

A vibrational model of F centres in alkali halides

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Abstract. A model of F-centres in alkali halides, which relates absorption energies in F-bands to the dynamic parameters of host lattices, is proposed. According to this model, the electrons trapped in F-centres are treated as classical particles with a proper mass $m^* = m\varepsilon_{loc}^4/\varepsilon_\infty^2$, m standing for the actual electron mass, ε_{loc} and ε_∞ for local high frequency and optical dielectric constants, respectively. Hence, by considering the trapped electrons as substitutional impurities of small mass, the dynamics of the lattice is investigated by means of the theory of local modes with the assumption of isotopicity. A simple equation allowing calculation of the local mode frequencies is obtained. Knowledge of the Debye frequency and of transverse and longitudinal mode frequencies at the long wavelength limit is required. With this model, F-band absorption energy is reasonably well accounted for.

PACS. 63.20.Pw Localized modes – 71.55.-i Impurity and defect levels – 78.40.Ha Other nonmetallic inorganics

1 Introduction

Halide vacancies in ionic crystals originate localized positive extra-charges which can trap electrons when crystals are excited by ionizing radiations. Electron centres thus formed, called F-centres, have been investigated for many years [1, 2]. They have served as a testing-bench for various methods of calculating the electronic structure of lattice defects in ionic crystals. Consequently, many studies have been engaged dealing with electronic wave functions and energies of F-centres. These studies are grounded on models, usually referred to as static models, leaving out the dynamics of the lattice coupled to electrons. The earliest works treated the lattice as a continuum characterized by low and high frequency dielectric constants [1, 3–6] (continuum models). The F-centres were represented by means of special potentials determined in a self-consistent way. More realistic models were implemented by means of numerical calculations. The lattices were treated as made up of point-like ions and the wave functions of trapped electrons were taken as superpositions of orbitals centred on the nearest alkaline ions [7, 8] (point-ion models). Improved results were obtained by anti-symmetrizing these wave-functions with that of the alkaline ion cores [9].

The numerical calculations spoken of showed that the lattice surroundings of ground state F-centres are substantially undeformed. Moreover, it was found that the ionic crystal field determines the extent of the trapped electron wave-function which scales according to the lattice

parameter a [9]. This explains the Mollwo-Ivey law which maintains that the F-centre principal optical absorption energy E can be connected to the lattice parameter by means of a noteworthy power law relationship, that is, $E = Ca^{-n}$, where exponent n is to be determined by experiments [2]. It is to be pointed out that systematic deviations from the Mollwo-Ivey law become significant for large cationic radii where exchange interactions are large [10].

Contrary to the previously quoted studies, many other theoretical investigations emphasize the electron-lattice dynamics (dynamic lattice models). By considering the coupling of the oscillating electron distributions with the optical longitudinal modes, the F-band shapes, as well as their dependence on temperature have been explained [11]. A different point of view on the dynamic lattice problem is established by the configuration-coordinate model which characterizes the interaction of electron centres with the lattice by an *ad hoc* vibrational coordinate (configuration coordinate) [12].

This brief overview gives an idea of the role played by F-centres in solid state physics. On the whole, the aforementioned studies give a good qualitative and quantitative account of F-centre properties, although some questions are still to be answered in full. It is known that the average lattice frequency, which is coupled to the electronic transitions, lies far below the frequency of the longitudinal branch [13]. It follows that electrons must also couple to other-than-longitudinal optical modes. Moreover, it remains to be explained the role of the local lattice

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modes in the electronic transitions. Actually, some issues concerning the relation between the optical properties of F-centres and lattice dynamics have not yet been explored. In the classical picture, this matter appears simple. Indeed, if trapped electron behave as classical particles of small mass, then F-centres will originate local vibrational modes whose frequencies lie far above the normal vibration spectra of host lattices. An external electromagnetic field, resonantly coupled with these local modes, forces electrons to perform large amplitude oscillations while nuclei remain frozen at their current positions. Thus, these resonances, which supposedly form the absorption band of F-centres, may be correlated to the lattice-dynamic features by means of existing theoretical models. Given the interest in this matter, it is advisable to investigate such a classical system. Of course, a classical model raises some problems since electron motion must be treated quantum-mechanically. However, if a suitable representation of F-centres is found, there is hope of properly address the investigation dealt with. In this case, the known theory of local modes can be applied to the perturbed lattice. The goal would be to show that the frequencies of local modes originated by the trapped electrons are those of photons absorbed in F-bands.

The basic tools for addressing the present investigation are the study of local modes in vibrational spectra of perturbed lattices and the classical description of the F-centres interacting with the host lattice. Owing to the explorative nature of this investigation, the matter will be dealt with using heuristic arguments and applying suitable simplifications. The specialized issues are dealt with in dedicated sections of this paper. In Section 2, the local mode frequency originated by a small mass defect in an alkali halide crystal is calculated in the harmonic approximation. Section 3 is concerned with the problem of the classic representation of electrons trapped in F-centres. In Section 4, the problem of ion polarization is briefly discussed in order to account for local effects. Finally, in Section 5, results are compared with experiments.

2 Local mode calculation

When impurity atoms are introduced into a crystal, localized modes may appear. Their frequencies lie in ranges forbidden to normal modes of the unperturbed host crystal, and their vibration amplitude decreases faster than exponentially when the distance from the defect increases [14]. This leads to special features of the dependencies on frequencies of scattering and absorption processes. In particular, absorption spectra in ionic crystals show peaks corresponding to the local vibrations of the various centres. In the simplest case of a mono-atomic Debye lattice constituted by atoms of mass M_h some of which are isotopically (without changes of the force tensor) substituted by impurity atoms of mass M_S , the local mode frequency at the defect sites is $\omega = (M_h/M_S)^{1/2} (3/5)^{1/2} \omega_D$, where ω_D stands for the Debye frequency [15]. This equation correctly predicts the ratio of local mode frequencies originated by light impurities such as H^- and D^-

(U -centres) replacing anions also when applied to alkali halides. Actually, the local modes dealt with have frequencies larger than those of the normal mode spectrum and the frequency ratio of absorbed photons is near the ratio $(M_D/M_H)^{1/2}$ of the isotope masses [16].

The simple mono-atomic model is, of course, unsuitable for predicting actual local mode frequencies in ionic crystals, since ion oscillations have components in both acoustic and optical branches. A powerful method based on the Green function, which is suited to address this kind of problems, has been developed [14,17,18]. In some favourable circumstances, this method leads to approximated analytical solutions. This occurs when the local modes lie so largely separated from the normal mode spectrum that their amplitude vanishes within the distance of nearest neighbours ions from defects [14,17]. This section is concerned specifically with strongly localized modes originated by very light substitutional impurities for which the vibration frequency is expected to lie far above the normal mode spectrum.

The equation of local modes has been derived in a detailed way by Dawber and Elliot in reference [17]. In their paper, the modes of vibration of isotopic defects were studied by considering the simplest case of a single mass defect in cubic lattice. In this case, the eigenvalue equations for the perturbed modes are reduced to consider a 3×3 diagonal matrix which give a threefold degenerate solutions for the eigenvectors of the dynamic matrix, that is,

$$\frac{\epsilon_i \omega^2}{N} \sum_{k,f} \frac{|\sigma_{X_i}(\mathbf{k}, f)|^2}{\omega^2(\mathbf{k}, f) - \omega^2} = -1, \quad (1)$$

where $\epsilon_i = (M_i - M_S)/M_i$, M_i standing for the mass of ion of index i ($i = 1, 2, \dots, s$) and M_S the mass of the substitutional ion, ω the frequency of the local mode, $\omega(\mathbf{k}, f)$ the frequencies of the lattice modes of branch f ($f = 1, 2, \dots, 3s$) and wave vector \mathbf{k} , N the number of lattice cells and $\sigma_{X_i}(\mathbf{k}, f)$ the x -component of the eigenvectors of the dynamic matrix which satisfy the relations [19]

$$|\sigma_{X_i}(\mathbf{k}, f)|^2 = |\sigma_{Y_i}(\mathbf{k}, f)|^2 = |\sigma_{Z_i}(\mathbf{k}, f)|^2 = \frac{|\sigma_i(\mathbf{k}, f)|^2}{3} \quad (2)$$

and the normalization conditions

$$\sum_j \sigma_j(\mathbf{k}, f) \cdot \sigma_j^*(\mathbf{k}, h) = \delta_{fh}, \quad (3)$$

$$\sum_f \sigma_i(\mathbf{k}, f) \cdot \sigma_j^*(\mathbf{k}, f) = 3\delta_{i,j}. \quad (4)$$

The factor 3 appearing in equation (4) (which is to be compared with equation (2.5) of reference [17]) is a consequence of equation (2) and of the sum over the vector components. Now, from equations (1–2), it follows

$$\frac{\epsilon_i \omega^2}{3N} \sum_{k,f} \frac{|\sigma_i(\mathbf{k}, f)|^2}{\omega^2(\mathbf{k}, f) - \omega^2} = -1,$$

which, by taking into account equation (4) and that $\omega^2 \gg \omega^2(k, f)$, can be re-written as

$$\frac{\epsilon_i}{3N} \sum_{kf} |\sigma_i(\mathbf{k}, f)|^2 \omega^2(\mathbf{k}, f) = (1 - \epsilon_i) \omega^2. \quad (5)$$

It is convenient to separate the sum over acoustic modes from that over optical modes and to rewrite equation (5) by using different labels for the two ion species of alkali halides. Let label α indicate one specie of substituted ions and β the other ion specie. So, equation (5) becomes

$$\begin{aligned} \frac{\epsilon_\alpha}{3N} \sum_{kf_{AC}} |\sigma_\alpha(\mathbf{k}, f_{AC})|^2 \omega^2(\mathbf{k}, f_{AC}) \\ + \frac{\epsilon_\alpha}{3N} \sum_k |\sigma_{\alpha LO}(\mathbf{k})|^2 \omega_{LO}^2(\mathbf{k}) \\ + \frac{2\epsilon_\alpha}{3N} \sum_k |\sigma_{\alpha TO}(\mathbf{k})|^2 \omega_{TO}^2(\mathbf{k}) = (1 - \epsilon_\alpha) \omega^2, \end{aligned} \quad (6)$$

where labels AC , TO and LO mean acoustic, transverse and longitudinal optical modes, respectively. The degeneration of optical transverse modes is accounted for by the factor 2. The actual normal vibrations in crystals are very complicated. Thus to obtain from equation (6) handy formula, some crude simplifications are required. The more conservative assumption is to consider the amplitudes of vibration vectors as independent of f and \mathbf{k} , both over the acoustic and the optical branches, that is,

$$|\sigma_\alpha(\mathbf{k}, f_{AC})|^2 = |\sigma_{\alpha AC}|^2 \quad (7)$$

and

$$|\sigma_{\alpha LO}(\mathbf{k})|^2 = |\sigma_{\alpha TO}(\mathbf{k})|^2 = |\sigma_{\alpha OP}|^2. \quad (8)$$

A possible choice for the eigenvector normalization is

$$|\sigma_{\alpha AC}|^2 = \frac{M_\alpha}{M_\alpha + M_\beta} \quad |\sigma_{\alpha OP}|^2 = \frac{M_\beta}{M_\alpha + M_\beta} \quad (9)$$

and

$$|\sigma_{\beta AC}|^2 = \frac{M_\beta}{M_\alpha + M_\beta} \quad |\sigma_{\beta OP}|^2 = \frac{M_\alpha}{M_\alpha + M_\beta}. \quad (10)$$

Accordingly, when in equation (6) $M_\beta = 0$, optical modes vanish. Owing to equations (7–8), sums in equation (6) apply only to the frequencies. For the acoustic modes, a Debye dispersion law is assumed which has been proved to be quite successful in thermodynamics [15, 20]. Thus, the sum over the acoustic modes becomes

$$\begin{aligned} \sum_{kf} |\sigma_\alpha(\mathbf{k}, f_{AC})|^2 \omega^2(\mathbf{k}, f_{AC}) &= 3 |\sigma_{\alpha AC}|^2 \sum_k \omega^2(\mathbf{k}) \\ &= \frac{9N}{5} \frac{M_\alpha}{M_\alpha + M_\beta} \omega_D^2, \end{aligned}$$

where factor 3 accounts for the three acoustic branches. As for optical modes, a flat dispersion law is assumed. This is accurate for transverse modes, but for longitudinal modes

it involves an error on the order of 10% [19]. It follows that

$$\begin{aligned} 2 |\sigma_{\alpha TO}|^2 \sum_k \omega_{TO}^2(\mathbf{k}) + |\sigma_{\alpha LO}|^2 \sum_k \omega_{LO}^2(\mathbf{k}) = \\ N \frac{M_\beta}{M_\alpha + M_\beta} (2\omega_{TO}^2 + \omega_{LO}^2), \end{aligned}$$

which allows equation (6) to be re-written as

$$\epsilon_\alpha \frac{[\frac{3}{5} M_\alpha \omega_D^2 + \frac{2}{3} M_\beta (\omega_{TO}^2 + \frac{1}{2} \omega_{LO}^2)]}{M_\alpha + M_\beta} = (1 - \epsilon_\alpha) \omega^2. \quad (11)$$

Finally, by taking into account that $\epsilon_\alpha = 1 - M_S/M_\alpha \simeq 1$ and $1 - \epsilon_\alpha = M_S/M_\alpha$, equation (11) leads to

$$\omega^2 = \frac{3}{5} \frac{M_\alpha}{M_\beta} \frac{\mu}{M_s} \omega_D^2 + \frac{2}{3} \frac{\mu}{M_s} \left(\omega_{TO}^2 + \frac{1}{2} \omega_{LO}^2 \right), \quad (12)$$

μ standing for the reduced ion mass $M_\alpha M_\beta / (M_\alpha + M_\beta)$. In the limit of $M_\beta \rightarrow 0$, that is for monatomic crystals, $\mu \rightarrow 0$ and $\mu/M_\beta \rightarrow 1$. Thus, according to equation (12), the local mode frequency becomes $\omega = (3/5)^{1/2} (M_\alpha/M_S)^{1/2} \omega_D$ as expected.

3 The classic F-centre oscillator

According to the classical representation of photon emitting or absorbing atomic systems, electrons are assumed to lie at equilibrium positions within the atoms and to react elastically to disturbances [21]. So, they perform forced oscillations when exposed to electromagnetic radiations. The amplitude and phase of these oscillations depend, according to simple laws of mechanics, on the characteristic frequency of the free oscillations, on their damping factor and on the frequency of the electromagnetic radiation. Maximum oscillation amplitude is attained at a resonance whose frequency, owing to the damping forces, is in general slightly different from the characteristic frequency. Isolated systems have resonances determined only by their internal structure. On the contrary, systems such as F-centres have dynamic properties strongly affected by interactions with the host medium. In these cases, resonances must be determined by taking into account the actual form of these interactions. If electrons behave as classical particles, this problem could be addressed along the lines of the local mode theory presented in Section 2. However, the quantum mechanical treatment cannot be avoided. Thus, to use equation (12), a suitable harmonic model for F-centres must be assumed, that is,

$$\omega^2 m^*_\alpha - \sum_\beta \frac{\partial^2 U}{\partial u_\alpha \partial u_\beta} \delta u_\beta = 0 \quad (13)$$

where m^* means a proper electron mass, δu the oscillation amplitude, ω the oscillation frequency corresponding to the F-band transition and $U = 1/2 K \delta u^2$ the potential energy. The associated elastic constant is $K = \omega^2 m^*$

which should be compared to the one resulting from equation (12) with $M_S = m^*$, that is,

$$K_{class} = \omega^2 m^* = \frac{3}{5} \frac{M_\alpha}{M_\beta} \mu \omega_D^2 + \frac{2}{3} \mu \left(\omega_{TO}^2 + \frac{1}{2} \omega_{LO}^2 \right). \quad (14)$$

The foregoing arguments are based on the Ehrenfest theorem, which states that on the average the evolution of a quantum system obeys classical laws, and on the hypothesis that equation (12) is indeed what classical mechanics predicts for the electron motion. Now, is the time to tackle the quantum mechanical problem. The Hamiltonian of a crystal containing F-centres is of the form [15,22]

$$H = H_R + H_r + V(\mathbf{r}, \mathbf{R}), \quad (15)$$

where H_R is the sum of the kinetic and potential energies of the ions, H_r the kinetic energy of the F-centre electron and $V(\mathbf{r}, \mathbf{R})$ its interaction energy with the ions. In reality, the interaction among electrons should be treated explicitly. But this is impracticable since too many electron coordinates would have to be taken into account. Thus, to deal with these interactions, $V(\mathbf{r}, \mathbf{R})$ is assumed to be a one-electron effective interaction energy. Interaction among F-centres is assumed to be negligible. The eigen-states of the Hamiltonian (15) can be searched for in the usual way, along the lines of the adiabatic potential method. Assuming the coordinates \mathbf{R} of the ions to be fixed, the eigenvalue equation

$$[H_r + V(\mathbf{r}, \mathbf{R})] \varphi_l(\mathbf{r}, \mathbf{R}) = E_l(\mathbf{R}) \varphi_l(\mathbf{r}, \mathbf{R}) \quad (16)$$

gives the adiabatic potential $E_l(\mathbf{R})$ for the l th electron state. In this electronic state, the motion of the nuclear system is determined by

$$[H_R + E_l(\mathbf{R})] \zeta_{lv}(\mathbf{R}) = E_{lv} \zeta_{lv}(\mathbf{R}). \quad (17)$$

Thus, a quantum state of the whole system is specified by the electron and phonon quantum numbers l and v , respectively, so that the wave function takes the form

$$\psi_{lv}(\mathbf{r}, \mathbf{R}) = \varphi_l(\mathbf{r}, \mathbf{R}) \zeta_{lv}(\mathbf{R}), \quad (18)$$

which is a good approximation for the stationary states [22]. Now, in the presence of an exciting field, the perturbation operator $H_I = e/c\mathbf{A} \cdot \mathbf{p}$ ($-e$ standing for the electron charge) is to be added to the Hamiltonian (15) [23]. When the radiation field is coupled with the F-centre electrons, the function of state may be written as a superposition of wave-functions like the one given in equation (18). Actually, the absorption consists of a series of narrow lines merging into a single broad band. Each line involves a narrow set of phonon levels of quantum numbers w for which the Bohr condition $h\nu = E_{bw} - E_{av}$ is satisfied, $h\nu$ standing for the energy of the absorbed photon and E_{bw} and E_{av} for the energies of the final and initial states of the transition dealt with, respectively. At zero K, only the lowest vibrational state $\zeta_{a0}(\mathbf{R})$ is occupied and absorption takes place only within a narrow band. This is the most favourable case for handling. Indeed, provided the photon energy is not close to system

resonance, the perturbative procedure can be applied. It follows that the wave-function of the perturbed F-centre is

$$\Psi(\mathbf{r}, \mathbf{R}, t) = \varphi_a(\mathbf{r}, \mathbf{R}) \zeta_{a0}(\mathbf{R}) \exp(-iE_{a0}t/\hbar) + \sum_v b_v(t) \varphi_b(\mathbf{r}, \mathbf{R}) \zeta_{bv}(\mathbf{R}) \exp(-iE_{bv}t/\hbar). \quad (19)$$

The mean force, acting on the F-centre electrons during the excitation with external fields, can be calculated by averaging on Ψ the derivative of electron momentum $\mathbf{P} = \mathbf{p} + e/c\mathbf{A}$ [23]. That is,

$$\left\langle \frac{d\mathbf{P}}{dt} \right\rangle = \left\langle \Psi \left| \frac{d\mathbf{P}}{dt} + \frac{e}{c} \frac{d\mathbf{A}}{dt} \right| \Psi \right\rangle = \left\langle \Psi \left| \frac{d\mathbf{P}}{dt} \right| \Psi \right\rangle - e\mathbf{E}, \quad (20)$$

\mathbf{E} being the electric field of the exciting radiation. By exploiting the hermitian character of the Hamiltonian H with respect to the wave-function (18), the derivative of momentum \mathbf{p} can be written as [23]

$$\frac{d\mathbf{P}}{dt} = -\frac{m}{\hbar^2} [H, [H, \mathbf{r}]].$$

In the lowest approximation order, equation (20) leads to

$$\left\langle \frac{d\mathbf{P}}{dt} \right\rangle = -\frac{m}{\hbar^2} (E_b - E_a)^2 \delta \mathbf{u}_e - e\mathbf{E}, \quad (21)$$

where $(E_b - E_a)$ is the energy of the transition dealt with and (see Appendix A),

$$\delta \mathbf{u}_e = \frac{-e\mathbf{E}/m}{(E_b - E_a)^2 / \hbar^2 - \omega^2}. \quad (22)$$

Consequently, equation (21) describes a forced harmonic oscillator of elastic constant

$$K = \frac{m}{\hbar^2} (E_b - E_a)^2. \quad (23)$$

Constant K thus defined still cannot be compared with the K_{class} of equation (14). Indeed, it is not known how equations (14) and (23) account for the electron-electron interactions. Therefore, some other considerations are required. Since this matter is difficult to handle, it will be addressed by means of heuristic arguments. For this purpose, it is convenient to subsume the electron-electron interactions in a suitable local dielectric constant ε_{loc} . Now, the problem at issue may be better illustrated by treating the F-centre as an hydrogen system immersed in a medium of dielectric constant ε_{loc} . By applying the procedure leading to equation (21), it is found that the frequency of the electron transition is $\omega = \omega_V / \varepsilon_{loc}^2$, where the “V” label means the “vacuum”, that is, the medium with $\varepsilon_{loc} = 1$. This is tantamount to saying that ω_V represents the oscillation frequency in a medium made up by non-polarizable ions. Thus, from equation (23) it follows that

$$\omega = \omega_V / \varepsilon_{loc}^2 = \sqrt{K/m}. \quad (24)$$

Concerning the oscillation frequency of an object of mass m , as given by the local mode theory, it is to be pointed out that in the right member of equation (14) only quantities not related to local features appear. Thus,

Table 1. F-band absorption energies (eV) of F-centres in alkali halides with NaCl structures. Top values in boxes were calculated by means of equation (34). The starred values are experimental figures measured at 5 K. Values in round brackets were measured at room temperature. Data are taken from reference [1]. Values in square brackets are taken from reference [26].

	F	Cl	Br	I
	4.96	2.80		
Li	5.10*, [5.102] (4.96)	[3.30] (3.22)	/	/
	3.88	2.85	2.37	2.04
Na	3.69*, [3.723] (3.65)	2.75*, [2.770] (2.67)	2.36*, [2.1] (2.30)	/ (2.11)
	2.81	2.21	2.19	1.84
K	[2.847] (2.75)	2.30*, [2.313] (2.20)	2.06*, [2.064] (1.97)	1.86*, [1.875] (1.81)
	2.37	1.81	1.82	1.59
Rb	[2.428] (2.43)	[2.050] (1.98)	[1.857] (1.72)	[1.708] (1.60)

in place of ε_{loc} , the optical dielectric constant ε_∞ is accounted for. The dependence on ε_∞ is expected to be different from that on ε_{loc} shown in equation (24). Indeed, the inverse of ε_{loc}^2 appears in this equation consequent to quantum mechanics since the state of the system is defined only by mutually commuting physical quantities. Thus, if the electron is localized in a region of dimension δr , its momentum goes as $\sim 1/\delta r$. But, in a medium of dielectric constant ε_∞ , the size of an atomic system goes as ε_∞ (indeed the effective Bohr radius is given by $a_0 = \varepsilon_\infty a_B$). This leads to $\delta r \sim \varepsilon_\infty$. Therefore, kinetic energy, and thus total energy, shows the dependence on $1/\varepsilon_\infty^2$. Of course, this is not the case with the local mode theory because the state of a classical system is defined by the contemporary assignments of r and p , that is, of a point in the phase space. Thus, a weaker dependence of the kind $1/\varepsilon_\infty^\alpha$ with $\alpha < 2$ is expected. As a working hypothesis, it can be assumed that

$$\omega_{class} = \omega_V/\varepsilon_\infty = \sqrt{K_{class}/m},$$

which leads to

$$\omega = \sqrt{\varepsilon_\infty^2 K_{class}/\varepsilon_{loc}^4 m}. \quad (25)$$

In this way, it follows from equations (14), (24) and (25) that

$$\frac{\varepsilon_{loc}^4}{\varepsilon_\infty^2} m \omega^2 = \frac{3}{5} \frac{M_\alpha}{M_\beta} \mu \omega_D^2 + \frac{2}{3} \mu \left(\omega_{TO}^2 + \frac{1}{2} \omega_{LO}^2 \right), \quad (26)$$

which calls for mass $m^* = m \varepsilon_{loc}^4 / \varepsilon_\infty^2$ being introduced in equation (14).

4 The effective dielectric constant

In Section 3, interactions of F-electrons with ion-electrons have been subsumed under the effective dielectric constant ε_{loc} which, owing to local effects, is in general different from ε_∞ . Local effects include both local polarizations and exchange interactions with electrons of nearest ions. For simplicity's sake, it can be assumed that exchange interactions do not significantly affect the constant ε_{loc} . This seems reasonable when alkali ions of small radius are considered [4]. On the other hand, a rigorous investigation

of the local effects is not the purpose of this paper, nor is it necessary. It is sufficient to find an approximated relation between ε_{loc} and ε_∞ including a free parameter η to be determined by means of fittings to experiments. Thus, in calculations of Section 5 a simple relation of the form $\varepsilon_{loc} = \eta \varepsilon_\infty$ will be adopted. To understand the meaning of parameter η , it is useful to recall that ε_∞ is a function of $\alpha_+ + \alpha_-$, symbols α_+ and α_- standing for the polarizabilities of positive and negative ions respectively [20]. Dependence on $\alpha_+ + \alpha_-$ is a consequence of the assumption about uniformity of the electric field. In the case of optical fields, this assumption is reasonable if a region, smaller than the wavelength of the field but larger than the lattice parameter, is considered. On the contrary, in the case of localized charges, the field can no longer be considered as uniform. Indeed, electric potential changes greatly even at a distance from the source of field as small as a few lattice spacings. Thus, owing to proximity of F-electron to the nearest positive ions, the role of α_+ in ε_{loc} is expected to be emphasized. However, if the actual number N_+ of nearest positive ions is less than the number N_- of nearest negative ions, the proximity effect may be counterbalanced by the N_+ to N_- disparity. In this case, ε_{loc} can be replaced with ε_∞ . This can occur in alkali halides with a NaCl structure for which $N_+ = 6$ and $N_- = 12$. As for the alkali halides with CsCl structure, for which $N_+ = 8$ and $N_- = 6$, the inequality $\alpha_+ < \alpha_-$ always holds [20], so allowing for $\varepsilon_{loc} < \varepsilon_\infty$.

By anticipating the results of the fits, it is found $\eta = 1$ and $\eta = 1/1.17$ for NaCl and CsCl structures, respectively, in agreement with the aforesaid expectations. More refined equations for ε_{loc} are left out because they are merely speculative in the present context. Further comment on this matter will be made at the end of Section 5.

5 Results

The F-band absorption energies of alkali halides belonging to NaCl structures are calculated by means of equation (26) with $\varepsilon_{loc} = \varepsilon_\infty$. The results obtained are shown in Table 1. Values of ε_∞ are reported in Appendix B, the optical frequencies ω_{TO} and ω_{LO} are taken from reference [24] and the Debye frequencies ω_D from

Table 2. F-band absorption energies (eV) of F-centres in alkali halides with CsCl structures. In boxes, the top values were calculated by means of equation (34). The values in brackets were measured at room temperature. Data are taken from reference [1].

	Cl	Br	I
Cs	1.83 (2.06)	1.82 (1.84)	1.78 (1.58)

reference [25]. Each calculated value is associated with the corresponding experimental figure. The starred values are those measured at 5 K, the others in round brackets are those measured at room temperature [1]. Values in square brackets are taken from reference [26]. For these latter, no information about temperature is available.

It can be seen that differences between theory and experiments are on the order of 10%. In some cases the agreement is better. When possible, comparison is to be made with starred values. It is to be pointed out, in this connection, that the present model does not account for the effect of temperature on absorption energy. Actually, this effect is related to the change in lattice frequencies originated by F-centres transitions [11]. In general, these frequencies decrease during the absorption processes so that the vibrational energy of the lattice decreases, thus allowing F-centres to be excited with less energy. Owing to the increase in phonon density, this effect becomes larger as temperature increases.

In some cases, the Debye frequencies ω_D are lacking or difficult to be found in literature. This occurs for LiBr and alkali halides with a CsCl structure. In these cases, the reststrahlen frequencies ω_{TO} were utilized in place of the Debye ones. This was done with some confidence because the ratio of frequencies ω_D and ω_{TO} approaches unity as their value decreases. Absorption energies for CsCl-like alkali halides were calculated using $\varepsilon_{loc} = \varepsilon_{\infty}/1.17$. Results are given in Table 2 together with experimental figures. The agreement is poorer than for NaCl structures. This probably depends on an inadequate fitting to local effects. In particular, exchange interactions may play a more significant role in CsCl- than in NaCl-like crystals, owing both to the larger alkaline ion radius and to the higher N_+ value.

In Table 3 are shown the ratios E_{th}/E_{exp} , where E_{th} and E_{exp} mean the energies of absorbed photons as calculated from equation (26) and found from experiments, respectively. Experimental data were obtained from room temperature measurements. It can be noted that for each halide series the ratio E_{th}/E_{exp} shows a maximum in correspondence to Na and K ions. To explain this behaviour, two contrasting effects should be considered: the exchange interactions effect and the local polarizations effect. The former lowers the energies of electron states, thus causing an increase in transition energy and, consequently, a decrease in E_{th}/E_{exp} . On the contrary, local polarization causes an increase in E_{th}/E_{exp} as ε_{∞} increases. This is due to the fact that the polarizabilities α_{\pm} increase as ionic radii increase [20], so that ε_{loc} is expected to increase faster than ε_{∞} . This latter effect is dominant for low

Table 3. Ratios of absorption energies E_{th} and E_{exp} obtained from equation (34) (see Tab. 1) and from experiments at room temperature, respectively.

E_{th}/E_{exp}	F	Cl	Br	I
Li	1	0.86	/	/
Na	1.06	1.07	1.03	0.97
K	1.02	1	1.11	1.02
Rb	0.97	0.95	1.05	0.99

r_+/r_- ratios, while for large r_+/r_- ratios the exchange interactions effect is prevalent.

6 Conclusions

A classical model is proposed for use in investigating F-centres in alkali halides by means of the local mode theory. The trapped electron is treated as an isotopic substitutional impurity with effective mass $m^* = m \varepsilon_{loc}^4 / \varepsilon_{\infty}^2$, m standing for the electron mass, ε_{loc} for an effective high frequency dielectric constant accounting for local effects and ε_{∞} for the usual optical dielectric constant. The vibrational spectrum of the lattice is simplified by using a Debye dispersion law for the acoustic modes and a flat dispersion law for the optical modes. The frequencies of transverse and longitudinal optical modes are taken at the long wavelength limit. With these assumptions, the local mode theory is applied in the harmonic approximation. This was done by means of the Green method developed by Dawber and Elliot [17] which, in this particular case, leads to a fairly simple equation for the frequency of the local mode. It is found that this frequency depends on the averages of optical and acoustic frequencies of the lattice. By putting $\varepsilon_{loc} = \varepsilon_{\infty}$ for NaCl-like crystals, the calculated frequencies agree, within an error of about 10%, with those of F-band photons. In some cases the agreement is closer. In the case of CsCl-like crystals, for which $\varepsilon_{loc} = \varepsilon_{\infty}/1.17$ was chosen, the agreement is not as good. Perhaps, this is due to an over-simplification of local effects. On the whole, the results are satisfying, thus encouraging their extension to crystals other than alkali halides.

Appendix A

To prove equation (22), it is to be taken into account that

$$\langle \psi_{bv} | H_I | \psi_{a0} \rangle = e/c \mathbf{A} \cdot \langle \psi_{bv} | \mathbf{p} | \psi_{a0} \rangle = i \frac{e \mathbf{A}}{\hbar c} \cdot \langle \psi_{bv} | [H, \mathbf{r}] | \psi_{a0} \rangle = e \mathbf{E} \cdot \langle \psi_{bv} | \mathbf{r} | \psi_{a0} \rangle, \quad (\text{A.1})$$

where, in the Condon approximation [1],

$$\langle \psi_{bv} | \mathbf{r} | \psi_{a0} \rangle = \langle \zeta_{bv} | \zeta_{a0} \rangle \langle \varphi_b | \mathbf{r} | \varphi_a \rangle = \langle \zeta_{bv} | \zeta_{a0} \rangle \mathbf{r}_{ab}.$$

Thus, according to perturbation theory [23], by putting $\mathbf{A}(t) = \mathbf{A}_0 \exp(-i\omega t) + \text{c.c.}$, $F = e/c \mathbf{A}_0 \cdot \mathbf{p}$ and by

omitting the c.c. terms, the oscillation amplitude is found to be

$$\delta \mathbf{u} = - \left[\frac{F_{ba}}{E_b - E_a - \hbar\omega} \mathbf{r}_{ab} + \frac{F_{ba}^*}{E_b - E_a + \hbar\omega} \mathbf{r}_{ab}^* \right] \times \sum_v \langle \zeta_{a0} | \zeta_{bv} \rangle \langle \zeta_{bv} | \zeta_{a0} \rangle \exp(-i\omega t). \quad (\text{A.2})$$

In the case of a narrow band, this equation can be simplified by extending the sum on the phononic quantum number over the whole set of functions ζ_{bv} . Indeed, by utilizing the completeness property

$$\sum_v \langle \zeta_{a0} | \zeta_{bv} \rangle \langle \zeta_{bv} | \zeta_{a0} \rangle = 1$$

and by taking into account equation (A.1), equation (A.2) can be rewritten in the simplified form

$$\delta \mathbf{u} = -e \left[\frac{\mathbf{E} \cdot \mathbf{r}_{ba}}{E_b - E_a - \hbar\omega} \mathbf{r}_{ab} + \frac{\mathbf{E} \cdot \mathbf{r}_{ba}^*}{E_b - E_a + \hbar\omega} \mathbf{r}_{ab}^* \right].$$

Now, since \mathbf{r}_{ab} is parallel to the electric field, it is easy to show that

$$\mathbf{E} \cdot \mathbf{r}_{ba} \mathbf{r}_{ab} = |r_{ba}|^2 \mathbf{E},$$

which leads to

$$\delta \mathbf{u} = - |r_{ba}|^2 \frac{2(E_b - E_a)/\hbar^2}{(E_b - E_a)^2/\hbar^2 - \omega^2} e \mathbf{E}.$$

Finally, by taking into account that the oscillator strength of the F-band transition is near unity [26], that is,

$$f_{ab} = 2m |r_{ba}|^2 (E_b - E_a)/\hbar^2 \simeq 1,$$

the oscillation amplitude becomes

$$\delta \mathbf{u} = \frac{-e \mathbf{E}/m}{(E_b - E_a)^2/\hbar^2 - \omega^2}.$$

Appendix B

Table 4. Dielectric constants of the alkali halides considered in Tables 1 and 2. Labels (a), (b) and (c) indicate references [19,24] and [27] respectively.

ε_∞	F	Cl	Br	I
Li	1.92 (a)	2.7 (b, c)	/	/
Na	1.79 (c)	2.25 (a, b)	2.69 (c)	2.91 (a, b)
K	1.83 (c)	2.13 (a)	2.33 (a)	2.69 (a, c)
Rb	1.9 (b)	2.19 (a, b, c)	2.33 (a, c)	2.63 (a, c)
Cs	/	2.60 (a)	2.78 (a)	3.0 (b)

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