Optical Dielectric Function of the Lithium-Fluoride Crystal*

W. Paul Menzel and Chun C. Lin
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706

and

Doyle F. Fouquet and Earl E. Lafon
Department of Physics, Oklahoma State University, Stillwater, Oklahoma 74074

and

Roy C. Chaney
University of Texas at Dallas, Dallas, Texas 75230
(Received 26 March 1973)

The method of tight binding has been applied in a calculation of the imaginary part of the dielectric function, ϵ_2, for a LiF crystal. The large variations of the transition matrix elements over portions of the Brillouin zone are found to have very pronounced effects on ϵ_2. Our results suggest a possible reinterpretation of the experimental 13- and 62-eV optical structure as band-to-band, instead of excitonic, transitions.

Recent works[1-3] on energy-band theory have shown that the method of tight binding [linear combination of atomic orbitals (LCAO)] is capable of giving accurate band structures for a wide variety of crystals. This method is ideally suited for calculating optical properties,[4] since the band structure and transition matrix elements are readily evaluated from first principles at all $\vec{k}$ points. In this paper we present the results of our calculation on the imaginary part of the dielectric function (ϵ_2) of LiF and compare them with experimental data.

A Hartree-Fock-Slater self-consistent-field (SCF) band structure of a LiF crystal, obtained by the LCAO method with ten basis functions ($1s$, $2s$, $2p$ of the Li and F atoms), was reported previously.[1] To improve the accuracy of conduction bands, we extended the basis set to a total of 54 functions which consist of ten Bloch sums of the $1s$, $2s$, and $2p$ orbitals plus twelve s-type, four p-type, and four d-type single-Gaussian Bloch sums, and calculated an SCF band structure using a three-point (Γ, X, L) quadrature scheme.[1] The energies of those high-symmetry points are given in Table I.

Following the prescription of Ehrenreich and Cohen,[5] we write

$$\epsilon_2(\omega) = (e^2/\pi m^2 \omega^2) \sum_{ij} \int_{BZ} \delta(E_{ij}(\vec{k}) - \hbar\omega)$$

$$\times T_{ij}(\vec{k}) d^3k, \qquad (1)$$

where $T_{ij}(\vec{k})$ is related to the matrix elements of the momentum operator between the ith and jth bands by

$$T_{ij}(\vec{k}) = \tfrac{1}{3} \sum_{\alpha=x,y,z} |\langle i,\vec{k}|p_\alpha|j,\vec{k}\rangle|^2. \qquad (2)$$

The calculation of ϵ_2, therefore, entailed evaluation of transition matrix elements for numerous $\vec{k}$ points. The numerical integration of Eq. (1) was facilitated by using the procedure outlined by Gilat and Dolling.[6] For this calculation we evaluated $E_n(\vec{k})$, $\nabla_k E_n(\vec{k})$, and $T_{ij}(\vec{k})$ over a uniform mesh of primary $\vec{k}$ points which divide the fundamental wedge of the Brillouin zone ($\frac{1}{48}$ of the entire zone) into nineteen primary regions. The numerical integration over a primary region was accomplished by further subdividing it into as many as 7000 secondary quadrature points.

Our calculated ϵ_2 for the soft-x-ray energy region of 56–68 eV is shown in Fig. 1; experimental data for the absorption coefficient[7] are presented in Fig. 2, in which the dominant structure at 62 eV was interpreted in Ref. 7 as being

TABLE I. SCF energy bands of a LiF crystal.

	Energy (a.u.)		Energy (a.u.)
Γ_{15v}	0.000	L_{1c}	0.466
X_{4v}'	−0.090	Γ_{15c}	0.929
X_{5v}'	−0.030	X_{1c}	0.701
L_{2v}'	−0.077	X_{5c}'	0.833
L_{3v}'	−0.007	L_{2c}'	0.658
Γ_{1c}	0.389	L_{3c}	0.812
X_{4c}'	0.587		

FIG. 1. Theoretical ϵ_2 for 56–68 eV.
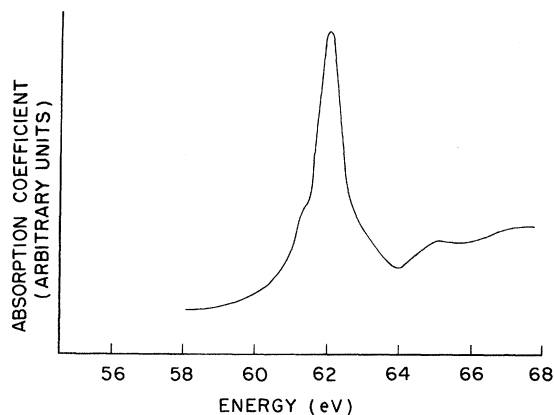
FIG. 2. Experimental photoabsorption data of Ref. 7 for 56–68 eV.

excitonic. A similar structure in photoabsorption was also reported by Brown et al.[8] However, the corresponding peak in the theoretical ϵ_2 at 64 eV is due to band-to-band transitions (from the Li core to the conduction band). We found that $T_{ij}(\vec{k})$ is large for transitions from the Li core to states near L_{3c} that have a predominant Li $2p$ character, which is understandable in view of the tightly bound nature of the Li $1s$ band and atomic selection rules. Furthermore, the joint density of states passes through a sharp maximum here. This combined enhancement produces a dominant peak at 64 eV in the theoretical ϵ_2. Our results suggest a possible reassignment of the dominant peak observed in the soft-x-ray region to an interband transition rather than excitonic excitation.

In Fig. 3 our ϵ_2 for the ultraviolet region computed using nineteen primary points (uniform dashed curve) is shown with the experimental data of Roessler and Walker.[9] Good qualitative agreement is seen between theory and experiment. In particular we found a strong peak in our theoretical ϵ_2 at nearly the same energy (13 eV) as and of comparable magnitude to the dominant peak of experiment (12.62 eV), which was identified by Roessler and Walker as an exciton transition. Again, we have investigated the origin of this peak and found that the joint density of states passes through a local maximum at 13 eV (corresponding to the energy gap at the L point), while at the same time the transition matrix elements undergo an abrupt increase in this narrow energy range but are greatly suppressed at higher energies. An inspection of the LCAO crystal wave functions explains this abrupt increase of matrix elements near L. The valence-band states
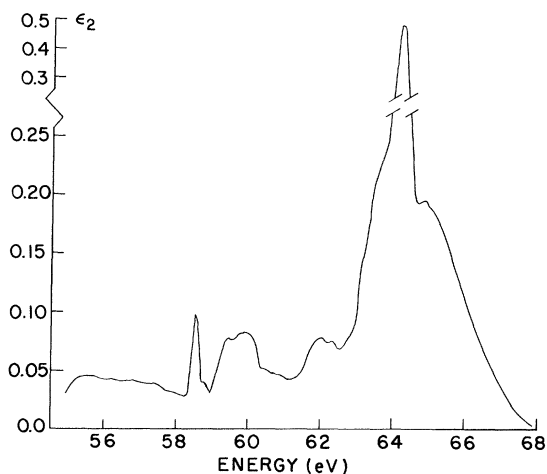
consist of chiefly fluorine p orbitals with little contribution from the Li orbitals. For the conduction-band states near L_{1c}, the wave functions have larger amplitude near F atoms than around Li atoms and gravitate toward F sites on approaching L_{1c}. In addition symmetry considerations require the L_{1c} functions to contain only s orbitals (not p) of F and only p orbitals (not s) of Li, making transitions from the valence to conduction band particularly favorable at the L point on account of atomic selection rules. The theoretical peak at 13 eV shown in the uniform dashed curve in Fig. 3 is considerably broader than the corresponding experimental peak. Part of the width of the theoretical peak may be attributed to the approximate nature of our numer-
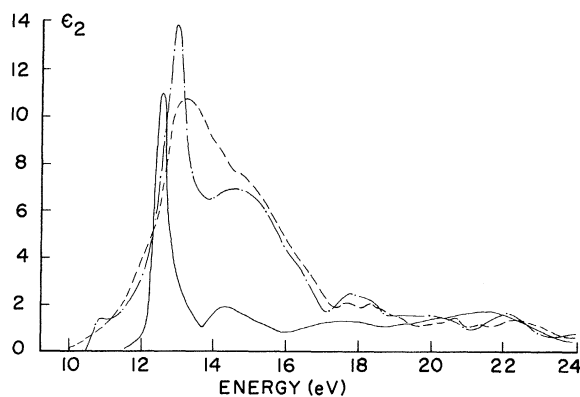
FIG. 3. Experimental ϵ_2 (Ref. 9) for 12–24 eV (solid curve). Uniform-dashed curve, theoretical ϵ_2 with nineteen primary points; long-short-dashed curve, for 28 primary points.

ical integration of Eq. (1) in which the values of $T_{ij}(\vec{k})$ and $\nabla_k E_n(\vec{k})$ are assumed to be constant for all secondary quadrature points inside a primary region. The large variations of T_{ij} and $\nabla_k E_n(\vec{k})$ found in the proximity of L_{1c} and L_{3v}' make this approximation less adequate. Because the L-point transitions are responsible for the calculated 13-eV peak, we sought to refine this peak by increasing the number of primary points from 19 to 28 to improve the mesh mainly around the L point. The volume associated with a primary point was again chosen to be the portion of the reduced zone closer to that point than to any other points. The theoretical ϵ_2 curve resulting from this improved $\vec{k}$ integration (long-short-dashed curve in Fig. 3) shows a strong narrowing of the 13-eV peak in better agreement with experimental data. (The small shoulder at 10.8 eV arises from a local peak in the joint density of states near the Γ point.) On the other hand, none of the structures above the 13-eV peak in the ultraviolet range can be attributed to a very localized region of the Brillouin zone, so to achieve comparable refinement for the higher energies would require much more than 28 primary points. A more detailed investigation of this problem is being initiated. We found little change in the shape of the 64-eV peak of Fig. 1 due to the improved integration because T_{ij} and $\nabla_k E_n(\vec{k})$ are rather constant in the neighborhood of L_{3c}, unlike the cases of L_{1c} and L_{3v}'.

The assignment of the experimental ultraviolet peak to an excitonic transition leads to a band gap of 13.6 eV.[9] Several recent papers[10-12] in this area parametrized the exchange potential ($X\alpha$ approach), and selected the exchange parameter consistent with this interpretation of the experimental data. Our calculations place the band gap at 10.6 eV but still show the same leading optical structure at 13 eV. Therefore, our Hartree-Fock-Slater band picture is compatible with the experimental data.

In conclusion we found that the method of tight binding can be used effectively for calculating ϵ_2. The variation of the transition matrix elements over $\vec{k}$ has very important effects on ϵ_2, especially in the ultraviolet region. The calculated ϵ_2 differ quite drastically from those deduced from consideration of joint density of states *only*, indicating the inadequacy of the usual assumption of constant transition matrix elements even for the higher-energy (soft-x-ray) transitions. Our calculations suggest that the 13- and 62-eV optical structure of LiF, previously identified as the exciton transitions, may be interpreted as band-to-band transitions.

[1] R. C. Chaney, E. E. Lafon, and C. C. Lin, Phys. Rev. B 4, 2734 (1971).

[2] R. C. Chaney, C. C. Lin, and E. E. Lafon, Phys. Rev. B 3, 459 (1971).

[3] J. Callaway and C. S. Wang, Phys. Rev. B 7, 1096 (1973).

[4] W. Y. Ching and J. Callaway, Phys. Rev. Lett. 30, 441 (1973).

[5] H. Ehrenreich and M. H. Cohen, Phys. Rev. 115, 786 (1959).

[6] G. Gilat and G. Dolling, Phys. Lett. 8, 304 (1964).

[7] R. Haensel, C. Kunz, and B. Sonntag, Phys. Rev. Lett. 20, 262 (1968).

[8] F. C. Brown, C. Gähwiller, A. B. Kunz, and N. O. Lipari, Phys. Rev. Lett 25, 927 (1970).

[9] D. M. Roessler and W. C. Walker, J. Phys. Chem. Solids 28, 1507 (1967).

[10] L. J. Page and E. H. Hygh, Phys. Rev. B 1, 3472 (1970).

[11] D. M. Drost and J. L. Fry, Phys. Rev. B 5, 684 (1972).

[12] N. E. Brener, Phys. Rev. B 7, 1721 (1973).