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Optical properties of LiF†

Daniel J. Mickish
Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801

A. Barry Kunz
Department of Physics and Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801
Aerospace Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433

T. C. Collins
Aerospace Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433

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In this paper, we examine the optical properties of LiF. The fundamental calculations performed are a self-consistent Hartree-Fock band-structure calculation. As has been found previously, such a calcualtion has substantial errors when compared with experiment. Correlation corrections are needed and are included by means of the electronic-polaron method. The usual electronic polaron is extended to include short-range polarization corrections which the usual model neglects but which are peculiarly large for LiF. The energy bands are evaluated directly by the linear-combination-of-local-basis-functions method along with the crystal wave functions for 89 points in the irreducible wedge of the first Brillouin zone. Using these results and the Lemann-Taut interpolation scheme the density of states, the joint density of states, and the imaginary part of the dielectric function are computed. These results which neglect the formation of excitons and "plasmons" are in poor agreement with experiment. The effect of the exciton formation is included by a Koster-Slater one-band–one-site calculation. We find that the inclusion of exciton effects substantially improves the level of agreement with experiment. This is in direct contrast with recent work of Menzel *et al.* in which energy-band theory alone is found to account for the optical properties of LiF. This disagreement is discussed in detail.

I. INTRODUCTION

There has been some speculation that the direct band gap in LiF is about 10.6 eV[1] and that the prominent absorption peak at 12.5 eV is due to band-to-band transitions. This speculation would seem to be highly unlikely in view of the technological use of LiF as an optical window[2] in the energy range below 12 eV. In this paper, we calculate the absorption by performing a Hartree-Fock calculation[3] and making the correlation corrections to the Hartree-Fock bands. From this we calculate $\epsilon_2(\omega)$ over the energy range of interest. The correlation corrections include the electronic-polaron method,[4] which is extended to obtain a local-field corrections. The exciton effect is also included by a Koster-Slater one-band–one-site calculation.[5] The oscillator strength of the $n=1$ exciton which amounts to approximately 40% of the absorption of the top valence and lowest conduction bands was estimated using the work of Elliot.[6]

The outline of this paper is as follows. In Sec. II, the Hartree-Fock energy-band model is presented. The correlation corrections to the Hartree-Fock bands are found in Sec. III and the comparison with experimental results is given in Sec. IV. The conclusions are then presented in Sec. V.

II. HARTREE-FOCK BAND MODEL

In order to obtain solutions of the Hartree-Fock equation, a linear combination of localized basis functions (LCLBF) was used. This basis set is a generalization of using linear combination of atomiclike self-consistent local orbitals[7–10] and "free" Slater-type orbitals (STO's). A similar approach has been used giving excellent results for diamond ground-state properties but poses similar difficulties with the excitations.[11]

The one-particle Bloch orbital $\psi_j(\vec{k},\vec{r})$ in terms of this basis set is

$$\psi_j(\vec{k},\vec{r})=\sum_{nlm} a^j_{nlm}(\vec{k})\frac{1}{\sqrt{N}}\sum_{\mu}\phi_{nlm}(\vec{r}-\vec{R}_\mu)e^{i\vec{k}\cdot\vec{R}_\mu}+\sum_{nlm} b^j_{nlm}(\vec{k})\frac{1}{\sqrt{N}}\sum_{\mu}\xi_{nlm}(\vec{r}-\vec{R}_\mu)e^{i\vec{k}\cdot\vec{R}_\mu}\quad . \tag{2.1}$$

In the above equation, the $\phi_{nlm}(\vec{r}-\vec{R}_\mu)$'s are the local orbitals, with $\vec{R}_\mu$ denoting the site, and nlm are the usual quantum numbers. Similarly, the ξ's are the free Slater-type orbitals defined as

$$\xi_{nlm}(\vec{r}-\vec{R}_\mu)=|\vec{r}-\vec{R}_\mu|^{n-1}Y^m_l(\hat{r}-\hat{R}_\mu)e^{-\alpha_{nl}|\vec{r}-\vec{R}_\mu|}\quad . \tag{2.2}$$

The coefficients $a^j_{nlm}(\vec{k})$ and $b^j_{nlm}(\vec{k})$ are determined by the variational theorem.

One is led to evaluating three types of matrix elements:

$$\begin{aligned} A&=\int\phi(\vec{r}-\vec{R}_\mu)\hat{O}\,\phi(\vec{r}-\vec{R}_\nu)\,d\vec{r}\quad ,\\ B&=\int\phi(\vec{r}-\vec{R}_\mu)\hat{O}\,\xi(\vec{r}-\vec{R}_\nu)\,d\vec{r}\quad ,\\ C&=\int\xi(\vec{r}-\vec{R}_\mu)\hat{O}\,\xi(\vec{r}-\vec{R}_\nu)\,d\vec{r}\quad . \end{aligned} \tag{2.3}$$

$\hat{O}$ stands either for the Fock operator $\hat{F}$ or the unit operator which determines the overlap matrix.

The set of orthonormal occupied band functions given in Eq. (2.1) determines the first-order density matrix $\rho(\vec{r},\vec{r}\,')$ which in turn gives the Fock operator

$$\rho(\vec{r},\vec{r}\,') = \sum_{jk} \psi_j(\vec{k},\vec{r})\,\psi_j^*(\vec{k},\vec{r}\,') \qquad (2.4)$$

and

$$F(\vec{r}) = -\nabla^2 - \sum_\mu \frac{2Z_\mu}{|\vec{r}-\vec{R}_\mu|} + 2\int \frac{\rho(\vec{r}\,',\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,' - 2\int d\vec{r}\,' \frac{\rho(\vec{r},\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,\hat{P}(\vec{r},\vec{r}\,') \quad . \qquad (2.5)$$

$\hat{P}(\vec{r},\vec{r}\,')$ is the permutation operator which changes $\vec{r}$ to $\vec{r}\,'$ before the integration is performed.

Instead of obtaining the self-consistent $\rho(\vec{r},\vec{r}\,')$ by iteration of the Fock equation,

$$F\psi_j(\vec{k},\vec{r}) = e_j(\vec{k})\psi_j(\vec{k},\vec{r}) \quad , \qquad (2.6)$$

the identical $\rho(\vec{r},\vec{r}\,')$ is obtained by adding a term to the Fock operator, namely, $-\hat{\rho}\hat{A}\hat{\rho}$.[8-10,12] The ground-state density operator ρ is described by the LCLBF's and these orbitals satisfy the equation

$$(F-\rho A\rho)\,\phi_{nlm}(\vec{r}-\vec{R}_\mu) = e_{nlm}(\vec{R}_\mu)\phi_{nlm}(\vec{r}-\vec{R}_\mu) \quad . \qquad (2.7)$$

In the limit of small overlap Eq. (2.7) becomes[8]

$$\Big(F_\mu + U_\mu - \sum_{j,k}\phi_j(\vec{r}-\vec{R}_\mu)\langle j\mu|U_\mu|k\mu\rangle\phi_k^\dagger(\vec{r}-\vec{R}_\mu)\Big) \times\phi_i(\vec{r}-\vec{R}) = e_i(\vec{R}_\mu)\phi_i(\vec{r}-\vec{R}_\mu) \quad . \qquad (2.8)$$

In the above equation,

$$U_\mu = \sum_{\nu\neq\mu}\frac{-2Z_\nu}{|\vec{r}-\vec{R}|} + 2\int\frac{\rho_\nu(\vec{r}\,',\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r} \quad ,$$

$$F_\mu = -\nabla^2 - \frac{2Z_\mu}{|\vec{r}-\vec{R}_\mu|} + 2\int\frac{\rho_\mu(\vec{r}\,',\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,d\vec{r}\,' - 2\int d\vec{r}\,'\frac{\rho_\mu(\vec{r},\vec{r}\,')}{|\vec{r}-\vec{r}\,'|}\,\hat{P}(\vec{r},\vec{r}\,') \quad ,$$

and

$$\rho_\nu(\vec{r},\vec{r}\,') = \sum_i \phi_i(\vec{r}-\vec{R}_\nu)\,\phi_i^\dagger(\vec{r}\,'-\vec{R}_\nu) \quad . \qquad (2.9)$$

Self-consistent $\rho(\vec{r},\vec{r}\,')$ using the above equations and the method of Roothaan[13] have been obtained for LiF.[10] The density matrix $\rho(\vec{r},\vec{r}\,')$ expressed in terms of the local orbitals becomes

$$\rho(\vec{r},\vec{r}\,') = \sum_{i\mu}\sum_{j\nu}\phi_i(\vec{r}-\vec{R}_\mu)\,S^{-1}_{i\mu,j\nu}\,\phi_j^\dagger(\vec{r}\,'-\vec{R}_\nu) \quad . \qquad (2.10)$$

where

$$S_{i\mu,j\nu} = \langle i\mu|j\nu\rangle \quad .$$

One is now in a position to make several approximations which have almost no effect on the results but make the computational problem much simpler. In making the approximations, the magnitude of $S_{i\mu,j\nu}$ was treated as a smallness parameter, as recommended by Gilbert.[14] Substituting Eq. (2.10) into Eq. (2.5) one sees that all four-center terms can be neglected, as well as all three-center exchange terms involving a two-site contribution to $\rho(\vec{r},\vec{r}\,')$. Similarly, all two-center or three-center Coulomb terms involving a two-site contribution to $\rho(\vec{r},\vec{r}\,')$ are neglected. All integrals are evaluated numerically by the Löwdin α-function expansions.[15] The magnitude of the off-diagonal terms of the local orbitals was found to be very small. In the cases of Ar and LiF, $|S_{i\mu,j\nu}| \leq 0.05$.

Since one only needed STO's which fall off rapidly past the midpoint of the nearest-neighbor distance it was necessary to include only six shells of unit cells around the central site in evaluating the Fock and the overlap matrix. Ions outside this region are included via a point-ion contribution. The convergence of the Fock and overlap matrix due to basis functions was extremely good (s-, p-, and d-type functions about each lattice site were included).

The Hartree-Fock bands are given in Fig. 1(a). As expected, the Hartree-Fock eigenvalues do not match experiment very well. The eigenvalue differences are much too large. For example, the fundamental gap in this calculation is 1.688 Ry. It is immediately obvious from the results of this section that correlation corrections are needed before the band structure of LiF can be used to analyze the results of experiment.

III. CORRELATION CORRECTIONS

The model we adopt at the outset is the electronic-polaron model introduced by Toyozawa[4] and extended by one of the authors.[4] The true wave function of the solid is assumed to be constructed by a simple expansion in terms of Slater determinants. Let us define the Hartree-Fock n-electron wave function $|\theta\rangle$ as

$$|\theta\rangle = (N!)^{-1/2}\det\|\phi_i(\vec{r}_\alpha)\| \quad . \qquad (3.1)$$

Let, for example, Ψ_0^T be the true ground-state wavefunction. We label states such that $1 < i < j \leq N < a < e$, and i labels occupied orbitals and a the virtual set. Then in terms of the fermion creation and annihilation operators $C^\dagger$ and C, one has

$$\Psi_0^T = |\theta\rangle + \sum_{j=1}^{N}\sum_{a=N+1}^{\infty} A_{0ja}C_a^\dagger C_j|\theta\rangle + \sum_{j,k=1}^{N}\sum_{a,b=n+1}^{\infty} B_{0jkab}C_a^\dagger C_b^\dagger C_j C_k|\theta\rangle + \cdots \quad . \qquad (3.2)$$

In the electronic-polaron model (EPM), we retain the first three terms on the right-hand side of the above equation and further restrict the system in

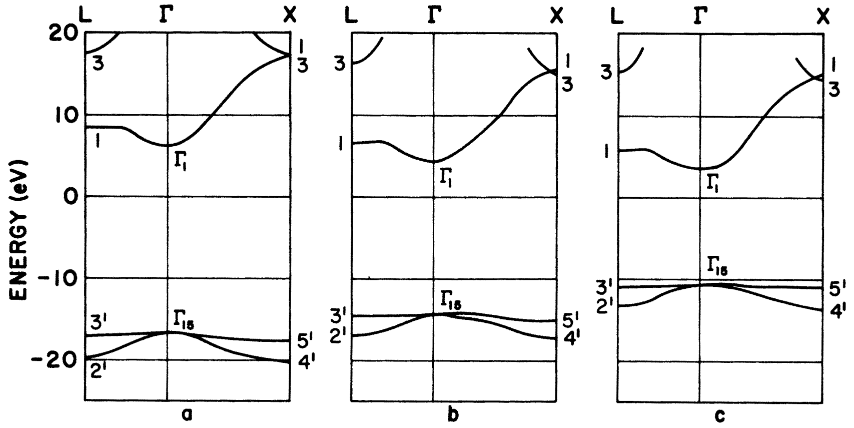

FIG. 1. Relevant part of the LiF band structure is shown here. In part (a), the Hartree-Fock bands are shown. In part (b), the bands corrected by the EPM are shown. In part (c), the bands computed using IEPM are given.

that we permit (i) scattering internal to the band in question, and (ii) formation of a single band of longitudinal excitons, corresponding to approximating the atomic spectron by a single averaged level per atom in the solid. The approximation (ii) has several immediate consequences. These are as follows: The exciton wave vector is rigorously restricted to lie in the first Brillouin zone and this then to a great extent justifies and dictates the first approximation, as has been pointed out by one of us.[4] There is one immediate and potentially important physical consequence of all this. That is, the EPM correctly describes correlation effects at a large distance from the electron or hole but neglects short-range correlations or polarizations.[16] This was in part seen by one of us,[4] and various related and important comments on the need for including short-range or central-cell correlations have been elucidated by Hermanson[16] and Perrot.[17] In this paper, we will use a model which is similar in philosophy to the polarization-potential model (PPM) introduced by Perrot, but which has the singular advantage of avoiding the adjustable constant which appears in the PPM. We term this model the improved electronic polaron model (IEPM).

The EPM which also yields the long-range correlation correction for the IEPM says that the self-energy Σ for electrons and for holes is given by

$$\Sigma_{\mathrm{el}}(\vec{k})=\sum_{\vec{K}}\frac{|V_{\vec{K}}(0)|^2}{e(\vec{k})-\epsilon-e(\vec{k}-\vec{K})} \tag{3.3}$$

and

$$\Sigma_{\mathrm{hole}}(\vec{k})=\sum_{\vec{K}}\frac{|V_{\vec{K}}(0)|^2}{e(\vec{k})+\epsilon-e(\vec{k}-\vec{K})}\ , \tag{3.4}$$

where

$$V_{\vec{K}}(0)=\frac{e[2\pi\epsilon(1-1/e_\infty)]^{1/2}}{V[i/|\vec{K}|\int\phi^2(\vec{r})e^{i\vec{K}\cdot\vec{r}}\,dr]^{-1}}\quad . \tag{3.5}$$

Here $e(\vec{K})$ are the Hartree-Fock band energies, ϵ is the average energy ($\vec{K}$ independent) of a longitudinal exciton, e is the electron charge, ϵ_∞ is the optical dielectric constant, V the volume of the crystal, and ϕ the Wannier function or local orbital for the band in question.

Before proceeding, it is worth commenting on the adequacy of the use of second-order perturbation theory here. The one-electron Hamiltonian in the EPM can be given in a polaron form in terms of the boson (exciton) creation and annihilation operators $b^\dagger$ and b as

$$h=\sum_{\vec{K}}C^\dagger_{\vec{K}}C_{\vec{K}}e(\vec{K})+\epsilon\sum_{\vec{K}}b^\dagger_{\vec{K}}b_{\vec{K}}$$
$$+\sum_{\vec{K}\vec{K}}V_{\vec{K}}(0)\{b_{-\vec{K}}-b^\dagger_{\vec{K}}\}C^\dagger_{\vec{k}+\vec{K}}C_{\vec{k}} \tag{3.6}$$

From this one develops an effective polaron coupling constant α. This has been found to be

$$\alpha=\left(\frac{e^2}{2(h/2m\epsilon)^{1/2}}\right)\left(\frac{1}{\epsilon}\right)\left(1-\frac{1}{\epsilon_\infty}\right)\quad . \tag{3.7}$$

For all the alkali halides or rare gases, one finds $0.25<\alpha<0.5$.[18] It is well known from ordinary polaron theory that if the coupling constant α is of order unity or less that the use of perturbation theory to second order is valid. Hence, we conclude that we introduce no significant errors by using perturbation theory. The EPM is evaluated for LiF and we find the effect is to lower the conduction band by 1.8 eV and the valence-band maximum is raised by 2.3 eV. Thus the Hartree-Fock band gap is reduced from 22.8 to 18.7 eV. We show the EPM band results in Fig. 1. The usually accepted band gap for LiF is 13.6–13.7 eV.[19,20]

It is highly unlikely that the above figures are in substantial error since the non-self-consistent Hartree-Fock band gap of Perrot[17] is found to be 22.5 eV and Fowler finds the long-range polarization corrections to be 4.7 eV in the band gap.[21] There are sufficient minor differences between the various models to account for the difference of about

0.5 eV or so which exist here, but not for the 4-eV error with respect to experiment. We can only agree with our previous analysis[22,23] and with that of Perrot[17] and Hermanson[16] and attribute it to the neglect of short-range correlation which the EPM neglects. Clearly then it is also possible to consider the effects of electron-hole interaction here. However, at present we are simply concerned with band states (i.e., those states for which the electron and hole are spatially uncorrelated) and here we will omit the effects of electron-hole interaction in formulating the IEPM for band states as they are negligible. We will, however, later consider this question in formulating the excitonic properties of LiF.

In improving the EMP, we are directly interested in including short-range correlation corrections. We do not employ here the PPM model of Perrot because of its use of an adjustable constant, and in part because the model is of a somewhat *ad hoc* nature and does not clearly fit into our concept of a systematic first principles study of correlation effects. We therefore postulate the extension of the EPM to the IEPM as follows. We assume here the dominant short-range correlation effect is the polarization of the central-cell atom or ion by the electron or hole on that ion. Such a model was used by Kunz, Mickish, and Collins[22] in a recent study of the soft-x-ray properties of LiF. In this model, then, we calculate using a series of atomic Hartree-Fock calculations the difference in energies needed to remove an electron from the system or to add on an electron to the system, as the case may be from the value for this given by using the Hartree-Fock eigenvalue (Koopman's theorem) and from the differences in energies for the self-consistent calculations for the two states. That is, this correction $\Sigma^{\rm local}$ is found, for example, for the creation of a valence hole on the $2p$F$^-$ ion to be (that is, going from F$^-$ to F)

$$\Sigma^{\rm local}_{p\,\rm hole} = -\epsilon^{F^-}_{2p} + E^{F^-}_{\rm HF} - E^{F}_{\rm HF} \approx 3.6 \text{ eV} .$$

Similarly, we perform such a calculation for adding an extra electron onto the Li$^+$-ion site, where we presume the conduction electron to be largely localized and find this correction to be about -1.0 eV. With these corrections included, the band gap is seen to reduce to 14.1 eV. The bands including these corrections are seen in Fig. 1.

It is worth noting that Gilbert, Kunz, and Mickish[23] have discussed this need for local-correlation-polarization corrections for the soft-x-ray absorption of the entire series of lithium halides. In that study, the approach was purely local and the model, which closely parallels our improvements to the EPM, was developed by consideration of the general valence-bond formalism. In this calculation, crystal effects were neglected because the excitation of interest was from the Li$^+$ *K* shell to the conduction band, which is mostly Li$^+$-ion functions. In general, however, the IEPM used here can either be considered a solid-state generalization of the work of Gilbert, Kunz, and Mickish or an atomic improvement to the EPM of the type the author used for improving the correlation results of Fowler.[4] Physically then we assume the electron or hole moves slowly enough to produce polarizations on the site it is occupying which are comparable to those of polarizing a free atom or ion by an electronic charge. This is quite reasonable since crystal electron velocities are slow enough to permit the other electrons to respond instantaneously to the position of a moving charge. Hence, the principal limitation is the use here of atomic rather than crystal wave functions to deduce the effect of such short-range polarization. Presumably, in the present case, where the maximum overlap of the local orbitals is -0.06, the neglect of overlap corrections is a trivial matter. Extension of the valence-bond model[23] to include such corrections is possible and most likely computationally tractable. Nonetheless, we argue that for the present case, LiF, the model employed is reasonable.

We show our computed state density from calculations to the bonds at some 2100 points in the first Brillouin zone for the F$^-$ $2p$ band in Fig. 2. A similar plot is shown in Fig. 3 for the LiF conduction bands. In Fig. 4, we show the calculated value of ϵ_2 for transitions from the $2p$ band in LiF to the conduction band computed in the Hartree-Fock limit. Here, in both ϵ_2 and the conduction-state den-

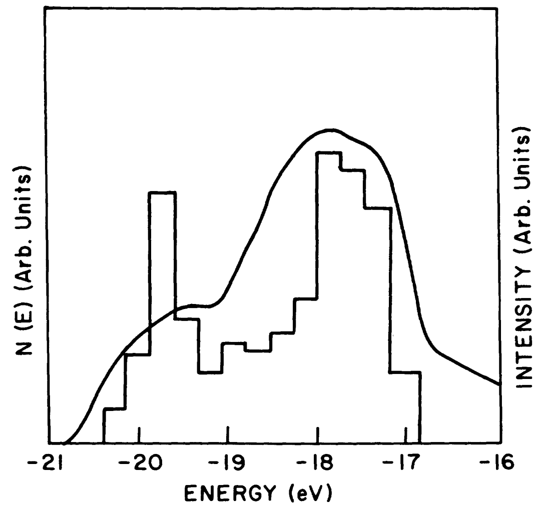

FIG. 2. Density of states for the occupied $2p$F$^-$ band is shown along with a superimposed figure of the x-ray emission data for this level obtained by O' Brian and Skinner (Ref. 27).

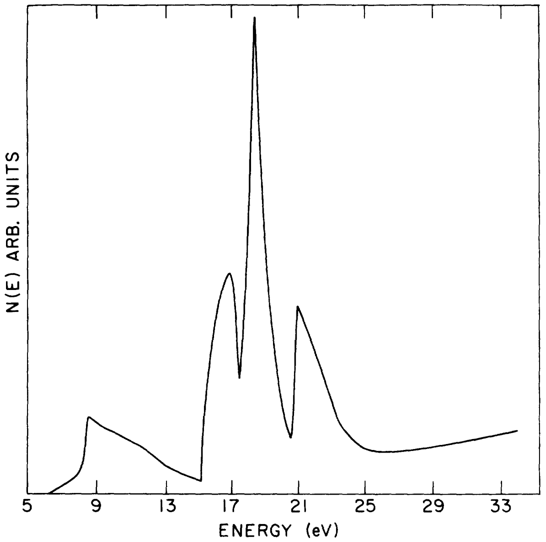

FIG. 3. State density of the virtual levels (conduction band) in LiF are shown in the Hartree-Fock limit.

sity, we employ an analytic interpolation scheme of Lemann and Taut[24] to construct our curve. In the case of ϵ_2, we interpolate both the band structure and the transition matrix elements. The joint density of states (and by obvious changes, the density of states) is defined to be

$$J(E)=\frac{2V}{(2\pi)^3}\sum_{i,j}\int_{BZ}\delta(e_i-e_j-E)\,d\vec{k}\quad ,\qquad (3.8)$$

where i is the initial and j the final state, and V is the volume of the Wigner-Seitz cell. The optical absorption ϵ_2 is seen to be

$$\epsilon_2(E)=\frac{e^2h^2}{m}\sum_{i,j}\frac{1}{(2\pi)^3}\int_{BZ}\frac{f_{ij}(\vec{k})}{e_j-e_i}\,\delta(e_i-e_j-E)\,d\vec{k} \qquad (3.9)$$

and

$$f_{ij}(\vec{k})=\frac{2}{3m}\,\frac{|\langle\vec{k}_j|P|\vec{K}_i\rangle|^2}{e_j-e_i}\quad . \qquad (3.10)$$

The $f_{ij}(\vec{k})$ are evaluated at 2100 points in the first Brillouin zone using our Hartree-Fock band eigenfunctions.

It is absolutely clear from our results as given above, and also from our results in Fig. 4 that we do not find it possible to interpret the optical spectrum in LiF in terms of band structure, as was possible in the calculation of Menzel *et al.*[1]

Since it is not possible to interpret the spectrum of LiF directly from our band structure, we decided to attempt a highly approximate inclusion of the exciton in our calculation. In what follows, we compute only the fundamental $n=1$ exciton and freely acknowledge that the effect of the $n\geq 2$ excitons are present and important. As a first approximation, one might wish to use the simple effective-mass approximation. This method has its defects, however, in that it is only good for excitons of radius much greater than the dimension of a unit cell, where, as one finds using this model, the radius of the exciton is smaller than but comparable to the nearest-neighbor distance. This suggests to us that an alternate model may be possible. This would be based upon the one-band–one-site model of Koster and Slater.[5] We chose to apply this model in the way used recently by Scifres *et al.*[25,26] for studies of the spectrum of N in III-V compounds. Clearly the Coulomb attraction of the valence hole is long range and hence seems to violate the one-site nature of the model; however, the results of effective-mass theory suggest that the conduction electron is so closely bound to the hole that it is quite irrelevant as to whether the potential extends to infinity or is only a Coulomb potential extending from the center of the cell to the cell boundary and then is set equal to zero. There is a great dividend available for using the results of the one-band–one-site model over simple effective-mass theory. This is, we permit our exciton's electron to draw its wave function from all parts of the band rather than from just a single minimum, which in this case would be at Γ. In view of the computed state density shown in Fig. 3 for the conduction band, and the experience of Scifres *et al.*, we anticipate that

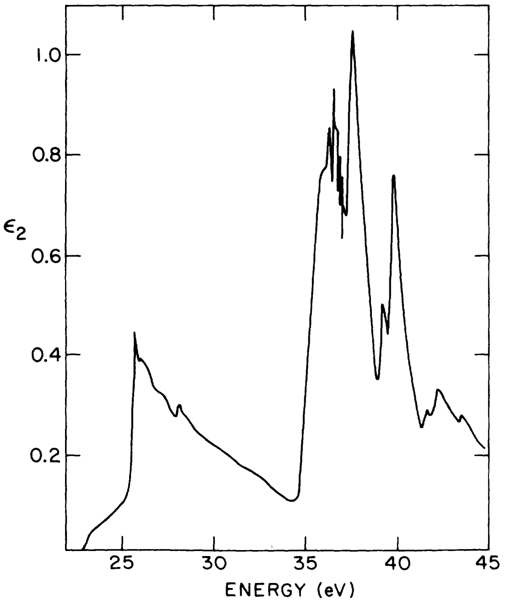

FIG. 4. Theoretical Hartree-Fock calculation of the imaginary part of the dielectric function is shown for LiF over an extended energy range. The transitions are from the 2*p* valence bands and the transition matrix elements are calculated from the actual Hartree-Fock crystal wave functions.

this may be important in practice.

In the one-band–one-site model, we assume that for our potential V the matrix elements in terms of Wannier functions are given by

$$\langle \vec{\mathrm{R}}_\mu, n | V | \vec{\mathrm{R}}_\nu, m \rangle = V_0 \delta_{\mu\nu} \delta_{n=c}\, \delta_{m=c} \quad . \qquad (3.11)$$

Here c stands for the conduction band. The $\vec{\mathrm{R}}_\mu$ and n are site and band indices for the Wannier states. The probability that the electron is in the cell containing the hole, $|\psi_E(0)|^2$, is given by

$$|\psi_E(0)|^2 = |1 - V_0 \Lambda(E)|^2 \quad , \qquad (3.12)$$

$$\Lambda(E) = \lim_{\delta \to 0^+} \int_{-\infty}^{\infty} dt\, N(E) | E - t + i\delta) | \quad . \qquad (3.13)$$

$N(E)$ is our computed state density for the conduction band. In order to proceed, it is necessary to estimate or compute the value of V_0. If one simply removes an electron from a F^- site to a nearest Li^+ site and includes an optical dielectric constant, the Coulomb attraction of electron and hole is found to be about 4.0 eV. This is clearly a crude estimate. It is possible to further refine the estimate by doing simple atomic-type calculations, that is, to evaluate the electron affinity of a fluorine atom (F^- ion with a hole on it) sitting at the bottom of a Madelung well and screening the interaction by the dielectric constant ϵ_∞. Such an estimate places a value of about 5.0 eV for V_0 and is the value we chose to use for our calculation. Doing this, we find the exciton is formed about 1.8 eV below the bottom of the conduction band or at 12.3 eV. It is interesting to note that the use of simple effective-mass theory also yields this result.

It is clear from a comparison of our band structure in Fig. 1 and the conduction density in Fig. 3 that for the first band the principal contribution comes from states at the L point which furnish the large shoulder and peak in the state density some 3 eV above the onset of the conduction band. It is states which are pulled off from L not Γ which we find by our calculation to be responsible primarily for the exciton in LiF. This state lies below the conduction-band minimum rather than being a resonance in the conduction-band structure because of the size of V_0. In the cases considered by Scifres *et al.*[25,26] this was not always the case. It is possible then in our model and, in fact, clearly likely that higher exciton lines will exist as resonances above the band edge and convergence on the shoulder in the state density at the L point. In the Sec. IV, we will postulate that such states are, in fact, seen experimentally.

IV. COMPARISON WITH EXPERIMENT

One obtains the density of states of the $2p$ valence band given in Fig. 2. The calculated results given contain only the Hartree-Fock density of states; however, the effect of adding the electron polaron did not change the structure very much. One sees that the experimental results obtained from x-ray emission measurements[27] has the same form. The experiment shows, in fact, that the bands are a little wider than that calculated. If one compares this with the results obtained by local-density approximations for the exchange term given in Ref. 1, the valence density of states is 30% too small. This trend of a too narrow valence-band density of states obtained from the local-density exchange approximation not only is true for alkali halides[28] but is found in most of the semiconductors[29] also.

In Fig. 3, the density of states of the conduction band is given. It is interesting to note here that the energy differences between the bottom of the conduction band (the Γ_{1c} energy) and the minimum at L (the L_{1c} energy) are approximately the same in the corrected Hartree-Fock calculations and the results of the local-density approximation. Thus the lower structure of the conduction-band density of states should not be too different in the two calculations. The imaginary part of the dielectric function, ϵ_2, for the uncorrected Hartree-Fock bands is shown in Fig. 4. This should be compared with Fig. 3 of Ref. 1. This figure of Ref. 1 is the

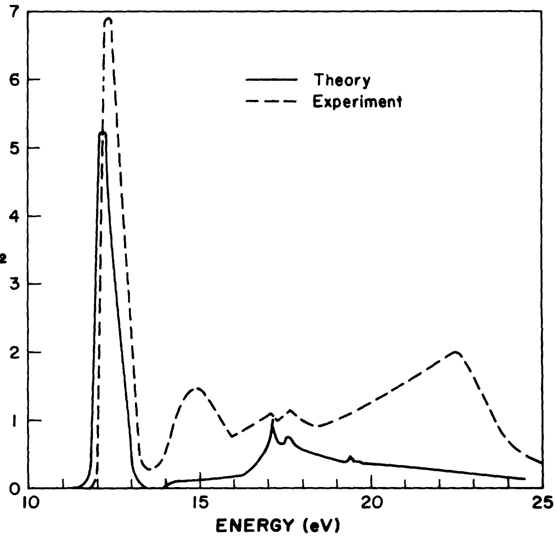

FIG. 5. Results of the measurements of Stephan (Ref. 20) for the imaginary part of the LiF dielectric function. Also shown are the results of our present calculation for this quantity. In obtaining the theoretical results the Hartree-Fock bands are corrected by the IEPM. However, owing to the computed small admixture of other wave functions in the Hartree-Fock one-electron orbitals in the IEPM calculation, the Hartree-Fock wave functions were used to compute the matrix elements $\langle i | \vec{p} | f \rangle$. The effects of the $n=1$ exciton are also included. This exciton is computed as described in the text and the transition strength into the band-to-band region is reduced to allow for the transition strength into the exciton.

imaginary part of the dielectric function where Slater's approximation to the exchange term[30] was used in deriving the electronic band structure. It should be made perfectly clear that Slater's approximation is for the exchange term and only the exchange term. One finds a difference of approximately 1 Ry in the band edge. There is a factor of 30 difference in the peak heights due to the *L* region of the BZ. These differences are the results of the fact that Slater's approximation is not at all accurate in simulating the exchange operator in this material. It is often said that the local-density approximation for the exchange term has somehow gone beyond the Hartree-Fock approximation. How is left to the imagination of the reader. It has been shown by Hedin and Lundquist[31,32] that the next-order terms beyond Hartree-Fock lead to a screened exchange term plus a Coulomb hole. The combination of these terms in the free-electron-gas system appears to behave as a local density but the coefficient is $\frac{2}{3}$ to $\frac{4}{5}$ the Slater value. This would result in the electronic structure being even further from experiment than it is now.

The corrected Hartree-Fock results (described in Sec. III) for the imaginary part of the dielectric function is displayed in Fig. 5. The first main peak at 12.3 eV is due to the exciton. The oscillator strength was estimated by using the theory of Ref. 6. It was calculated to be approximately 40% of the total oscillator strength into the first band and the amplitude of the first band ϵ_2 is reduced here to reflect this. The structure at 15 eV in the experimental curve looks like the envelope of the higher exciton states which also overlap the lower conduction band. This structure was not included in the theory. The third structure matches extremely well and is the result of a high joint density of states around *L* in the BZ. This is an entirely new interpretation of this structure in ϵ_2. The last main broad peak in the experiment at 22.5 eV has been shown to be a scattering state of the electron polaron by two of the authors[18] and is well understood.

V. CONCLUSIONS

It has been demonstrated that one can match experiment by including exciton effects and correcting Hartree-Fock bands as outlined in Sec. III. This leads to new interpretation of the structure; namely, that structure is associated with the *L* region of the BZ. It has also been pointed out that the local-density approximations one generally uses for the exchange terms are not applicable to this kind of crystal.

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