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-muffic-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.