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Optical absorption of F_A centres in mixed ionic crystals

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Abstract. The shift with concentration variation of the optical absorption F_A band in KCl–KBr mixed crystals, with Li impurities is studied by means of the method of Bartram *et al.* The distortion around the F_A centre is calculated considering the change in the repulsive and polarisation energies due to the impurity. The energy due to this distortion is obtained by a perturbative method. This correction gives good agreement with the experiment values for one of the two absorption bands of the F_A centre, but not for the other. Our calculations, using several types of wavefunction, are in approximate agreement with the experimental observations of Asami and Ishiguro.

1. Introduction

The F_A centre consists of an F centre adjacent to a substitutional impurity cation in an ionic crystal. The earliest theoretical work on F_A -centre absorption was done by Kojima *et al* [1] for KCl:Na. Their work was based on a simplified molecular orbital approach. Smith [2] studied KCl:Na and KCl:Li crystals using a pseudopotential method. He obtained results in qualitative agreement with experimental results. Alig [3] used an ion-size correction very similar to that of Bartram *et al* [4], with several pseudo-wavefunctions and including lattice relaxation for the F_A -centre's six nearest neighbours. He found that $\alpha = 0.53$ gave an inappropriate F_A absorption value and that $\alpha = 1$ gave qualitative agreement with experiment. Weber and Dick [5] also found that the empirical factor $\alpha = 0.53$ gave absorption splitting in the wrong direction and, when they set $\alpha = 1$, qualitative agreement with experiment was obtained. Evarestov [6] obtained similar results for KCl:Na. Ong and Vail [7] and Ong [8] have further used the lattice static method to include the non-harmonic displacement of the impurity ions in F_A and F_B centres. Kung *et al* [9] have done an unrestricted Hartree–Fock cluster analysis of F_A centres in KCl:Li and KBr:Li. Their calculated optical absorption is in good qualitative agreement with experiment.

The F and F_A centres have also been studied in cesium halides [10–14].

The research on colour centres in alkali halide crystals has led to the development of lasers in the visible and infrared (IR) regions. At IR frequencies [15, 16] the colour centres in alkali halide crystals are indispensable for laser function. In a recent paper, Asami and Ishiguro [17] have considered the possibility of using mixed alkali halide

crystals in IR laser operation. They have obtained experimental results on KCl–KBr crystals with lithium impurities. In this work the F and F_A centres are studied. Recently Rodríguez and Ruíz-Mejía [18] have conducted a theoretical study of the optical absorption of the F centre in coloured KCl–KBr and KCl–RbCl crystals, using semicontinuum models [19] and also the point-ion model and ion-size correction [20].

Experimentally the x-ray spectrum of a mixed crystal [19] gives a lattice constant a_M which is different from the lattice constants of the two crystals which form the mixed crystal. In our previous papers [18, 20], we considered a mixed crystal that has specific intrinsic constants such as a lattice constant a_M derived from Vegard's rule [21]. These considerations do not assume effects of a perturbative nature, which in fact have not been detected such as a splitting of the excited state of the F centre in a mixed lattice. Other theoretical work by Logatchov and Evarestov [22, 23] on the mixed crystal $K_{0.5}Cl-Na_{0.5}Cl$ has been carried out. They considered a statistical distribution of different types of positive ion around the F centre and assume that the substitution of ions at a lattice place has a perturbative effect on the F centre electron. They used the point-ion model in their calculations.

The aim of the present paper is to extend the calculations for the optical absorption of coloured KCl–KBr mixed crystals to the case of the F_A centre and to compare our results with the experimental work of Asami and Ishiguro [17].

2. Pseudopotential method

Within the framework of the pseudopotential method, the point-ion model is a prerequisite to calculate the ion-size effects. The variational method to obtain the energy levels of the F centre in the point-ion approximation consists of the minimisation of the energy functional E_{lm} , i.e.

$$E_{lm} = \int \Phi_{lm}^* [-\frac{1}{2}\nabla^2 + V_{PI}(r)] \Phi_{lm} d\tau \quad (1)$$

where $V_{PI}(r)$ is the point-ion potential which is of the form [23]

$$V_{PI}(r) = \sum'_{x_i, y_i, z_i = -\infty}^{\infty} (-1)^{x_i + y_i + z_i} [(x - ax_i)^2 + (y - ay_i)^2 + (z - az_i)^2]^{-1/2} \quad (2)$$

where a is the nearest-neighbour distance, (ax_i, ay_i, az_i) are the coordinates of the i th nucleus, and the prime on the summation sign means that the point $(0, 0, 0)$ is omitted.

It is possible to expand $V_{PI}(r)$ in spherical harmonics, i.e.

$$V_{PI}(r) = \sum_l \sum_{\mu_l} V_{l, \mu_l}(r) Q(\Gamma_l^p, l, \mu_l | \theta, \varphi) \quad (3)$$

where the Q -values are the Kubic harmonics and the individual $V_{l, \mu_l}(r)$ -values are determined by expanding each term in the potential about the centre of the vacancy. Since the potential energy $V_{PI}(r)$ is invariant under the full cubic group, every solution of equation (1) must belong to an irreducible representation of the cubic group, i.e. Φ_{lm} must be of the form

$$\Phi(\Gamma_l^p, l, \mu) = \sum_{l=0} \sum_{\mu_l} R(\Gamma_l^p, l, \mu_l | r) Q(\Gamma_l^p, l, \mu_l | \theta, \varphi). \quad (4)$$

For the model of Bartram *et al* [4] the pseudopotential V_P has the form

$$V_P = V_{PI} + \sum_{\gamma} [A_{\gamma} + (\bar{V}_P - U_{\gamma})B_{\gamma}]\delta(r - r_{\gamma}) \quad (5)$$

where U_{γ} is the potential at the γ th ion due to all the other ions, \bar{V}_P is the expectation value of V_P , and A_{γ} and B_{γ} are characteristic parameters of the ions alone.

The ground- and first-excited-state energies are obtained by minimising an energy functional of the form

$$E(\xi) = \bar{T} + \bar{V}_{PI} + \sum_{\gamma} [A_{\gamma} + (\bar{V}_P - U_{\gamma})B_{\gamma}]|\Phi_{lm}(r_{\gamma})|^2 \quad (6)$$

where ξ is the variational parameter which is varied to minimise the right-hand side of equation (6) with \bar{V}_P fixed. In the case of the F_A centre there is a little change for equation (5). Now V_P for the F_A centre denoted V_P^{FA} is given by

$$V_P^{FA} = V_P - V_{PI} + [A_I - A_C + (\bar{V}_P - U_I)(B_I - B_C)]\delta(r - r_I) \quad (7)$$

where the subscripts I and C mean impurity and cation, respectively. The trial wavefunctions are again of the form given by equation (4). The expectation value of the Hamiltonian

$$\langle \Phi_{lm} | H_P | \Phi_{lm} \rangle = \langle \Phi_{lm} | T + V_{PI} + V_P^{FA} | \Phi_{lm} \rangle \quad (8)$$

is minimised with respect to the parameter ξ for a fixed value of \bar{V}_P . Then \bar{V}_P is recomputed (not V_P^{FA}), and the procedure is continued to self-consistency.

The wavefunctions used were types I, II and III of Gourary and Adrian [24].

3. Distortion around the F_A centre

The functions for the excited state are not perturbed by the impurity if lattice relaxation is ignored [5]. The p function which lies on the z axis gives the excited-state energy of the F_A centre. The other p functions lie in the plane orthogonal to the z axis and behave like the F centre ones. In that case, only the ion-size effect is taken into account, and the absorption line splitting can be obtained from the difference between the values for F_{A2} and F_{A1} (see table 4).

Logatchov and Evarestov [22, 23] have studied KCl-NaCl mixed crystals and obtained the peak position of the F band in KCl:Na with a 50% concentration of NaCl. Here we are considering a slightly different problem, i.e. a KCl-KBr mixed crystal with Li impurities. In our case each mixed crystal of KCl-KBr is considered as a new crystal with lattice constant $a_M = a_1(1 - x) + a_2x$, where x depends on the concentration. In this way our problem is reduced to that of a simple crystal with one impurity by taking the adequate crystal parameters.

As the distortion around an F centre is small [4, 24–27], we have considered the problem of the F_A centre equivalent to the problem of the distortion around a Li impurity in a KCl-KBr crystal. This means that the F centre is ignored. In order to solve this problem we have used a method developed by Dick and Das [28]. They took into account all the interactions that occur in the crystal, and this procedure has the advantage, compared with other methods, that it is computed in a simple way. The change in energy

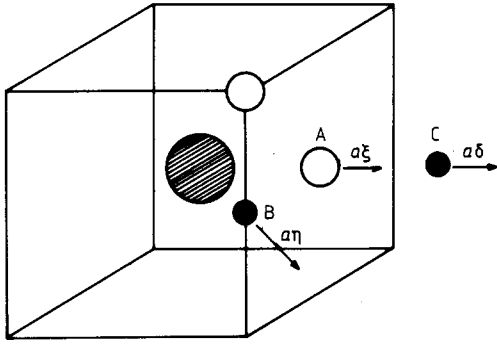


Figure 1. Displacements ξ , η and δ around the impurity represented by the shaded circle. The origin of the F_A centre is localised in the position of ion A.

due to the impurity is given by

$$\Delta E = \Delta E_r + \Delta E_e + \Delta E_s + \Delta E_v^{(1)} + \Delta E_v^{(2)} \quad (9)$$

where

$$\begin{aligned} \Delta E = & 6[B \exp(-a/\sigma) - A \exp(-a/\rho)] + 6[(a/\rho)A \exp(-a/\rho) - (a/\sigma)B \exp(-a/\sigma)]\xi \\ & + 6[(a^2/2\rho^2 - 2a/\rho)A \exp(-a/\rho) + (a^2/2\sigma^2)B \exp(-a/\sigma)]\xi^2 \\ & + 6(a^2/\rho^2 - 2a/\rho)A \exp(-a/\rho)(2\eta^2) + 6A \exp(-a/\rho)(a^2/2\rho^2)\delta^2 \\ & - 6(a/\rho)[A \exp(-a/\rho)]\delta - (24/\sqrt{2})(a/\rho)[A \exp(-a/\rho)]\eta \\ & + 12\sqrt{2}(A \exp(-a/\rho))\xi\eta - 6(a^2/\rho^2)[A \exp(-a/\rho)]\xi\delta. \end{aligned} \quad (10)$$

ΔE_r is the change in the repulsive energy to second order in the displacements due to the impurity. The ξ , η and δ are the displacements around the impurity (figure 1). The dipole interactions with one another give

$$\begin{aligned} \Delta E_e = & (3e^2/a)[(3/\sqrt{2} + \frac{1}{4})M_A^2 + (\frac{3}{4} + 7/3\sqrt{6} + 5/\sqrt{2} + 1/4\sqrt{2})M_B^2 \\ & + (\frac{1}{32} + 3/8\sqrt{2})M_C^2 + 2(1 + 2/3^{3/2} + 13/2^{5/2})M_B M_C \\ & + 4(1 - \frac{1}{27} - 12/5^{5/2})M_C M_A \\ & - 2(2^{3/2} + 52/25\sqrt{10} + 4\sqrt{2}/3^{3/2})M_A M_B] \end{aligned} \quad (11)$$

where $M_A = \xi + \mu_A$, $M_B = \eta - \mu_B$ and $M_C = \delta - \mu_C$, and μ_A , μ_B , μ_C are the electronic dipoles. The dipole self-energies ΔE_s are given by

$$\Delta E_s = 3e^2 a^2 (\mu_A^2/\alpha_A + 2\mu_B^2/\alpha_B + \mu_C^2/\alpha_C). \quad (12)$$

The van der Waals energies $\Delta E_v^{(1)}$ (dipole–dipole) and $\Delta E_v^{(2)}$ (dipole–quadrupole) are not given, because they have not been taken into account in our calculations, as was done by other researchers [29]. We assume Vegard's law for all the constants in the KCl–KBr mixed crystals.

By minimising the expression ΔE in equation (9) with respect to the six variables ξ , η , δ , μ_A , μ_B and μ_C one gets the minimum value ΔE_{\min} , and the equilibrium values for ξ , η , δ , μ_A , μ_B and μ_C . The point A in figure 1 represents the position of the F_A centre, and the shaded circle represents the position of the impurity. Then there are four ions which are displaced as B, and one ion displaced as C; ξ represents the displacement of the impurity with respect to the origin of the F_A centre.

In order to take into account the energy change in the energy levels due to the displacement, we consider a perturbative potential in the following way. The potential for an F_A centre with displacement can be considered as the sum of the F_A centre without displacement and the potential

$$V_{\text{add}} = \sum_{i=1}^6 \left(\frac{1}{|r_i^D|} - \frac{1}{|r_i|} \right) \quad (13)$$

where r_i are the positions of the first six ions around the F_A centre when there is no displacement and r_i^D are the positions of those ions calculated by minimising ΔE .

Using the Gourary–Adrian wavefunction type I, for the ground state, we obtain

$$\begin{aligned} \langle \Psi_s | V_{\text{add}} | \Psi_s \rangle &= \sum_i \left(\left\langle \Psi_s \left| \frac{1}{r_i} \right| \Psi_s \right\rangle - \left\langle \Psi_s \left| \frac{1}{r_i^D} \right| \Psi_s \right\rangle \right) \\ &= \sum_i \left[\alpha \left(1 + \frac{2}{2\alpha r_i} \right) \exp(-2\alpha r_i) - \alpha \left(1 + \frac{2}{2\alpha r_i^D} \right) \exp(-2\alpha r_i^D) \right] \end{aligned} \quad (14)$$

and for the excited state

$$\begin{aligned} \langle \Psi_p | V_{\text{add}} | \Psi_p \rangle &= \sum_i \left(\left\langle \Psi_p \left| \frac{1}{r_i} \right| \Psi_p \right\rangle - \left\langle \Psi_p \left| \frac{1}{r_i^D} \right| \Psi_p \right\rangle \right) \\ &= \sum_i \left[\beta \left(F_1(\beta r_i) - \frac{1}{\beta r_i} + P_2(\cos \theta) F_2(\beta r_i) \right) \right. \\ &\quad \left. - \beta \left(F_1(\beta r_i^D) - \frac{1}{\beta r_i^D} + P_2(\cos \theta) F_2(\beta r_i^D) \right) \right] \end{aligned} \quad (15)$$

where

$$F_1(\beta x) = (1/x) \exp(-2x) \left(\frac{1}{3}x^3 + x^2 + \frac{2}{3}x + 1 \right) \quad (16)$$

$$F_2(\beta x) = (1/x^3) [\exp(-2x) \left(\frac{2}{3}x^5 + 2x^4 + 4x^3 + 6x^2 + 6x + 3 \right) - 3] \quad (17)$$

α and β are the parameters of the wavefunctions, $P_2(\cos \theta)$ is the Legendre polynomial of order two, and θ is the angle that r makes with the wavefunction axes.

4. Calculations and results

Bartram *et al* [4] found that good agreement with experimental F-centre transition energies could be obtained if all calculated parameters A_γ were reduced in magnitude by a factor of $\alpha = 0.53$. Gash [30] showed that α described the variation in the F-centre wavefunctions across the ion cores. In this way, α should be close to unity for very compact core functions and a factor $\alpha = 0.5$ would be appropriate for diffuse ions. In the case of the F_A centre, Weber and Dick [5] found that the empirical factor $\alpha = 0.53$ gave absorption splitting in the wrong direction. When they set $\alpha = 1$, qualitative agreement with experiment was obtained. In our case we take $\alpha = 1$. We let the lattice

Table 1. Energy levels for wavefunction types I, II and III of Gourary and Adrian [24], for an F_A centre in KCl-KBr:Li mixed crystals as a function of the concentration x . The values were obtained using the method of Bartram *et al* [4] for the empirical parameter $\alpha = 1$.

x	$-E_{1s}^{(1)}$ (au)	$-E_{2p}^{(1)}$ (au)	$-E_{1s}^{(2)}$ (au)	$-E_{2p}^{(2)}$ (au)	$-E_{1s}^{(3)}$ (au)	$-E_{2p}^{(3)}$ (au)
0	0.1790	0.1035	0.1814	0.0956	0.1874	0.1026
0.25	0.1796	0.1022	0.1805	0.1005	0.1865	0.1047
0.50	0.1800	0.1127	0.1797	0.1054	0.1856	0.1095
0.75	0.1805	0.1172	0.1789	0.1100	0.1846	0.1128
1.00	0.1808	0.1212	0.1780	0.1143	0.1836	0.1168

Table 2. Calculated F_A -centre absorption energies for KCl-KBr:Li mixed crystals as a function of the concentration x .

	Type I	Type II	Type III	Type IV
ΔE_0 (eV)	2.0536	2.3337	2.3065	2.4969
$\Delta E_{0.25}$ (eV)	1.9421	2.1760	2.2249	2.3392
$\Delta E_{0.5}$ (eV)	1.8305	2.0209	2.0699	2.1814
$\Delta E_{0.75}$ (eV)	1.7217	1.8741	1.9529	2.0291
ΔE_1 (eV)	1.6211	1.7326	1.8169	1.8849

Table 3. Energy levels for wavefunction types I, II and III of Gourary and Adrian [24] for an F centre in KCl-KBr:Li mixed crystals as a function of the concentration x . The values were obtained using the method of Bartram *et al* [4] for the empirical parameter $\alpha = 1$.

x	$-E_{1s}^{(1)}$ (au)	$-E_{2p}^{(1)}$ (au)	$-E_{1s}^{(2)}$ (au)	$-E_{2p}^{(2)}$ (au)	$-E_{1s}^{(3)}$ (au)	$-E_{2p}^{(3)}$ (au)
0	0.1762	0.0817	0.1804	0.0664	0.1860	0.0748
0.25	0.1768	0.0866	0.1796	0.0729	0.1850	0.0811
0.50	0.1774	0.0919	0.1788	0.0790	0.1841	0.0871
0.75	0.1778	0.0973	0.1779	0.0853	0.1832	0.0926
1.00	0.1782	0.1022	0.1771	0.0914	0.1822	0.0977

Table 4. Theoretical and experimental values of the F_{A1} and F_{A2} absorption shifts of F_A centres relative to F-centre absorption in KCl-KBr:Li as a function of the concentration x .

Centre	Absorption shift (eV)				
	$x = 0$	$x = 0.25$	$x = 0.50$	$x = 0.75$	$x = 1$
F_{A1}^{exp}	-0.315	-0.310	-0.305	-0.285	-0.250
F_{A2}^{exp}	-0.035	-0.055	-0.070	-0.075	-0.070
F_{A1}^{theor}	-0.468	-0.495	-0.474	-0.468	-0.446
F_{A2}^{theor}	0.076	0.076	0.070	0.073	0.070

Table 5. Values of the displacement ξ of the impurity, the displacement η of the ions type B and the displacement δ of the ion C as functions of the concentration x .

	$x = 0$	$x = 0.25$	$x = 0.50$	$x = 0.75$	$x = 1$
ξ	0.03789	0.03972	0.04198	0.04477	0.04829
η	0.05736	0.05844	0.05997	0.06212	0.06513
δ	0.04629	0.04079	0.03446	0.02699	0.01790

constant a_M be given by

$$a_M = a_1(1 - x) + a_2x \quad (18)$$

according to Vegard's rule [21] where x depends on the concentration, and a_1 and a_2 are the lattice constants of the crystals which form the mixed crystal. Also the A_γ and B_γ constants used in this paper are given by

$$A_\gamma = A_\gamma^{(1)}(1 - x) + A_\gamma^{(2)}x \quad (19)$$

and

$$B_\gamma = B_\gamma^{(1)}(1 - x) + B_\gamma^{(2)}x \quad (20)$$

where $A_\gamma^{(1)}$, $B_\gamma^{(2)}$ correspond to one type of crystal and $A_\gamma^{(2)}$, $B_\gamma^{(1)}$ to another type which are the components of the mixed crystal. In equations (19) and (20) we have assumed that the ion-size correction has the same behaviour as the lattice constant in the case of mixed crystals (equation (18)). This procedure is justified in the appendix. The constants $A_\gamma^{(1)}$, $A_\gamma^{(2)}$, $B_\gamma^{(1)}$ and $B_\gamma^{(2)}$ were taken from the paper by Bartram *et al* [4]. Table 1 shows the ground and excited states as functions of the concentration x for KCl-KBr:Li. For $x = 0$ we have a KCl pure crystal and for $x = 1$ a KBr pure crystal. The superscript corresponds to wavefunction types I, II and III. Table 2 gives the optical absorption energies as a function of x for the same wavefunctions. Type IV, in table 2, corresponds to the absorption energy which is obtained using $E_{1s}^{(3)}$ for the ground state and $E_{2p}^{(2)}$ for the excited state.

The ground and excited state energies for the F centre in KCl-KBr:Li for wavefunction types I, II and III and $\alpha = 0.53$ were reported by us [20]. In table 3 the same values

Table 6. Matrix elements related to equation (13), i.e. $\langle \Psi_s | \Sigma_i (1/r_i) | \Psi_s \rangle$, $\langle \Psi_s | \Sigma_i (1/r_i^D) | \Psi_s \rangle$, $\langle \Psi_p | \Sigma_i (1/r_i) | \Psi_{p/x,y,z} \rangle$ and $\langle \Psi_p | \Sigma_i (1/r_i^D) | \Psi_{p/x,y,z} \rangle$. $\langle \Psi_s | V_{\text{add}} | \Psi_s \rangle$ and $\langle \Psi_p | V_{\text{add}} | \Psi_p \rangle$ are also given.

	$x = 0$	$x = 0.25$	$x = 0.50$	$x = 0.75$	$x = 1$
$\langle \Psi_s \Sigma_{i=1}^6 (1/r_i) \Psi_s \rangle$ (au)	-1.0114	-0.9989	-0.9869	-0.9752	-0.9638
$\langle \Psi_s \Sigma_{i=1}^6 (1/r_i^D) \Psi_s \rangle$ (au)	-0.8987	-0.8858	-0.8725	-0.8586	-0.8438
$\langle \Psi_p \Sigma_{i=1}^6 (1/r_i) \Psi_{p/x} \rangle$ (au)	-1.0162	-1.0040	-0.9924	-0.9806	-0.9696
$\langle \Psi_p \Sigma_{i=1}^6 (1/r_i^D) \Psi_{p/x} \rangle$ (au)	-0.9019	-0.8890	-0.8758	-0.8621	-0.8470
$\langle \Psi_p \Sigma_{i=1}^6 (1/r_i) \Psi_{p/z} \rangle$ (au)	-1.0214	-1.0092	-0.9980	-0.9859	-0.9859
$\langle \Psi_p \Sigma_{i=1}^6 (1/r_i^D) \Psi_{p/z} \rangle$ (au)	-0.9055	-0.8926	-0.8797	-0.8663	-0.8511
$\langle \Psi_s V_{\text{add}} \Psi_s \rangle$ (au)	-0.1126	-0.1130	-0.1143	-0.1166	-0.1200
$\langle \Psi_p V_{\text{add}} \Psi_{p/x} \rangle$ (au)	-0.1143	-0.1150	-0.1166	-0.1185	-0.1226
$\langle \Psi_p V_{\text{add}} \Psi_{p/z} \rangle$ (au)	-0.1158	-0.1166	-0.1182	-0.1196	-0.1242

are given but with the empirical parameter $\alpha = 1$. Table 4 shows the experimental values of F_{A1} and F_{A2} , obtained from the results of Asami and Ishiguro [17], and the theoretical values.

Table 5 shows the displacements of the impurity, the ions B and the ion C (see figure 1) around the ion A, as functions of the concentration x , for KCl–KBr mixed crystals with a Li impurity. In table 6 the matrix elements $\langle \Psi_s | \sum_{i=1}^6 (1/r_i) | \Psi_s \rangle$, $\langle \Psi_s | \sum_{i=1}^6 (1/r_i^D) | \Psi_s \rangle$, $\langle \Psi_p | \sum_{i=1}^6 (1/r_i) | \Psi_p \rangle_{x,y,z}$ and $\langle \Psi_p | \sum_{i=1}^6 (1/r_i^D) | \Psi_p \rangle_{x,y,z}$ are given as functions of the concentration x .

5. Conclusions

Owing to the Li ion impurity the symmetry of the potential acting on the F-centre electron is reduced from O_h to C_{4v} . Consequently the excited p state of the unperturbed F centre will split into two levels. Transitions between the ground state and these two levels are characterised by the label F_{A1} and F_{A2} . The optical absorption associated with these transitions consists of two bands [19]: one (F_{A1}) which occurs at somewhat longer wavelengths than F_{A2} and is polarised parallel to the vacancy–impurity axis; the other (F_{A2}) is centred near the absorption band of the unperturbed F centre and is polarised in a plane perpendicular to the vacancy–impurity axis. Table 4 shows the experimental and theoretical values of F_{A1} and F_{A2} shifts.

Table 1 gives the energies of the ground and excited states for the three types of wavefunction. In table 2 the theoretical transition energies as a function of the concentration x are shown, and in table 3 the F-centre energies for the ground and excited states for $\alpha = 1$ are given. The values reported in [20] were for $\alpha = 0.53$.

As we can see from table 4, the sign of F_{A1}^{theor} is the same as that of F_{A1}^{exp} ; it is also very close in value and its behaviour as a function of the concentration is correct. In the case of F_{A2}^{theor} the sign is incorrect and the magnitude is close for $x = 0.5, 0.75$ and 1. As we obtained the values of F_{A1}^{exp} and F_{A2}^{exp} from the experimental curve in the paper by Asami and Ishiguro [17], perhaps the values of F_{A2}^{exp} for $x = 0$ and $x = 0.25$ that we obtained are inexact. $x = 0$ corresponds to pure KCl for which the F_{A2}^{exp} value is -0.06 [19], and $x = 1$ corresponds to pure KBr for which the F_{A2}^{exp} value is -0.06 [19]. So it seems evident that the magnitude of our F_{A2}^{theor} value is correct but has the wrong sign. Alig [3] and Ong and Vail [7] also found the last problem when they studied KCl:Li and KBr:Li, but they obtained the correct sign for KCl:Na.

In order to obtain the distortion around the F_A centre, we have assumed that there is no distortion around the F centre. This problem has been discussed in some detail by Ruíz-Mejía [25]. Other researchers [4, 24, 26, 27] have calculated these small displacements. This means that the charge distribution of the electron F centre is approximately equivalent to that of the halogen ion for which it substitutes. In that way the relaxation around the F_A centre is due mainly to the cation impurity, and the distortion problem can be solved by considering the distortion around an impurity in a simple crystal (which does not have an F centre). In that case the displacement of the ion A with respect to the impurity is the same as the displacement of the impurity with respect to the origin of the F_A centre.

As we can see from table 6, the change in energy of the ground and excited states due to the relaxation ($\langle \Psi_s | V_{\text{add}} | \Psi_s \rangle$ and $\langle \Psi_p | V_{\text{add}} | \Psi_p \rangle$) is important, but the change in the absorption energy due to this effect is small. These energies were calculated using a perturbative method. Ong and Vail [31] and Vail and Harker [31] have calculated the

distortion by directly minimising the total energy. As far as we know, they [31, 32] did not take into account the polarisation energy. Vail and Harker [32] made a calculation ignoring lattice distortion except for a static displacement of $0.08a$ (a is the interionic distance) of the Li impurity. We found that the Li impurity is displaced about $0.037a$ in KCl, but we also found that the other first neighbours (see table 5) are displaced as well.

For KCl the experimental energy for the F centre is 2.31 eV and for the $F_A(\text{Li})$ the absorption energies are 2.25 and 1.98 eV [19]. Because the perturbative energies due to the distortion of the F_A centre are negative, the theoretical energy due to the F_A centre, in the case of the x and y wavefunctions, is equal to the energy of the F centre (for x and y wavefunctions there is no ion-size correction) plus the perturbative energy. For KCl:Li that energy is equal to -0.0462 eV. Experimentally that energy level is equal to the energy of the F centre plus -0.06 eV. From table 6, we can see that the theoretical value is -0.0685 eV and the experimental value 0.06 eV. For the z wavefunction the contribution to the energy due to the distortion (-0.086 eV for KCl:Li and -0.1142 eV for KBr:Li) makes the theoretical results worse owing to the ion-size correction which is negative with respect to the energy of the F centre. For KCl:Li the theoretical energy is -0.516 eV (and the experimental value -0.33 eV) and for KBr:Li the theoretical value is -0.462 eV (and the experimental value -0.24 eV).

Vail and Harker [32] found good agreement between their calculations and the experimental results if they used flexible symmetry-adapted trial pseudowave functions and a form of the method of Bartram *et al* [4]. This type of wavefunction could be used in order to improve our calculations.

Appendix

In the method of Bartram *et al* [4], A_γ and B_γ are given approximately by

$$A_\gamma = 4\pi Q_\gamma (r_{\text{ion}\gamma})^2 \quad (\text{A1})$$

and

$$B_\gamma = \frac{4}{3}\pi (r_{\text{ion}\gamma})^3 \quad (\text{A2})$$

where Q_γ is the net charge of the ion γ , and $r_{\text{ion}\gamma}$ the radius of the r ion.

Table A1. Values of A_γ^a and B_γ^a calculated from equations (A4) and (A5), and A_γ^b and B_γ^b calculated from equations (A8) and (A9) as functions of the concentration x for KCl-KBr and KCl-RbCl mixed crystals. In the first case, $r_{\text{ion}\gamma}^{(1)}$ and $r_{\text{ion}\gamma}^{(2)}$ are the radii of the Cl^- and Br^- ions, and in the second case they are the radii of the K^+ and the Rb^+ ions. The units of $A_\gamma^{a,b}$ are $\text{Ryd } a_0^3$ and the units of $B_\gamma^{a,b}$ are a_0^3 , where a_0 is the Bohr radius.

x	$-A_\gamma^a$	$-A_\gamma^b$	B_γ^a	B_γ^b
KCl-KBr				
0.25	166.16	165.97	201.73	201.05
0.50	159.81	159.56	190.42	189.52
0.75	153.46	153.27	179.10	178.10
KCl-RbCl				
0.25	93.62	93.43	85.43	84.83
0.50	88.89	88.64	79.15	78.47
0.75	84.16	83.97	72.85	72.36

Table A2. Crystal constants used in these calculations. A , B , ρ and σ are constants in the repulsive energy expression, α is the polarisability and a is the interionic distance.

A_{K-Cl} (10^{-9} erg)	1.59	α_{Cl^-} (10^{-24} cm)	2.97
A_{K-Br} (10^{-9} erg)	1.55	α_{Br^-} (10^{-24} cm)	4.17
B_{Li-Cl} (10^{-9} erg)	1.44	α_{K^+} (10^{-24} cm)	1.33
B_{Li-Br} (10^{-9} erg)	1.42	a_{K-Cl} (Å)	3.139
ρ_{K-Cl} (Å)	0.337	a_{K-Br} (Å)	3.293
ρ_{K-Br} (Å)	0.346		
σ_{Li-Cl} (Å)	0.330		
σ_{Li-Br} (Å)	0.344		

From Vegard's rule [21] the lattice constant a_M of the mixed crystal is given by

$$a_M = a_1(1 - x) + a_2x \quad (A3)$$

where x depends on the concentration, and a_1 and a_2 are the lattice constants of the crystals which form the mixed crystal. Approximately ionic radii are additive quantities. Then from equation (A3) we can conclude that in one approximate way the ionic radii also obey Vegard's rule. Therefore A_γ^a and B_γ^a of the mixed crystals can be written as

$$A_\gamma^a = 4\pi Q_\gamma [(1 - x)r_{ion\gamma}^{(1)} + xr_{ion\gamma}^{(2)}]^2 \quad (A4)$$

and

$$B_\gamma^a = \frac{4}{3}\pi [(1 - x)r_{ion\gamma}^{(1)} + xr_{ion\gamma}^{(2)}]^2 \quad (A5)$$

where $r_{ion\gamma}^{(1)}$ and $r_{ion\gamma}^{(2)}$ are the radii of the ions which form the mixed crystals. The A_γ - and B_γ -values (equations (10) and (11)) used in this paper for the mixed crystals are given by

$$A_\gamma = A_\gamma^{(1)}(1 - x) + A_\gamma^{(2)}x \quad (A6)$$

and

$$B_\gamma = B_\gamma^{(1)}(1 - x) + B_\gamma^{(2)}x. \quad (A7)$$

The equations equivalent to equations (A6) and (A7) in terms of the ionic radii would be

$$A_\gamma^b = 4\pi Q_\gamma [(1 - x)(r_{ion\gamma}^{(1)})^2 + x(r_{ion\gamma}^{(2)})^2] \quad (A8)$$

and

$$B_\gamma^a = \frac{4}{3}\pi [(1 - x)(r_{ion\gamma}^{(1)})^3 + x(r_{ion\gamma}^{(2)})^3]. \quad (A9)$$

Using the approximate expressions (A1) and (A2) for A_γ and B_γ the corresponding values for the mixed crystal would be A_γ^a and B_γ^a . In order to see the magnitude of the error that we have made using equations (A6) and (A7) for our calculations, table A1 in which the values of A_γ^a and B_γ^a are compared with A_γ^b and B_γ^b should be consulted. We conclude that our approximation is good enough for our purposes. The values of $A_\gamma^{(1)}$, $B_\gamma^{(1)}$, $A_\gamma^{(2)}$ and $B_\gamma^{(2)}$ were taken from table 1 in the paper by Bartram *et al* [4] (see table A2). Equations (A4) and (A5) cannot be used in the calculations of the absorption energy of the F centre because A_γ (equation (A1)) and B_γ (equation (A2)) are not close to the values in table 1.

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