

Extended-ion approximation and pressure shifts in *F*-band energies

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Abstract. Pressure variation of maximum *F*-band absorption energies in the halides of lithium, sodium and potassium has been investigated employing the extended-ion approximation for the calculation of the *F*-electron energy eigenvalues and using values of local compressibility in the neighbourhood of the *F*-centres which include the effect of vacancy and pressure. The results obtained agree with the experimental results.

Keywords. Alkali halides; *F*-band energies; pressure shifts.

1. Introduction

Pressure dependence of maximum *F*-band absorption energy ϵ_m has been one of the biggest challenges to the solid state theoreticians. Jacobs (1954) and Bartram and Stoneham (1968) suggested that the experimentally observed stronger pressure dependence of ϵ_m might be due to the change in compressibility in the neighbourhood of the *F*-centre because of vacancy, and the latter tried to explain the stronger pressure dependence of ϵ_m on this basis. Recently, Singh and Joshi (1978) attempted to account for this stronger pressure dependence in the case of lithium halides using the extended-ion approximation for the calculation of *F*-electron energy eigenvalues and attributed it to the effect of vacancy and pressure on the local compressibility λ_p in the neighbourhood of the *F*-centre and obtained satisfactory results. In the present work, we have extended these studies to the halides of sodium and potassium also using the same approach. Here, instead of using an empirical relation for λ_p containing two arbitrary parameters (Singh and Joshi 1976), we have proposed another empirical relation containing three parameters which have been evaluated by the method of least squares fit. The results obtained in the case of lithium halides (Singh and Joshi 1978) have also been revised in the light of this modification. The results obtained agree with experimental results.

2. Theory

The *F*-electron energy eigenvalues have been evaluated by variational method using simple vacancy centred trial wavefunctions (Singh and Joshi 1978). For the ground state we have used

$$\psi_{2s}(\mathbf{r}) = (a^5/3\pi)^{1/2} r \exp(-ar), \quad (1)$$

and for the excited state we have tried the two functions

$$\psi_{2p}(\mathbf{r}) = (\beta^5/\pi)^{1/2} r \cos \theta \exp(-\beta r), \quad (2)$$

$$\psi_{3p}(\mathbf{r}) = (2\beta'^7/15\pi)^{1/2} r^2 \cos \theta \exp(-\beta' r), \quad (3)$$

where α , β and β' are variational parameters. The ground and the excited state energy eigenvalues ϵ_q ($q=2s, 2p$ and $3p$) have then been calculated.

The wavefunctions $\psi_q(\mathbf{r})$ ($q=2s, 2p$ and $3p$) of the F -centre have been orthogonalised to the core orbitals $\phi_n^j(\mathbf{r}-\mathbf{R}_n)$ (j th orbital at the n th ion) of the six nearest neighbour (nn) alkali ions following Wood and Korrynga (1961). The energy eigenvalues for the orthogonalised wavefunctions ϵ_q^0 have been evaluated as in Singh and Joshi (1978).

A sodium or a potassium ion contains 8 electrons in the outermost shell. The F -electron wavefunction will automatically be orthogonal to the core orbitals of half of these electrons through spin coordinates. Thus, orthogonalisation will be done only for the core orbitals of the remaining half of the electrons. Following Wood and Joy (1964) the ground state core-orbital of the Na^+ ions has been taken to be given by

$$\begin{aligned} \phi_n^{2s}(\mathbf{r}) = & -0.284358 (\eta_1^5/3\pi)^{1/2} r \exp(-\eta_1 r) \\ & + 1.092445 (\eta_2^5/3\pi)^{1/2} r \exp(-\eta_2 r), \end{aligned} \quad (4)$$

and the radial part of the excited state core-orbital by

$$R_{2p}(r) = (\eta^5/3\pi)^{1/2} r \exp(-\eta r), \quad (5)$$

where the distance r is measured from the n th sodium ion; ϕ_n^{3s} has the same value for all the 6 nn ions and the parameters are

$$\eta_1 = 10.626, \quad \eta_2 = 3.281 \quad \text{and} \quad \eta = 3.403. \quad (6)$$

For the ground state core-orbitals of K^+ ions we have used

$$\phi_n^{3s}(\mathbf{r}) = (2\xi^7/45\pi)^{1/2} r^2 \exp(-\xi r), \quad (7)$$

where $\xi = 2.583$. The radial part of the excited state core-orbital $R_{3p}(r)$ has also been taken to be given by (7). F -electron energy eigenvalues ϵ_q^0 have then been obtained.

The effect of lattice distortions has been considered only for nn ions. After evaluating the energy eigenvalues $\epsilon_u^{0'}$ for the distorted lattice the maximum F -band absorption energy for the state u ($=2p$ or $3p$) has been obtained from

$$\epsilon_m^u = \epsilon_u^{0'} - \epsilon_{2s}^{0'} \quad (8)$$

In the present work, instead of using a linear relation for λ_p containing two arbitrary parameters (Singh and Joshi 1976) we have used an exponential form of the relation containing three parameters, viz.

$$\lambda_p = \bar{\gamma} + (\bar{a} - \bar{\gamma}) \exp(-\bar{\beta} \Delta a_0/a_0), \quad (9)$$

and have evaluated these parameters by the method of least squares fit.

3. Calculations, results and discussion

Table 1 shows our calculated values of the maximum *F*-band absorption energy at room temperature and normal atmospheric pressure, $\epsilon_m(0)$, for *2p* and *3p* excited

Table 1. Maximum *F*-band absorption energy at normal atmospheric pressure $\epsilon_m(0)$ for *F*-centres in alkali halides.

Alkali halide	Present calculations		Experimental values*		
	For <i>2p</i> excited state	For <i>3p</i> excited state	Mollwo (1931) & (1933)	Rabin and Klick (1960)	Molnar (1940)
LiF	0.1480	0.1383	0.1823	0.1875	0.1723
LiCl	0.1127	0.1054	0.1184	—	—
LiBr	0.1058	0.0961	—	—	—
LiI	0.0964	0.0847	—	—	—
NaF	0.1355	0.1243	0.1340	0.1356	0.1336
NaCl	0.1006	0.0914	0.0980	0.1013	0.0995
NaBr	0.0905	0.0817	0.0844	0.0866	—
NaI	0.0858	0.0757	0.0775	—	—
KF	0.1065	0.0946	0.1002	—	—
KCl	0.0860	0.0747	0.0809	0.0846	0.0820
KBr	0.0785	0.0684	0.0723	0.0757	0.0730
KI	0.0728	0.0638	0.0665	0.0684	0.0662

*Gourary and Adrian (1960)

Table 2. A comparison of the slopes of the theoretical curves, $\partial \log [\epsilon_m/\epsilon_m(0)]/\partial \log (d/d_0)$ and those of the experimental curves for various alkali halides in the low pressure regions.

Alkali halide	Present values		Experimental values		
	For <i>2p</i> excited state	For <i>3p</i> excited state	Smakula (1961)	Buchenauer and Fitchen (1968)	Eppler and Drickamer (1960)
LiCl	1.45	1.50	0.567	1.15	1.57
LiBr	0.98	1.00	0.567	1.00	—
LiI	1.00	1.10	0.567	—	—
NaF	1.15	1.18	0.546	1.17	—
NaCl	1.51	1.50	0.546	1.52	1.52
NaBr	1.65	1.60	0.546	0.87	1.67
NaI	1.50	1.50	0.546	1.48	—
KF	0.75	0.73	0.517	0.74	—
KCl	1.18	1.17	0.517	1.10	1.16
KBr	1.42	1.45	0.517	1.25	1.51
KI	0.98	1.00	0.517	1.23	1.00

states. These results have been compared with the experimental results of Mollwo (1931, 1933), Rabin and Klick (1960) and Molnar (1940). Our calculated values for both $2p$ and $3p$ excited states are very close (within 10%) to the experimental results for all the alkali halides except LiF. This shows that the present model, *viz.*, the extended-ion approximation is quite satisfactory for the calculation of F -band absorption energies.

Table 2 presents the values of the slopes $\partial \log [\epsilon_m/\epsilon_m(0)]/\partial \log (d/d_0)$ for all the halides of lithium, sodium and potassium in the low pressure regions for both $2p$ and $3p$ excited states obtained by using fitted values of the parameters $\bar{\alpha}$, $\bar{\beta}$ and $\bar{\gamma}$. These values have been compared with the empirical values of Smakula (1961), the experimental values of Buchenauer and Fitchen (1968) and Eppler and Drickamer (1960). The slopes of the theoretical curves are very close to those of experimental curves. In the case of $2p$ excited state the agreement is within 2.5% for all the halides except KBr for which it is within 6%. Similarly, for $3p$ excited state the agreement is within 4%. However, for LiF our results are very low.

In figure 1 we have plotted $\log [\epsilon_m/\epsilon_m(0)]$ against $\log (d/d_0)$ for LiCl, NaCl, NaBr, KCl, KBr and KI using $3p$ excited state. The calculated values have been compared with the experimental values of Eppler and Drickamer (1960). The agreement is very nice. For $2p$ excited state also we get similar results.

We therefore conclude that the extended-ion approximation can very satisfactorily explain the pressure variation of maximum F -band absorption energies ϵ_m in alkali halides by considering the effect of vacancy and pressure on the local compressibility in the neighbourhood of the F -centre using simple vacancy centred wavefunctions. Both the $2p$ and $3p$ excited states give equally good results. It is difficult to decide which state is better. Poor results in the case of LiF, however, seem to be due to the effect of polarisation which we have not considered.

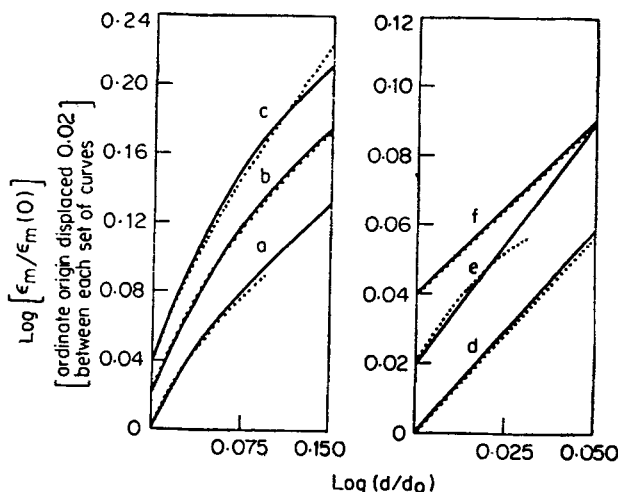


Figure 1. $\log [\epsilon_m/\epsilon_m(0)]$ versus $\log [d/d_0]$ for alkali halides. — present calculations for $3p$ excited state; ... experimental curves of Eppler and Drickamer (1960); a, LiCl; b, NaCl; c, NaBr; d, KCl; e, KBr; f, KI

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