SOFT X-RAY SPECTRA OF THE LITHIUM HALIDES AND THEIR INTERPRETATION*

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The photoabsorption of LiF, LiCl, and LiBr has been investigated with high resolution at quantum energies from 60 to 230 eV using synchrotron radiation from an electron storage ring. It is found that the spectra can be understood largely in terms of transitions from the various core levels to the final-band density of states as obtained from recent band calculations. Features are found which may possibly be due to replication of the edge with the emission of one or more collective excitations.

Substantial progress has recently been made toward a detailed understanding of the optical response of LiF, LiCl, and LiBr over a wide range of energies in the extreme ultraviolet. The lithium K shell provides especially suitable initial states because of large dipole matrix elements with the final band states and also the lack of strong resonances in the continuum beyond threshold.[1] Previous results on the lithium halides have been reported by Haensel, Kunz, and Sonntag in the spectral range 60-70 eV.[2] The present measurements extend some 150 eV higher in energy, and they provide values of absorption coefficient so that the importance of transitions from the various core states, for example, the Li^+ K, the Cl^- $L_{\mathrm{II,III}}$, the Br^- $M_{\mathrm{IV,V}}$, and the Br^- $M_{\mathrm{II,III}}$ can be assessed. Moreover, it has recently been possible to carry out a self-consistent Hartree-Fock energy-band calculation including the principal polarization or many-body corrections for LiCl[3] and also for LiBr.[4] This permits the comparison of theoretical and experimental optical spectra so as to determine the importance of core excitons and multiple excitations.

The absorption coefficients were determined by observing the transmission of thin films of various thicknesses evaporated in situ onto thin Formvar substrates. Film thicknesses were determined by a quartz crystal monitor calibrated by the Tolansky technique. The synchrotron continuum from the 240-MeV electron storage ring at the University of Wisconsin Physical Science Laboratory was used as a light source. Radiation transmitted by the substrates (and by the substrates plus samples) was dispersed by a 2-m grazing-incidence spectrometer with 10-μm entrance slits and a 576-line/mm grating. Digital recording of the photon counting rate as well as monitor and wavelength information was employed during scans of about 30 min each. When structure appeared it was possible to slow down the scanning rate so as to include many more points in the same wavelength interval. Scans were repeated and later combined during the computer analysis. The data reduction techniques, methods for filtering out stray light, etc., are described elsewhere.[5] Absolute absorption coefficients were determined to 30% accuracy and the wavelength resolution was 0.1 Å. Measurements were made with the film at room temperature since little narrowing of the observed structure occurred upon cooling to 77°K.

Figure 1 shows the experimental results for the three materials over a wide spectral range. The absorption coefficients $\alpha(\mathrm{cm}^{-1})$ are plotted vertically, and it is easy to convert to the imagi-

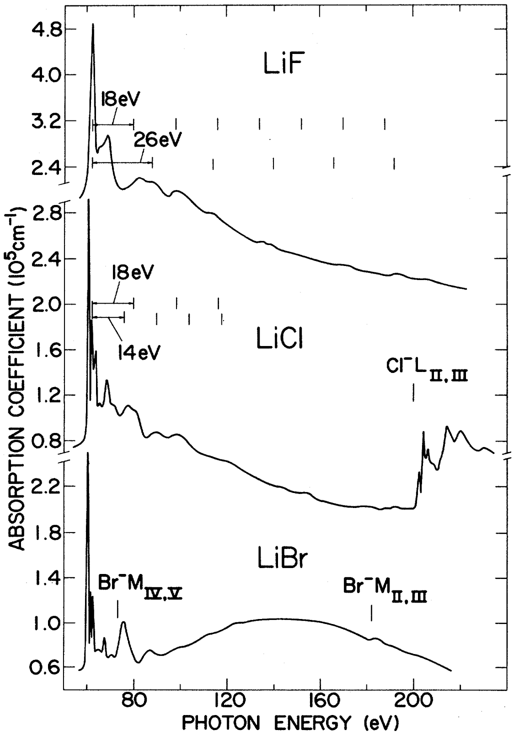

FIG. 1. The absorption coefficients in the range 50-230 eV for LiF, LiCl, and LiBr as determined by thin-film transmission measurements. All the peaks shown are reproducible and certain periodicities are noted as discussed in the text.

nary part of the dielectric functions $\epsilon_2 = nc\alpha/\omega$ since the index n is very close to 1.0 in this region of the spectrum. The prominent structure beginning near 60 eV is due to excitation of the Li^+ K shell. In the case of LiCl the chlorine $L_{\mathrm{II,III}}$ structure ($2p^6$ shell) can be seen at 200 eV. Spectral details are similar to those previously reported by Iguchi et al.[6] These high-energy transitions appear weaker than those at 60 eV when α is plotted. On the other hand, the transition probability W_{if} is proportional to $\omega\alpha$, and on this basis it can be seen that the $2p^6$ spectrum is actually stronger overall than the $1s^2$ spectrum, in agreement with the larger number of electrons involved. In the case of LiBr we see nearly the same Li^+ K spectrum as for LiCl and in addition structure beginning at 73 eV due to the Br $M_{\mathrm{IV,V}}$ levels ($3d^{10}$ electrons) as well as the Br^- $M_{\mathrm{II,III}}$ levels ($3p^6$ electrons) at 182 eV. These thresholds agree approximately, but not precisely,[7] with values estimated from electron-emission data. In order to make this comparison one must add half the band gap to the core energies listed in the tables.[8]

Since the various core bands are flat and extremely narrow (~0.1 eV), the observed structure at 60 and at 200 eV should closely follow the final-band density of states, at least to a first approximation of constant transition matrix elements. In order to obtain the band states, self-consistent Hartree-Fock energy-band calculations were performed for LiCl[3] and LiBr.[4] These calculations are expected to be more nearly correct than previous attempts in that the usual effective exchange approximation was avoided even though the result is truely self-consistent. Since details of the method will appear elsewhere[3] only a few remarks will be made here. The ground-state wave functions of the crystal are obtained self-consistently and from these the electron-charge density in the crystal is formed. Excited states are obtained within the framework of Koopman's theorem. The starting point for obtaining the appropriate localized orbitals to be used in the Fock operator is an alternate form of the Adams-Gilbert[9] equation. In order to generate the band structure including the excited states of the system the mixed basis method[10] is used. The principal approximations involved in this program are the following: (1) In computing a self-consistent charge density, only those terms which are linear in interatomic overlap are considered. (2) In considering those matrix elements of the exchange operator between two plane waves, only the first five terms of the expansion of $|r_{12}|^{-1}$ in spherical harmonics are retained. (3) The usual Born-Oppenheimer approximation as well as Hartree-Fock approximations are employed; however, some of the principal many-body effects can be included using the method of Fowler.[11] These electronic polarization corrections, which could in principle be incorporated directly into the exchange terms of the Fock operator, have the effect of shifting the conduction bands rigidly with respect to the valence bands, i.e., narrowing the band gap by about 3 to 4 eV. With these corrections the Hartree-Fock calculations yield band gaps and core energies which can be directly compared with experiment. Figure 2 shows the calculated band structure for LiCl in the ⟨100⟩ and ⟨111⟩ directions.[3] Very similar bands result for LiBr[4] and also for LiF[13] at least throughout the lower conduction bands. Note that the zero level of Fig. 2,

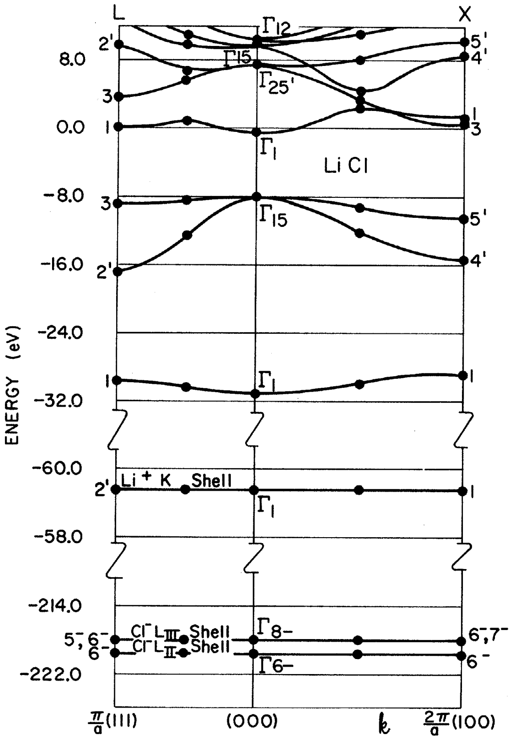

FIG. 2. The Hartree-Fock energy-band structure for LiCl after Ref. 3. The dots show the points actually computed self-consistently. An absolute energy scale is used and electronic polarization corrections have been included as discussed in the text. Notice that the calculated L_{III}-shell to conduction-band energy (218 eV) is about 8% greater than the observed threshold (202 eV). This is because the model used does not allow for relaxation of the outer Cl^- electrons during core excitation.

which in this calculation has meaning, lies very close to the minimum of the conduction band. This indicates that the electron affinity of these materials should be very close to zero, which may explain why the photoemissive yield of LiF peaks on the high-energy side of the first exciton band as observed by Duckett and Metzger.[12] It should also be noted that the calculated band gap for LiCl (Fig. 2) is 7.7 eV which is in reasonable agreement with an optical gap slightly in excess of 8.6 eV.[13]

In order to compare theory with experiment in the extreme ultraviolet, a joint Li^+ K shell to conduction band density of states was computed. A pseudopotential method was used to interpolate between computed points in the conduction-band structure, and the density of states was then evaluated throughout the Brillouin zone. The pseudo-Hamiltonian was of the form

$$\mathcal{H}_{\mathrm{ps}} = \alpha p^2/2m + \sum\nolimits_{\vec{k}} v(\vec{k}) e^{i\vec{k}\cdot\vec{r}}, \qquad (1)$$

where for LiCl as an example $\alpha = 1.383$ and the nonzero v's are $v(000) = -15.87$ eV, $v(111) = 6.59$ eV, $v(200) = -3.76$ eV, $v(220) = -0.845$ eV, $v(311) = 2.17$ eV, and $v(222) = -1.03$ eV. Assuming that the transition-matrix element is not a function of $\vec{k}$ or of energy, the final density computed in this way can be compared with the measured absorption (the initial bands are flat and not spin-orbit split for the K shell). Figure 3 shows the state density in the range 60 to 74 eV along with the experimental results for this region plotted on an expanded scale. Excellent agreement is found between the positions and widths of peaks in the two curves and also as regards the decrease in absorption at 73 eV. On the other hand, the relative heights of the peaks are not in precise agreement, most likely because of the assumption of constant transition-matrix elements. Although electron-hole interaction is included in the calculation, bound exciton states as such are excluded and it would seem that they are not required to explain the observed spectrum.[7] The spectral bandwidth of the apparatus was small enough to resolve structure as narrow as 0.1 eV or less. Since no evidence for core-exciton lines was found we conclude that (a) little or no oscillator strength is concentrated in such lines and (b) such states if formed are probably broadened by lifetime effects.

It should be noticed that the threshold corresponding to the Γ_1 minimum is very weak and is not clearly seen in the experimental data below the strong first band. This is probably the result of the strictly forbidden character of the transition and the fact that s-like character is preserved well out towards the zone boundary at L_1 in the lowest conduction band (see Fig. 2). The high-energy spectrum for LiCl at 200 eV is somewhat different in that spin-orbit splitting of the initial states is involved. A broad rise is also superimposed upon the $L_{\mathrm{II,III}}$ spectrum 10 or more eV beyond the edge. Part of this is thought to be due to a p-to-d resonance beyond threshold.[14] The gradual d-to-f increase for excitation of the Br^- $3d^{10}$ shell is seen in Fig. 1 beginning near 80 eV. Here structure is broadened and tends to merge into the underlying continuum.

Returning to further interpretation of the Li^+ K-shell spectra we note that peaks or bands are observed in LiCl 14 or more eV above the main band (at 74, 78, 88, 96 eV, etc.) Although the state density is not as well computed in this region, indications are that it simply decreases monotonically above 74 eV. These broad high-energy bands appear to be periodic with periods 18 and 14 eV as shown for LiCl in Fig. 1. A similar periodicity can be discerned for LiBr although some of the structure is coincident with the Br^- $3d$-shell excitations. From a comparison of optical and energy-loss data it can be said that both salts have plasmon frequencies of about 16 eV.[15] In LiCl there is also a lower frequency (surface plasmon?) of 14 eV observed in energy loss but not in normal-incidence optical data. We suggest that the 18- and 14-eV periodicities

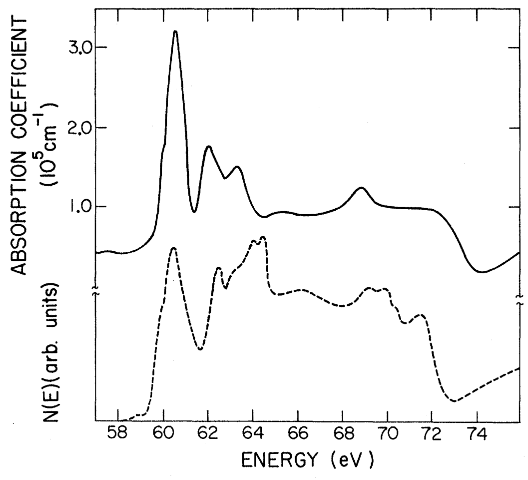

FIG. 3. The upper curve shows the observed absorption coefficient for LiCl. Lower curve (dotted) shows the theoretical density of states for the LiCl conduction band with the first peak aligned for best agreement. A very similar comparison between theory and experiment can be made for LiBr.

in Fig. 1 are plasmon replicas of the principal electron-hole transitions centered around 62 eV.[16] Such structure should be seen in soft x-ray absorption as well as emission spectra where plasmon satellites are well known. The idea of an electron-hole transition accompanied by a collective mode was discussed some years ago by Ferrell and Noziéres and Pines.[17] The fact that the main periodicity for LiCl gives $\hbar\omega_p$ slightly larger than the volume plasmon frequency may be due to dispersion or to a slightly inaccurate assignment of the latter frequency. It is also true that the additional core electron is involved in the final state and perhaps should be taken into account. These ideas are further born out by the spectrum for LiF (see Fig. 1) where the 26-eV (volume) and 18-eV (surface) periodicities extend all the way out to beyond 190 eV. Although the higher energy peaks shown are slight they are all reproducible when the scans are repeated under proper conditions with high intensity and good signal-to-noise ratio. Because of a relatively small unit cell, LiF has a volume plasmon frequency of 25.3 eV,[15] just less than the 26-eV periodicity noted in Fig. 1.

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CYCLOTRON PHASE-RESONANCE TRANSMISSION IN COPPER

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In a field-normal microwave-frequency transmission experiment we observe strong resonant oscillatory bursts of microwave-field transmission through sheets of single-crystal copper. These bursts occur at field values appropriate to cyclotron resonance and its harmonics, but are not associated with Azbel'-Kaner cyclotron resonance. Instead we attribute the effect to a mechanism in which electrons propagating across the sample all arrive at the second surface with the same microwave phase, whenever the dc magnetic field satisfies the condition for cyclotron resonance.

This Letter discusses a phenomenon we have observed in microwave transmission experiments, in which we examine the microwave field transmitted through single-crystal metal plates oriented normal to a dc magnetic field, H. At first glance the observed signals show a striking similarity to field-parallel Azbel'-Kaner cyclotron resonance.[1] However, as we shall show, the phenomenon does not involve resonance in the usual sense, but rather concerns a resonance