\Delta V_0 = 0$ for a = 5.76 a.u. as cornpared to the crystal parameter of 5.31 a.u. for the sodiurn chloride crystal.

By assigning the well width values equal to the sum of the nearest-neighbaur distance plus the ionic radius of the neighbouring cation one allows the defect electron to exchange with the electrons of the surrounding nearest-neighbour cations. The results of these calculations are presented in Table 3. Increased values of "a" increase the well strength, and from the table, we see that this treatmentresults in one additional bound s-state for each crystal except RbBr.

6. SELF CONSISTENT SQUARE WELL POTEMTIAL (SCSWP)

To force our model to be mathematically consistent, we can require that the well depth be independent of the orbital angular momentum quantum number. The results of requiring $\Delta V_0 = 0$ through the variation of the well width pararneter for the crystals are listed in Table 4. As a consequence of this variation we arrive at one additional bound s--state for NaCl and KCl. Also, by forcing this self-consistency on the model, we obtain a different well width value which may have physical significance. We define the "effective penetration range" as the difference of the well width for which AV, = 0 and the nearest-neighbour dis-

Table 4. Calculation of the Effective Penetration Range for the F-centre in Alkali Halide Lattices for a self--consistent square well potential

Lattice	Well Width a a (1)	Effective Penetration Range (au)(2)	V_0a^2 for s-states	V_0a^2 for p-states	I, for s-states	V_0 for p-states	no. of bound s-states	no. of bound p-states	E_{2s} (au)	E_{3p} (au)
LiF	4.09	0.29	8.0331	8.0388	0.4802	0.4806	1	1	-	-
NaF	4.86	0.49	9.5931	9.5938	0.4061	0.4062	1	1	-	-
LiCl	5.20	0.34	10.0666	10.0707	0.3723	0.3724	1	1	-	-
NaCl	5.76	0.45	11.1857	11.1863	0.3371	0.3372	2 (barely)	1	-0.0000	-
KCl	6.43	0.50	12.4193	12.4240	0.3004	0.3005	2	1	-0.0102	-
RbBr	7.32	0.84	14.4434	14.4369	0.2696	0.2694	2	1	-0.0309	-

(1) The well width a has been calculated using the SCSWP criterion that $\Delta V_0 = V$ (s-states) - V (p-states) = 0. The values of E_{1s} and E_{2p} listed in Table 1 were empioyed in the calculation.

(2) The effective penetration range is the difference of the well width a and the nearest-neighbour distance given as the well-width in Table 1. This difference can be regarded as a measure of the exchange interaction between the F-centre electron and the outer-shell eiectrons of the neighbouring metal cations.

tance for the crystal. This effective penetration range goes in value from a minimum of 0.29 a.u. in LiF to 0.84 for RbBr. The effective penetration range may be viewed as a measure of the interaction between the defect electron and the electrons of the neighbouring cation. It is seen from Table 4 to have roughly the same percentage change from the crystal parameter in each case.

A plot similar to Figure 6 can be employed to determine the well width of a lattice for which "a" is unknown, provided the values of AE and E_{1s} or equivalently E_{1s} and E_{2p} are known, by use of SCSWP. The desired value of "a" is then simply that for which AV, = 0. The values of "a" and V_0 so determined enable one to find an effective Madelung energy for the crystal, For the exampleof NaCl, a = 5.76 aiid V_0 = 0.3372, while the Madelung energy for NaCl is, in atomic units,

$$V_{\text{Madelung}} = M/R_0 = \frac{1.7475}{5.31} = 0.3291 \text{ a.u.} ,$$

where R_0 is the crystal parameter and M is the Madelung constant. Using the values of "a" and V_0 cited above, we find an effective Madelung constant aV_0 of 1.94.

If the Madelung constant and nearest-neigbour distance are known, Figures 2 and 3 can be employed to estimate values for thenumber

and energies of the bound states. For the case of the E-centre in NaCl, we have a well strength of 9.2793, which gives one bound s-state and one bound p-state with energies of -0.213 a.u. and -0.102 a.u., respectively. The F-band is predicted to occur at 4110 A as compared to the experimental value of 4580 A. For the F-centre in RbBr this approximation yields a predicted F-band at 5640 A as compared to the experimental value of 6940 A. For RbI the predicted band is at 6350 A while the experimental value is 7560 A. In this case, where energy levels have not been calculated by Gourary and Adrian[1], we find E_{1s} = -0.184 a.u. and E_{2p} = -0.112 a.u.

7. DISCUSSION

The results of this study demonstrate the relative simplicity of this model. The condition that AV, = 0 gives the required consistency of the SCSWP model and yields qualitatively useful results. Inthe potential function used here we have eliminated the asymptotic $-1/r$ behaviour which means that we can only have a finite number of bound states. By making use of the experimental ΔE value we have a good spacing of the first two energy levels and furthermore have sufficient additional structure in the F-centre to give a good account of the experimental features that have been observed. In the case of NaCl we have high-energy tail on the Pband while in KCl and RbBr we have a second bound s-state that could account for the observed K-band. Our interpretation of F-centre transitions is consistent with the conductivity data as well, and our suggestion that the K-band is primarily due to transitions from the $2p$ level to excited levels is consistent with experimental results. We could also have considered d-type energy levels but this added complication was not needed in order to give an adequate description of the data. A number of considerably more-complicated models have been applied to this problem, although they do not capitalize on the available experimental data[9,17].

Since we have suggested that the K-band may be due primarily to excitation from the $2p$ state, a few words are in order on the splitting of the 2s and $2p$ energy levels. In the potential used here the

splitting is in the opposite direction to what one might expect on the basis of atomic electronic structure. If we treat the square-well potential as a perturbation on a coulombic potential, the first-order energy corrections give (E_{2s} - E_{2p}) as positive and proportional to the well depth V_0. Thus the square-well model gives a $2p \rightarrow 2s$ absorption transition while in the coulomb model perturbed by many-electron effects one considers the $2s \rightarrow 2p$ absorption. The energy difference predicted by the square-well model is considerably too large for a good fit to the K-band. Once the $2p$ level is occupied, the lattice will undergo relaxation, thus shifting the energy levels to higher values that could reasonably decrease the predicted energy difference. However, this is a complicated phenomenon, and it is also possible that the bound $2s$ level would be moved into the continuum. Since the colour-centre properties are specific and characteristic, we prefer to view the defect particle as localized within the defect cavity*. Therefore, we feel that equation (1) is the predominant component in the potential and consequently that the ordering of energy levels found here more accurately reflects the actual situation in the crystal.

The discussion of V_0 and "a" in terms of the lattice crystal energy has considerable interpretative value. When V_0 and "a" are determined via the requirement that $\Delta V_0 = 0$, the values of V_0 in Table 4 are in good agreement with the Madelung crystal lattice energies. Thus this procedure accounts for the electrostatic potential energy of the lattice. When we employ a value of "a" equal to the lattice parameter plus the cationic radius, the resulting V_0 values (Table 3) give reasonable agreenient with the Born-Mayer crystal energy, which is the electrostatic potential plus a correction for electron repulsion effects between the nearest neighbours.

For the "a" value obtained by the $\Delta V_0 = 0$ condition, the well width for the defect electron extends beyond the centre of the nea-

* The $1s$ states are about 95% localized. For those crystals showing a K-band the $2p$ state is also highly localized (KCl and RbBr). The $2p$ state of NaCl is diffuse.

rest-neighbour cation site. While this model is based on the concept of a particle localized in the potential well, the extent of the wellwidth suggest a description of the F-centre defect particle as a solvated electron.

In conclusion, this study, for which a simplified model has been applied to a system where considerable quantitative data are available, is seen to be qualitatively consistent and allows itself to be interpreted in an intuitively appealing manner. Studies of the relaxed excited F center[18] and perturbation of the *F* band via increased pressure[19] or an electric field[20] are other methods used to study the colour centres that have provided further understanding of the electronic properties of the trapped electron. The SCSWP model is now being applied to the study of more cornplicated systerns where the defect particle has internal structure and for systems where the particle trapping medium is a non-periodic matrix.

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