

DEFECT STATE MODEL FOR LOCALIZED EXCITATIONS IN LiF*

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Received 26 November 1976

We find that a defect state treatment of localized excitations in LiF within the local density functional formalism accounts remarkably well for the observed experimental (core plus optical gap) excitations — in contrast to the failure of the one-electron band model. We show that when electron relaxation, self-interaction and charge polarization effects are taken into account by treating the excitation as a localized point defect, the improved band model predicts the correct excitation and interband states.

Despite extensive investigations, the nature of the fundamental optical gap and core excitations in ionic solids — of which LiF is considered the prototype — remains as a challenge to experimentalists and theorists alike. Theoretically, two basic models have been extensively applied: the restricted Hartree-Fock (HF) model [1] and the local density (LD) model [2–3]. With the recent advances in linear combination of atomic orbitals (LCAO) techniques, the more conventional non-self-consistent muffin-tin schemes were abandoned in favor of the more sophisticated extended basis set self-consistent (non-muffin-tin) LCAO methods for both models. Their applications have, however, yielded mixed results: (i) local exchange calculations [3] with an exchange coefficient α close to 1.0 could reproduce the optical gap but an extended Gaussian basis ($\alpha = 1$) study [2] gave calculated one-electron energies substantially lower than experiment in the interband region [4] and yielded the suggestion that the observed spectra both in the optical gap region (11–12 eV) and in the Li–K excitation region (60–62 eV) be reinterpreted as Bloch-type interband transitions instead of as bound excitons — in marked contradiction with recent experiments [4–8]. (ii) restricted HF calculations [1] revealed a pronounced disagreement of the one-electron eigenvalue differences with experimental transition energies in the whole spectral region and indicated that electron correlation, electron-hole interactions and relaxation corrections (calculated

using a simplified atomic model) are necessary to bring the results into agreement with experiment. It was further stated by these authors [1] that the local exchange model is inadequate for describing excitations in these materials.

We report results which show that a proper treatment of localized excitations in the LD model accounts remarkably well for all the observed experimental data in contrast to the failures of the one-electron band model. Our method goes beyond the conventional band model by considering excitation processes as transitions involving point-defect states in a solid and uses *total (statistical) energy* differences between separately calculated ground and excited states rather than *one-electron* energy differences of a ground state calculation to evaluate the relevant excitation energies. Specifically, this is done by our “small periodic cluster” (SPC) model [9] in which we perform a fully self-consistent band structure calculation but with a large crystallographic unit cell (8–16 atoms) containing a locally excited atom at its center instead of the usual (perfect crystal) primitive cell. The model allows for explicit electron-relaxation effects, self-interaction corrections (for the non-existence of Koopmans’ theorem in the local density model even in the unrelaxed limit), charge polarization correction and correlation (treated in the free-electron approximation) effects.

Our starting point is the self-consistent (SC) band structure obtained by solving the one-particle LD functional Hamiltonian with a free-electron exchange potential (using $\alpha = 2/3$) and the electron correlation potential of Singwi et al. [10]. Our LCAO basis set con-

* Supported by the National Science Foundation and the Air Force Office of Scientific Research.

sists of an extended *numerical* set (i.e., exact solutions of the LD one-particle equation, but for the free ions, in the presence of a localizing external potential) of type 1s, 2s, 2p, and 3s for Li^+ and 1s, 2s, 2p, 3s, and 3p for F^- . Full self-consistency (i.e., all non-spherical components of the charge density are included in the SC iterations) is obtained and all non-muffin-tin contributions to the potential as well as multi-center interaction terms are included using a direct three-dimensional Diophantine integration technique [11]. The model yields good agreement with experimental ground state observables (e.g., calculated X-ray scattering factors agree to 1% with experiment, a cohesive energy of 0.70 Ryd/Pair versus the measured value of 0.79 Ryd/Pair and an equilibrium lattice constant of 4.09Å (versus 4.02Å). The transition energies, however, determined as band eigenvalue differences, are in gross disagreement with experiment for both the core excitation and the fundamental optical gap region (table 1). A calculation with $\alpha = 1$ (but with the correlation potential excluded) yielded results that agree very closely to those obtained under the same conditions by Menzel et al. and Chaney et al. [2] (with a completely independent computational model) and disagree with earlier results [3]; by repeating their calculations, we find the disagreement to arise from their muffin-tin approximation to the exchange.

To go beyond the band model, we chose a unit cell containing either 8 atoms (simple cubic) or 16 atoms (face centered cubic) with a locally excited ion in its center and performed a SC band structure calculation (SPC model). The total kinetic and potential energy per cell were then calculated by the method previously developed [11] using the charge density sampled at the 4 (and 2) spacial k -points in the Brillouin zone (BZ) [12] appropriate for the 8- (and 16-) atom cells. The difference in total energies, ΔE_T , between the excited and ground state cells (obtained in independent calculations) was identified with the corresponding crystal transition energy. The errors involved in computing numerically the total energy as well as those introduced by the limited BZ sampling are estimated from convergence tests to be ± 0.7 eV and ± 0.3 eV, respectively. Whereas the SPC model used a superlattice representation for the locally excited defects [with defect-defect distances of a (and $\sqrt{2}a$) for the 8 (and 16) atom cells, where a is the LiF nearest-neighbor distance], the actual physical situation corresponds to a single ex-

citation in the crystal. Comparison between the results obtained for the 8- and 16-atom cells shows that this poses no practical difficulty, since the perturbed states considered here are characterized by rather short-range wavefunctions and narrow bands so that the residual defect-defect interactions are vanishingly small.

The SPC model for localized excitations completely avoids the unphysical boundary conditions (and resulting charge inhomogeneity and surface states) characteristic of simple cluster models. Solid state one-electron effects (i.e., the influence of the SC Coulomb, exchange, and correlation potential exerted by all the particles on a given state) are fully included, as are electronic relaxation and self-interaction effects (not present in the conventional band model for excitations). The model also offers likewise a substantial improvement over the conventional Slater-Koster one-band one-site defect model (previously used for the exciton model [1]) in that all unit cells, as well as an effectively large number of band levels are allowed to interact in forming a localized state. In contrast with simple free-ion models previously used to correct the HF band model [1], our present treatment does not assume in advance the degree of localization of the electron or hole states and properly accounts for the orthogonality of these states to all other band states. The following calculations were performed with the results indicated:

The Li^+ and F^- K-shell ionization energies were calculated as ΔE_T with a locally excited species [i.e. $\text{Li Li}^{++}(1s^1 2s^0 2p^0 2p^0 3s^0)$ or $\text{F}^0(1s^1 2s^2 2p^6 3s^0 3p^0)$]. The close agreement found for the 8- and 16-atom SPC (63.6 and 63.5 eV for Li^+ and 694.5 and 694.6 eV for F^-) indicates the adequacy of the superlattice representation used. A "transition state" model for these ionization [i.e. placing $\text{Li}^{+1.5}(1s^{1.5} 2s^0 2p^0 3s^0)$ or $\text{F}^{-0.5}(1s^{1.5} 2s^2 2p^6 3s^0 3p^0)$ in the SPC and taking the appropriate *eigenvalue* difference] yields excitation energies of 61.4 eV and 693.1 eV indicating incomplete orbital relaxation in this limit. Interestingly, the choice of $\alpha = 1$ which seemed to yield good agreement with optical data in the band model [3] produces very poor results in ΔE_T in the SPC model (e.g. 720.1 eV for F^- K-ionization).

To estimate solid state effects we compared our results with those obtained by a simple free-ion model. Here one computes the *atomic* total energy difference between the $\text{Li}^+(1s^2)$ and $\text{Li}^{++}(1s^1)$ configurations (76.24 eV) and adds that to the 1s eigenvalue of $\text{Li}^+(1s^2)$

Table 1

Excitation energies in LiF calculated in the one-electron band-structure model (for exchange coefficients $\alpha = 2/3$ and 1) and in the SPC model, compared with experimental data. "Vac" indicates the vacuum state. Values are given in eV.

Transition	Type	Band Model		SPC Model $\alpha = 2/3$	Exp
		$\alpha = 2/3$	$\alpha = 1$		
$\Gamma_{15v} \rightarrow \Gamma_{1c}$	Interband	9.8	10.5	13.9	13.6 - 14.2 ^a
	Exciton	—	—	11.7	12.2 - 12.6 ^a
Li 1s \rightarrow Γ_{1c}	Interband	47.2	57.2	63.3	64.4 ^b
	Exciton	—	—	61.3	60.8 ^c
Li 1s \rightarrow L_{3c}	Interband	58.1	68.5	71.4	64 - 71 ^d
	Exciton	—	—	62.2	61.9 ^d
Li 1s \rightarrow Vac	Ionization	47.6	58.4	63.5	64 ^e
F 1s \rightarrow Vac	Ionization	655.2	680.9	694.5	693.2 ^e

^a Ref. [4].

^b The separation between the Li 1s and the top of the valence band is measured from energy distribution curves [7] to be 50.2 eV and the optical gap is 14.2 eV [4].

^c Ref. [8].

^d Ref. [5].

^e Ref. [15] (Fermi reference level: 7.07 eV).

(-57.72 eV). This energy correction is then applied to the $-\epsilon_{\text{is}}$ properly corrected for the crystal point-ion Madellung field (45.2 eV) to yield a net 1s ionization energy of 63.7 eV, in good agreement with the SPC value. We found that this agreement stems in part from a fortuitous cancellation of effects: the negative of the point-ion corrected 1s eigenvalue is lower by some 2.4 eV than the corresponding band result (table 1) (due to neglect of wavefunction overlap, effects of short range Coulomb and exchange potentials of other sites, lack of proper orthogonality constraints in the free-ion limit and arbitrary assumption of an ideal ionic charge of +1) while the electronic relaxation and self-energy corrections in this limit are about 2 eV *higher* than in the crystalline case (mainly due to first order polarization of all band states by the localized hole). We note that when correlation and relaxation corrections are applied to the HF bands [1] in a way that is consistent with previous suggestions[‡], one obtains a

[‡] Taking the Li⁺ 1s HF ionization potential at the Koopmans' limit as 65 eV and using the value of 3.5 eV for the polaron-model long-range correlation correction, 3.0 eV for the first-order polarization in the Mott-Littleton model and 1.0 eV for the atomic relaxation correction (values obtained in ref. [1]) one gets 57 eV for the Li K-ionization.

value of 57 eV for the Li K-ionization, in poor agreement with experiment (64 eV).

Excitation from the Li⁺K-shell or from the F⁻ valence band edge at Γ_{15v} into the *delocalized* conduction band states (e.g. the Γ_{1c} band edge having a 97% Li 2s character or the maximum density of states L_{3c} level having 93% Li 2p character) are modeled by placing a localized hole in the initial state [e.g. $\text{Li}^{+(1-1/N)}(1s^1 2s^{1/N} 2p^0 3s^0)$ for Li K \rightarrow Γ_{1c} transitions or $\text{F}^0(1s^2 2s^2 2p^5 3s^0 3p^0)$ for the $\Gamma_{15v} \rightarrow \Gamma_{1c}$ transition] while the excited electron is initially allowed to spread equally among all Li 2s or 2p states with a probability of $1/N$ (N being the number of atoms in the SPC). In this limit our model corrects the one-electron band scheme for self-interaction effects, initial state electron relaxation effects and charge redistribution in the valence states due to the presence of a localized hole, but not for electron-hole interactions (which vanished in the limit of localized-to-delocalized excitations). The exciton transition is modeled by allowing also final state localization (and hence also relaxation) on a particular site (e.g. on $\text{Li}^+ 1s^1 2s^1 2p^1 2p^0 3s^0$ for the one-site exciton progression converging to the $\text{Li}^+ \text{K} \rightarrow \Gamma_{1c}$ transition or on a nearest-neighbor $\text{Li}^0(1s^2 2s^1 2p^0 3s^0)$ site for the anion-cation exciton state below the

$\Gamma_{15v} \rightarrow \Gamma_{1c}$ transition) and repeating the ΔE_T calculation. At this limit the short range electron-hole interaction is present (via Coulomb and exchange-correlation interactions, the latter being ignored in previous studies [1]) and acts to stabilize the exciton state relative to the edge of the continuum. The ΔE_T results obtained are summarized in table 1.

The experimental soft X-ray absorption [5, 8, 14] and emission [6–8] spectra indicates a knee at 60.8 eV assigned to the forbidden Li 2s exciton (calculated value 61.3 eV) followed by the Li 2p exciton at 61.9 eV (calculated value 62.2 eV), and the interband threshold at 64.4 eV (calculated value 63.3 eV). Sonntag [13] has observed a long structureless absorption tail extending down to 53.0 eV and suggested that this might be a Li 2s exciton state. We think that this tail is more likely to be due to the F 2s absorption tail: the observed F^- 2s ionization is at 37.6 eV [14] and our calculations show that the lowest F^- virtual states lie about 15 eV above the bottom of the conduction band. Moreover, the free-ion $Li^+ 1s \rightarrow 2s$ excitation is at 60.8 eV [15] and it would seem improbable that the analogous excitation in the crystal is about 8 eV lower (the multiple⁺/average free-ion $Li^+ 1s$ -2p excitation is at 61.5 eV [15] compared with the observed 2p exciton at 61.9 eV). This conclusion is also consistent with the close relation found between the exciton lines and the atomic absorption in rare-gas crystals [16]. The calculated transition probability (using our numerical basis functions) indicates a ratio of 4.1 between the strength of the transitions 2p to 2s, in fair agreement with the experimental ratio of about 3. The sharp 2p exciton line is followed by a valley in the absorption spectra at 64 eV which we assign to the series ionization limit (calculated value: 63.5 eV). The broad structure observed at 64–72 eV was previously assigned to electronic polaron excitations [1] while our calculation suggests a possible interpretation of the absorption in this region as being due to resonant interband transitions past the ionization threshold, having no counterpart in the free ion limit (calculated limit: 71.4 eV). Our results for the 58–64 eV region are thus in direct conflict with the suggestion [2] of a pure interband character to this region. We found that the exciton binding energies (2.0 and 9.2 eV for the Li 2s and 2p excitons, respectively) contain considerable contributions from the electron-hole exchange and correlation interaction (some 20%) and that the self-energy

and relaxation corrections are about 2.1 eV lower than those obtained in a simplified free-ion model, in conflict with the model of Kunz et al. [1].

Our results for the optical transitions across the fundamental gap indicate an exciton transition at 11.7 eV (binding energy of 2.2 eV) followed by a series limit at 13.9 eV. These results are in good agreement with recent experimental studies [4] indicating a bound exciton at 12.2–12.6 eV and a series limit at 13.6–14.5 eV. A simple free-ion model predicts an increase of 5.3 eV (and 6.97 eV for $\alpha = 1$) in the calculated band gap while the actual increase obtained in the SPC model is significantly lower than this effect, and is due to charge rearrangement effects tending to partially offset the wavefunction contraction caused by the single site atomic relaxation. Similarly, the final state relaxation in the calculated interband transition of only 0.02 eV while a “full” atomic relaxation (2.37 eV in the LD formalism and 1 eV in HF) was postulated in previous studies [1].

We conclude that the one-electron band structure cannot predict the correct excitation spectra for narrow-band materials like LiF where the partial localization of the electron and hole states cause severe on-site relaxation and charge redistribution effects. In contrast, our local exchange ΔSCF (*total energy* difference) model brings the results for both interband and exciton transitions into excellent agreement with experiment. We note that polarization and relaxation corrections cannot be simply superposed on the calculated band structure eigenvalues obtained in the LD formalism and that due to the non-existence of Koopmans' theorem even for unrelaxed orbitals, self-interaction corrections should be applied first. The apparent successes of atomic models to simulate relaxation effects in the solid, as tested here and in previous HF calculations, may be fortuitous.

We are indebted to Drs. E. Lafon and A.B. Kunz for clarifying discussions of their results. We also thank Dr. T.C. Collins for helpful discussions on the subject.

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