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Absorption of Soft X Rays by Insulators with a Forbidden Exciton Transition*

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In this note, we consider the absorption of soft x-ray radiation by an insulating crystal for which the lowest excitonic transition from the core state to the conduction band is forbidden. We argue that a proper description must go beyond simple Hartree-Fock band theory and should include substantial energy corrections due to the hole being a local phenomenon during the absorption process, as well as substantial corrections due to electron-electron interactions. Approximate calculations are made for LiF.

We direct our attention to a study of the soft-x-ray absorption of an insulating crystal for which the transition from the core state to the lowest conduction band is forbidden, e.g., LiF for transitions from the Li K shell (1s level) to the lowest conduction band which is s-like. In such crystals there should be at best a forbidden exciton and higher members of the exciton series preceding the band-to-band transition. We develop our ideas by computing the soft-x-ray spectrum of LiF for the Li K shell in the restricted Hartree-Fock model and then adding approximately various corrections to this calculation. We find that the effect of these corrections is to modify the Hartree-Fock absorption peak for the LiF, Li^+ K-shell absorption by about 20 eV. The principal effect is due to the localization of the core hole during the absorption process and its interaction with the conduction electron. The calculation is begun by obtaining a set of self-consistent Hartree-Fock energy bands for LiF. One such set has been reported[1] by us. These bands are in good agreement with the non-self-consistent results for LiF reported by Perrot.[2] These self-consistent energy bands are computed at 89 nonequivalent points in the irreducible portion of the first Brillouin zone (BZ) and are shown in Fig. 1. (Note that these bands are relatively spread out as is usual in Hartree-Fock bands using Koopman's theorem.)

The next step is to construct a joint density of states and to compute ϵ_2 for transitions from the Li K shell. The joint density J is defined as

$$J(\omega)=2v(2\pi)^{-3}\textstyle\sum_{ij}\int_{\mathrm{BZ}}\delta(E_i-E_j-\hbar\omega)\,d^3k, \tag{1}$$

where i is the core state, j the conduction state, and v the volume of the Wigner-Seitz cell. The relevant quantity for optical absorption ϵ_2 is just given by

$$\epsilon_2(\omega)=\frac{e^2h^2}{m}\sum_{i,j}(2\pi)^{-3}\int_{\mathrm{BZ}}\frac{f_{ij}(\vec{\mathrm{k}})}{(E_j-E_i)}\times\delta(E_i-E_j-\hbar\omega)\,d^3k, \tag{2}$$

and

$$f_{ij}(\vec{\mathrm{k}})=(2/3m)\,|\langle\vec{\mathrm{k}}_j|p|\vec{\mathrm{k}}_i\rangle|^2/(E_j-E_i). \tag{3}$$

If $f_{ij}(\vec{\mathrm{k}})$ and E_j-E_i are essentially constant, one sees that aside from trivial factors, $\epsilon_2(\omega)$ and $J(\omega)$ are the same. This approximation is often used.

In the present calculation, we compute the $f_{ij}(\vec{\mathrm{k}})$ directly from our energy-band eigenstates. This is the first time such a calculation using Hartree-Fock orbitals has been reported for soft-x-ray spectra. Having evaluated the bands and $f_{ij}(\vec{\mathrm{k}})$ at 89 nonequivalent points in the irreducible wedge, we fit the results by a linear analytic interpolation which allows us to compute $\epsilon_2(\omega)$ and $J(\omega)$ to great accuracy and resolution.[3] Our results for $\epsilon_2(\omega)$ and $J(\omega)$ are shown in Fig. 2. It becomes clear from the experimental measurements of the Li K-shell absorption in LiF that there is a great deal of similarity between our calculation and experiment, except that our calculated structure is some 20 eV higher than the experimental structure. The experimental situation is seen in Fig. 3.[4] The remainder of this note is concerned with finding the sources of this discrepancy. These results are in direct contradiction to the results of Menzel *et al.*[5] They used

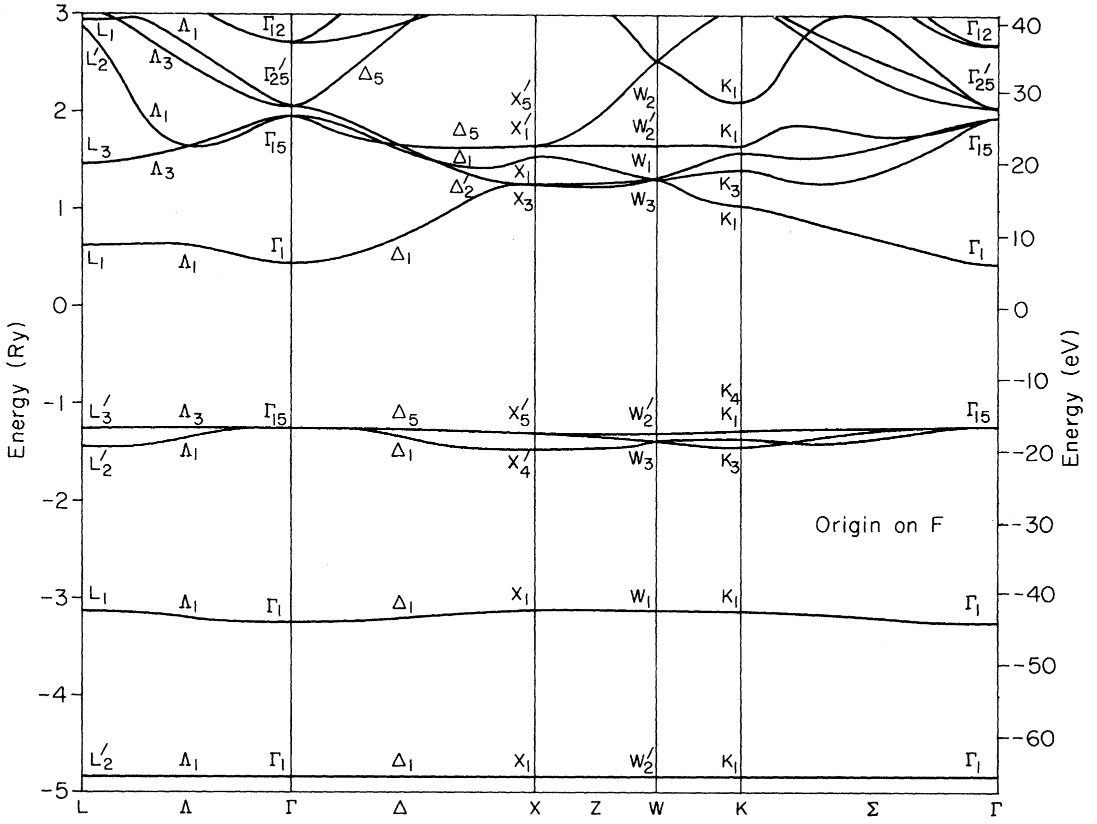

FIG. 1. Self-consistent energy bands for LiF in the restricted Hartree-Fock approximation.

a free-electron-gas approximation for the exchange operator and find very large enhancement of the L-transition peak. They also find structure some 3 eV below the fundamental gap in their band calculation.

We do not expect that the experimental absorption is due to excitons below the band edge since the exciton transition is s to s and hence not al-

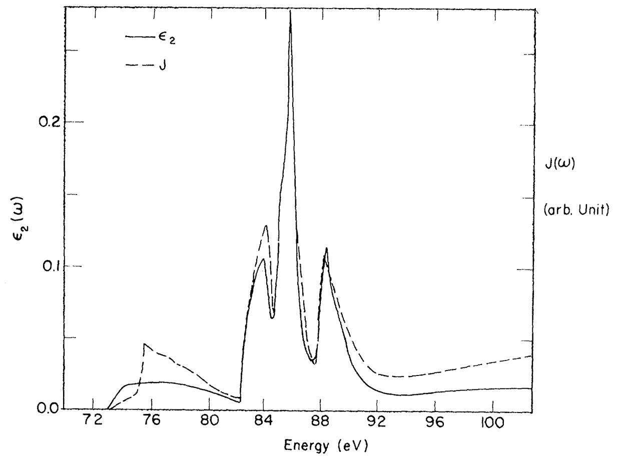

FIG. 2. Joint density of states and ϵ_2 as calculated by the authors using the Hartree-Fock energy bands for the Li K shell in LiF.

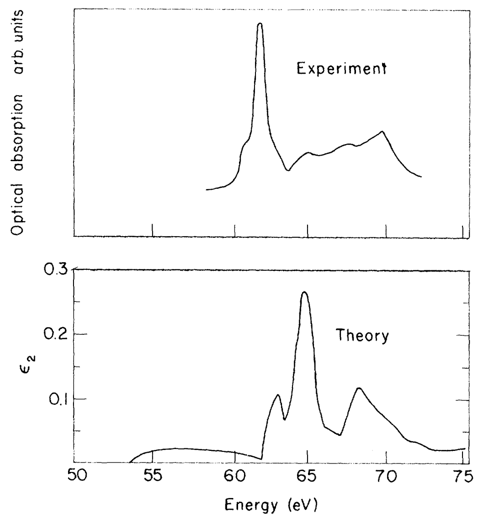

FIG. 3. Optical absorption from the Li K shell in LiF as determined experimentally. The calculated ϵ_2 from the Hartree-Fock bands corrected in energy for correlation and local-field effects is also shown. The experimental data are due to Brown *et al.* (Ref. 4).

lowed. In addition, recent calculations for such excitonic absorption in the silicon soft–x-ray spectrum by Altarelli and Dexter[6] have found such effects to be small. In Si the exciton transition is allowed, and hence the effect should be greater than in the present case. The first possible correction is due to correlation effects involving the electron or the hole and the remainder of the electrons in the crystal. We compute these effects using the electronic-polaron model.[7] We find that this correction raises the hole state by 3.5 eV and lowers the conduction state by 2.0 eV for a net correction of 5.5 eV or about 25% of the difference between theory and experiment.

Clearly, then, additional effects which go beyond band theory are needed. The most likely source of such an effect is the fact that the core hole is localized rather than being in a band state. The effects of local fields on the calculation of the *transition strength* have been recently given by Bergstresser and Rubloff.[8] They find these effects are non-negligible, but also that they are not very important in the present context since they do not create new structure or destroy structure which might exist in a Hartree-Fock band calculation. What is needed is an estimate of the size of the energy correction due to the presence of a localized hole in the $1s$ orbital of Li in LiF. The principal effects will be these: (1) The occupied $1s$ orbital on the Li ion containing the $1s$ hole is polarized by the hole. (2) The valence-electron cloud on the fluorine ions surrounding the Li ion with the $1s$ hole will be polarized from the band orbitals they are in. (3) The local hole in the Li $1s$ shell will have a Coulomb attraction for the electron excited to the conduction band. This gives the change from a V^N potential seen by a conduction electron in the Hartree-Fock theory to that of a V^{N-1} potential. This is of course the physical case. Such effects will include the formation of excitons and localized atomic excitations, and we are not able to distinguish between these effects in our model.

Effect (1) is simple to estimate. We compute the difference in the energy needed to remove a Li^+ $1s$ electron from a Li^+ ion in free space using Koopman's theorem and using the relaxed Hartree-Fock final state. This correction is found to be 1.5 eV. Effect (2), which is a first-order perturbation effect rather than a second-order effect, calculated using the electronic polaron, may be estimated using a Mott-Littleton model to compute the effect of a static hole on a Li^+ ion on the surrounding F^- ions.[9] The size of this effect is about 3.0 eV if contributions due to the electronic polaron are not included at this stage. Effect (3) is most difficult to evaluate. We do this using an atomic model. We compute the energy of an extra electron on a Li^+ ion; this corresponds to the usual band model in the Hartree-Fock limit and for the same excited state of the ion in a model in which a hole is present in the core. The difference in the energy of the outer electron corresponds to the effect of the hole on that electron. The energy correction is

$$[E(1s, \mathrm{Li}^{++}) - E(1s2p, \mathrm{Li}^+)] - [E(1s^2, \mathrm{Li}^+) - E(1s^2 2p, \mathrm{Li})] \approx 10.0 \text{ eV}.$$

This value seems reasonable in that careful analysis of the conduction wave functions which contribute most to the main ϵ_2 peak were found to be dominantly Li^+ atomic virtual states in character. Thus the correction due to the hole localization is estimated to be about 14.5 eV and the total correction from all effects is estimated to be 20.0 eV. By means of comparison, we show our previously computed ϵ_2 now shifted by the 20-eV correction in Fig. 3. This neglects the effect of the local field and of the many-body corrections on the transition matrix elements and is clearly highly approximate. The agreement between theory and experiment is seen to be reasonable, but in view of the approximate nature of the calculation of the corrections, this must be considered to be accidental. Nonetheless, this calculation shows that the effect of local-field corrections on the energy is large and that they should be included in such calculations whether or not one uses local exchange potentials[5] or Hartree-Fock potentials; this is to say that bands and excitons are shifted by these electron-hole interactions.

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The Mahan Soft-X-Ray Anomaly in Lithium: Relationship to the Knight Shift

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The Li soft-x-ray absorption-threshold shape is expressed in terms of the pressure-dependent Knight shift, using a one-electron model and accounting for the indirect interaction of the lattice with the 1*s* core, but neglecting the final-state interactions currently thought responsible for the anomalous shape.

In recent years, studies of "many-body effects" on the optical properties of metals have centered on the "x-ray anomalies" and their relationships to Mahan's model[1] of the final-state interaction. The primary prediction of the Mahan theory (in its current form[2-4]) is that the soft-x-ray absorption spectrum of a simple metal, $\epsilon_2(\omega)$, should exhibit an "anomalous" threshold behavior, corresponding to electronic transitions from a core level to a conduction-band state above the Fermi energy E_F:

$$\epsilon_2(\omega) \propto (\hbar\omega - E_F - E_{\text{gap}})^{-\alpha}\, \theta(\hbar\omega - E_F - E_{\text{gap}}).$$

Here the zero of energy is taken at the center of the core band, E_{gap} is the energy of the bottom of the conduction band, and $\theta(x)$ is the unit step function. The Mahan exponent α can be expressed in terms of the partial-wave phase shifts at the Fermi energy,[5] and may be either positive or negative.

The three principal experimental data cited as support for the Mahan theory are spikes in the soft-x-ray (30-60 eV) absorption spectra of metallic Na and Mg ($\alpha > 0$) and a rounded soft-x-ray absorption threshold in Li ($\alpha < 0$).[6] The spectra of a number of other materials (e.g., Al, Be) exhibit structures tentatively but ambiguously assigned to either "Mahan anomalies" or "band-structure effects."

The observed rounded threshold of Li [Fig. 1(b)] is currently thought to be conclusive evidence for the validity of the Mahan theory,[4] which predicts rounding whenever α is negative; Ausman and Glick[4] calculate $\alpha = -0.104$ for Li. However, this many-electron explanation seems deficient in at least three ways. First, the Mahan threshold shape $(\hbar\omega - E_F - E_{\text{gap}})^{-\alpha}$, as calculated using the Ausman-Glick exponent, disagrees qualitatively with the data [Fig. 1(b)]. Second, the observed Li emission[7,8] [circles in Fig. 1(b)] and absorption spectra overlap throughout an energy interval approximately equal to the edge breadth. In contrast, the many-electron theory gives mirror-image absorption and emission edges, which do not overlap but meet in a cusp.[5] Third, in calculating α, Ausman and Glick take the excited electron's angular momentum to be a good quantum number.[9] Band-structure effects and electron-phonon interactions combine to destroy both rotational and inversion symmetry, allowing