PHYSICAL REVIEW B VOLUME 11, NUMBER 6 15 MARCH 1975

Electronic excitation energies and the soft-x-ray absorption spectra of alkali halides*

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(Received 24 June 1974)

The interpretation of the soft-x-ray absorption spectra of alkali halides has been very controversial. Many of the observed spectra have been interpreted by several authors in terms of transitions to the Bloch states of the conduction bands, allowing the possibility of excitonic enhancement of peaks but excluding the possiblity that excitons are formed below the band edge. Other interpretations have ranged from the identification of excitons below the band edges with relatively small binding energies (~1 eV), excitons within the band continuum associated with critical points, and free-atom-like transitions shifted in energy by crystal fields. This controversy can be conclusively resolved by determining the position of the threshold for band transitions on the energy axis. Any structure appearing below this threshold can then unambiguously be identified as pure excitons, i.e., bound states of the electron to the core hole. Structure above this threshold must be carefully checked against theories predicting interband spectra. In this paper we present the theory governing soft-x-ray excitations and use x-ray photoelectron spectroscopy (XPS) and optical-gap data to determine band thresholds for a total of 39 soft-x-ray absorption spectra. In almost all cases we present a detailed analysis of the observed structure. Our main conclusions are: (a) In the case of excitations from the alkali-ion core levels, the observed spectra are almost entirely excitonic in nature. Electron-hole interaction is overwhelmingly large since the core hole in the alkali ion is not effectively screened by the valence-electron cloud, which lies almost completely on the halogen ions: This interaction *mixes* band states over the range of a rydberg and resulting binding energies of excitons are very large. No critical-point association for the observed excitons can thus be supported. (b) In the case of excitations from the halogen-ion core levels, electron-hole interaction is weaker due to effective screening by the valence electrons. Excitons are still found in all cases and binding energies are again larger than hitherto accepted. Critical-point analysis of excitons is again doubtful but transitions to band states may be responsible for some of the observed structure. (c) Transitions to states above the conduction-band edge do *not* reflect the structure present in the density of states of the conduction bands; this is also a consequence of the strong electron-hole interactions. We believe that the the present analysis gives a conclusive interpretation of the major features of each spectrum which is not always in agreement with either the latest publication on the given spectrum or, sometimes, any of the interpretations proposed in the past.

I. INTRODUCTION

The interpretation of optical spectra of nonmetals in the neighborhood of the fundamental energy gap is a well-established art. It has generally been feasible to unambiguously isolate one or more sharp peaks at the onset of absorption as excitons and thus identify accurately the threshold for interband transitions. In the one-electron energy-band picture this threshold is simply the difference between the top of the valence band and the bottom of the conduction band. Quite accurate experimental values for these band gaps are thus available in the literature.[1] As for the interpretation of the observed spectra above the fundamental gap, energy-band theory has been quite valuable since it allows one to predict the shape of the observed spectrum. Excitonic effects may alter such an interband spectrum, but identification of the observed structure in terms of particular transitions has generally been possible

In contrast, the interpretation of soft-x-ray absorption spectra is still a developing art. These spectra generally exhibit a mixture of sharp and broad peaks on structured background with no easily identifiable band edge. One common approach to their interpretation has been the use of energy-band theory. From such a point of view, during a soft-x-ray absorption experiment, electrons are excited from dispersionless (flat) core bands to the conduction-band continuum. Assuming that the matrix elements for such transitions are approximately constant, the absorption coefficient becomes proportional to the density of states (DOS) of the conduction bands. Such a calculation of course cannot account for any excitons that may be formed below the band edge. In view of the difficulties involved in computing accurate transition energies even for band-to-band transitions,[2] which would help locate the band edge, a common practice has been to freely shift the computed DOS on the energy axis and look for a position which yields the best one-to-one correspondence between structures in the DOS and the observed spectrum. This has led to the interpretation of a wide variety of soft-x-ray spectra in insulators entirely in terms of transitions to the conduction bands, allowing for possible excitonic enhancement of peaks, but *excluding* *the possibility that core excitons are formed below the band edge.*[3–10] Similar results have been reached in some cases without freely shifting the DOS but by calculating the transition energy directly.[11,12]

These interpretations based on energy-band theory have generally contradicted suggestions by experimental groups that one or more of the peaks near the onset of absorption may be excitons.[13–24] Such suggestions were based on a variety of considerations: Comparisons with transition energies in free atoms; experimental studies, such as changes in the spectrum upon cooling the sample, or comparisons with photoelectric-yield data; guesswork in identifying shoulders in the observed spectra as band thresholds; partial knowledge of the critical points in the conduction bands; and theoretical studies on the shape of metastable excitons.[25–28] Excitons below the band edge were in general found to have binding energies of order 1 eV and, in many cases, excitons were associated with critical points of the conduction bands.

Finally, the interpretation of soft-x-ray spectra has also been approached from the point of view of atomic models in which one starts from transitions in the free atom and attempts to systematically include crystal effects.[29–32]

Most of the controversy that has resulted from the various approaches can be resolved *if the threshold for interband transitions can be determined accurately in each case.* Any structure below such a threshold can then unambiguously be described as excitons and a meaningful comparison of density-of-states calculations can be made with observed structure above the threshold. From a strictly theoretical point of view, one would seek to determine this most important quantity through an energy-band calculation. It turns out, however, that the approximation one uses for the crystal potential is extremely crucial. In particular, the use of a local approximation to the exchange term in the Fock operator (such as the $X\alpha$ method) is not reliable. It is often claimed that the local exchange contains a certain amount of correlation as well, but the fact is that the eigenvalues of the $X\alpha$ Hamiltonian are a set of approximate eigenvalues and no systematic and reliable method of correcting them is available. Quite often α is adjusted to fit an observed transition, such as the fundamental band gap, but this is no guarantee that the position of the core levels would then be accurately predicted. An illustrative example is the Hartree-Fock-Slater calculation for LiF by Menzel *et al.*[11] In that case, their calculated optical gap was in reasonable agreement with experiment, but their threshold for transitions from the Li 1*s* level to the conduction bands can be shown[33,34] to be off by 10 eV! (See Sec. III.)

A rigorous Hartree-Fock calculation with nonlocal exchange also gives transition energies which are off by large amounts.[35] In this case however, one can *systematically* correct the Hartree-Fock results for correlation effects. Such correlation corrections have been discussed by a number of authors.[36–40] We recently performed such Hartree-Fock–plus–correlation calculations for the core, valence and conduction bands of MgO and the predicted interband energies agreed well with experimental values.[40,41]

An alternative approach is to seek to determine a value for the crucial interband threshold from independent experiments. For such a determination one can use x-ray emission data or x-ray-photoelectron-spectroscopy (XPS) data (also called ESCA: electron spectroscopy for chemical analysis), both of which may provide an accurate value for the position of the top of the valence band relative to the core bands. Combining this with optical-gap data,[1] one then obtains the position of the bottom of the conduction band relative to the core level. This is just the interband threshold in question. X-ray emission data have been used in the past for this purpose by a number of authors.[18,19,31,42,43] XPS data were used recently by Scheifley and Brown[44,45] who analyzed a number of spectra in the rubidium halides. They found that at least one exciton is formed below the band edge and made a detailed comparison with a computed density of states positioned at the determined threshold. Recently, Pantelides and Brown[33] and the author,[46] reported a similar analysis of some soft-x-ray spectra of lithium and sodium halides. Large excitonic effects were found. Similar results for the Li^+ K spectrum of LiF have also been reported by Gudat, Kunz, and Petersen.[34]

In this paper we present a comprehensive study of a total of 39 soft-x-ray spectra of 12 alkali halides. We will refer to these spectra by their spectroscopic notation which is summarized in Table I. The approach we will follow is to make use of recent accurate XPS data[47,48] and optical-gap data from the literature[1,5] to pin down the threshold for interband transitions for each spectrum. We

TABLE I. Spectroscopic notation for excitation of given core levels.

Core level	Spectroscopic notation
$1s$	K
$2s$, $2p_{1/2}$, $2p_{3/2}$	L_1, L_2, L_3
$3s$, $3p_{1/2}$, $3p_{3/2}$, $3d_{3/2}$, $3d_{5/2}$	M_1, M_2, M_3, M_4, M_5
$4s$, $4p_{1/2}$, $4p_{3/2}$, $4d_{3/2}$, $4d_{5/2}$	N_1, N_2, N_3, N_4, N_5
$5s$, $5p_{1/2}$, $5p_{3/2}$, $5d_{3/2}$, $5d_{5/2}$	O_1, O_2, O_3, O_4, O_5

will then proceed to a detailed interpretation of the structure, whenever possible, making use of available density-of-states calculations. In cases where Hartree-Fock energy-band calculations exist and core levels have been reported in the literature, we will proceed to calculate correlation-corrected interband thresholds and compare with the ones determined from the XPS and optical-gap data. For this reason, in Sec. II we present a summary of the theory governing electronic excitations in solids as approached from the rigorous Hartree-Fock-plus-correlation point of view. This also provides a rigorous justification for the use of XPS and optical-gap data in the subsequent sections. In Secs. III–V we discuss the soft-x-ray spectra arising from excitations of electrons in the core shells of the metallic *cation* (the alkali ion) in lithium, sodium, and potassium halides. In Secs. VI–IX, we discuss the soft-x-ray spectra arising from excitations of electrons in the core shells of the nonmetallic *anion* (the halogen ion) in the same alkali halides. In many cases, contradictory interpretations of the spectra exist in the literature and we attempted a review in chronological order. (We do not attempt nor do we claim any completeness in these brief reviews. A review paper has recently appeared by Brown.[45]) We believe that the present approach resolves the existing controversies and, indeed, not always in favor of the most recent, or, sometimes, any published interpretation of a given spectrum. Whenever possible, we present detailed interpretations of the observed structures. In the process, we arrive at a number of conclusions which shed considerable light on the nature of the processes involved. The most important is that electron-hole interactions are so overwhelmingly large in the cases of excitations of the *cation* core electrons, that each such spectrum is almost entirely excitonic in nature. Binding energies are much larger than suggested by previous interpretations by many authors[18–24] and no identification of excitons with critical points in the bands can be supported. This is not quite so in the case of excitations of the *anion*, where electron-hole attraction is more effectively screened. This and other conclusions are discussed in Sec. X.

II. EIGENSTATES OF THE ELECTRONIC SYSTEM AND EXCITATION ENERGIES

The eigenstates of a perfect crystalline solid containing N electrons are, in principle, determined from the eigenvalue problem

$$H^{(N)}\Psi_\alpha = E_\alpha^{(N)}\Psi_\alpha , \tag{1}$$

where $H^{(N)}$ is the complete N-electron Hamiltonian. Excitation energies are thus differences between the energies $E_\alpha^{(N)}$ of excited states and the total ground-state energy $E_0^{(N)}$.

A. Hartree-Fock picture

In the Hartree-Fock (HF) approximation, Eq. (1) is solved variationally by taking Ψ_α to be an antisymmetrized product (Slater determinant) of one-electron functions. One then ends up solving a one-electron eigenvalue problem

$$F\psi_{l\vec{k}}(\vec{r}) = \epsilon^0_{l\vec{k}}\psi_{l\vec{k}}(\vec{r}) , \tag{2}$$

where F is the Fock operator. The $\psi_{l\vec{k}}(\vec{r})$ are the well-known Bloch functions and the eigenvalues $\epsilon^0_{l\vec{k}}$ form the HF band structure of the solid. The index l labels bands and $\vec{k}$ is the wave vector in the first Brillouin zone. (Hereafter, the index $\vec{k}$ will be suppressed unless needed in the discussion.) In the case of insulators, the one-electron bands in the ground state are either full or empty; hereafter, we will use Latin letters such as l, m, n to denote occupied bands and Greek letters such as λ, μ, ν to denote empty bands.

The eigenvalues $\epsilon^0_{l\vec{k}}$ are given meaning via Koopmans's theorem[49,50] according to which

$$\epsilon_l^0 = E_0^{(N)} - E_l^{(N-1)0} \quad \text{(ionization energy)}, \tag{3}$$

$$\epsilon_\lambda^0 = E_\lambda^{(N+1)0} - E_0^{(N)0} \quad \text{(electron affinity)}. \tag{4}$$

Here $E_0^{(N)0}$ is the total ground-state energy of the N-electron system computed in the HF approximation; $E_l^{(N-1)0}$ is the total HF energy of the $(N-1)$-electron system when the missing electron was removed from the state $l\vec{k}$; $E_\lambda^{(N+1)0}$ is the total HF energy of the $(N+1)$-electron system when the extra electron occupies the state $\lambda\vec{k}$. In this context, excitations of the N-electron system are *one-electron interband transitions*. The excited states have total energies denoted by $E_{l\lambda}^{(N)0}$, meaning that an electron has made a transition from the state $l\vec{k}$ to the state $\lambda\vec{k}$. The excitation energy is given by

$$\Delta\epsilon^0_{l\lambda} = E_{l\lambda}^{(N)0} - E_0^{(N)0} = \epsilon^0_\lambda - \epsilon^0_l . \tag{5}$$

In view of Eqs. (3) and (4), we have

$$\Delta\epsilon^0_{l\lambda} = (E_\lambda^{(N+1)0} - E_0^{(N)0}) - (E_0^{(N)0} - E_l^{(N-1)0}) , \tag{6}$$

which means that this process of excitation amounts to taking an electron to infinity and then bringing it in a conduction-band state without it knowing that there is a hole in the occupied manifold. The electron and the hole are not allowed to interact. A consequence of this is that the various excitations are describable by a unique band structure. This is illustrated schematically in Fig. 1 where

$$\Delta\epsilon^0_{ll'} + \Delta\epsilon^0_{l'\lambda} = \Delta\epsilon^0_{l\lambda} . \tag{7}$$

Equation (7) represents the fact that HF energy bands are *additive* or *rigid*.

B. Energy bands beyond the Hartree-Fock approximation

The Hartree-Fock approximation has been shown to be quite inadequate in that HF energy bands re-

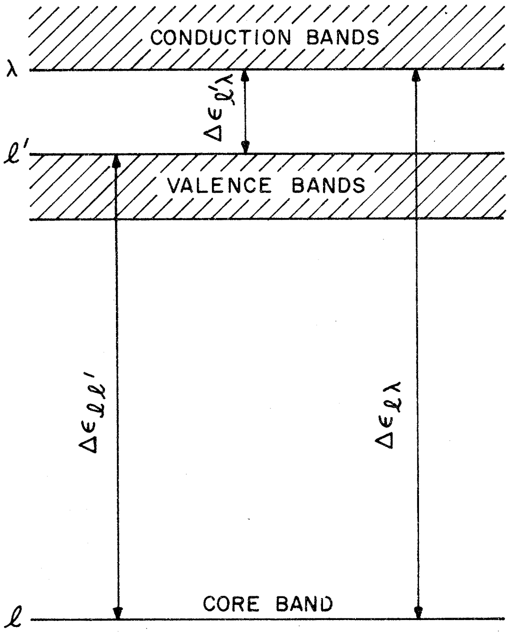

FIG. 1. Illustration of the rigidity of band structures beyond the Hartree-Fock approximation. The relations $\Delta\epsilon_{l\lambda}=\Delta\epsilon_{ll'}+\Delta\epsilon_{l'\lambda}$ is true at any $\vec{k}$ point.

sult in excitation energies which are off by as much as (30–100)% in some cases.[6–8,10,12,36,40,41,51] The energy-band picture may, however, be retained beyond the HF approximation.[40,52] In general, the *exact* total energy of an M-electron system in the αth eigenstate is given by

$$E_\alpha^{(M)}=E_\alpha^{(M)0}+C_\alpha^{(M)}, \tag{8}$$

where $C_\alpha^{(M)}$ is by definition the correlation energy. Exact expressions for it may be written down[40,53] but will not concern us here. One can then write, by analogy to Eqs. (3) and (4),

$$\epsilon_l=E_0^{(N)}-E_l^{(N-1)}, \tag{9}$$

$$\epsilon_\lambda=E_\lambda^{(N+1)}-E_0^{(N)}, \tag{10}$$

and by using Eqs. (8), (3), and (4) to get

$$\epsilon_l=\epsilon_l^0+\mathcal{E}_l, \tag{11}$$

$$\epsilon_\lambda=\epsilon_\lambda^0+\mathcal{E}_\lambda, \tag{12}$$

where

$$\mathcal{E}_l=C_0^{(N)}-C_l^{(N-1)}, \tag{13}$$

$$\mathcal{E}_\lambda=C_\lambda^{(N+1)}-C_0^{(N)}. \tag{14}$$

The quantity $\mathcal{E}_l$ is known as the self-energy of a hole and reflects the change in the correlation energy of the system when the electron from state $l\vec{k}$ is removed. $\mathcal{E}_\lambda$ is known as the self-energy of an electron and reflects the change in the correlation energy of the system when an electron is added in the state $\lambda\vec{k}$. These quantities contain all correlation and relaxation effects beyond the HF-Koopmans result and have been discussed in detail elsewhere.[40] It is found that in insulators $\mathcal{E}_l$ and $\mathcal{E}_\lambda$ have two distinct contributions:

(a) The first, referred to as long-range correlations and denoted by $\mathcal{E}^{(\mathrm{lr})}$, is the sum total of polarizations of the valence electron cloud induced by the hole or the electron independently. It can be calculated by simple dielectric response theory either in the semiclassical Mott-Littleton approach[54,36] or via models which simulate the excited spectrum of a crystal with a single band of excitations. Such models are Toyozawa's electronic polaron,[55,37,38,40] (the elementary excitations are taken to be a dispersionless band of excitons) and the Overhauser-Hermanson model[39,40] (the elementary excitations are taken to be a band of plasmons). These models result in $\mathcal{E}^{(\mathrm{lr})}\sim 1$–4 eV (Ref. 36–39) but calculations by different authors, even within the same model, may differ by 0.5 to 1.0 eV. Different models[37,39] disagree by 1–2 eV.[56]

(b) The second, referred to as short-range correlations and denoted by $\mathcal{E}^{(\mathrm{sr})}$, is the polarization of the core electrons in the central cell. The electron or hole carries this polarization well with it as it moves through the crystal. For electrons in the conduction bands these polarizations may be of order 1–2 eV (Refs. 40, 41, and 51) but no reliable method to compute them has been proposed. For holes in the core states, they are very large, particularly for deeper states. They may be estimated by making use of atomic calculations[40,51] but the uncertainty is probably again of order 1–2 eV or more. Overall, correlation corrections to Hartree-Fock transition energies introduce an uncertainty of at least 2–3 eV in most cases. Such accuracy may not be adequate to decide whether the first few peaks near the onset of soft-x-ray absorption are excitons below the band edge or not.

The most important aspect of definitions (8)–(14) is that the energy-band picture is retained. A set of excitation energies can be defined by analogy to (6):

$$\Delta\epsilon_{l\lambda}=(E_\lambda^{(N+1)}-E_0^{(N)})-(E_0^{(N)}-E_l^{(N-1)}), \tag{15}$$

whereby, via Eqs. (9) and (10),

$$\Delta\epsilon_{l\lambda}=\epsilon_\lambda-\epsilon_l=\Delta\epsilon_{l\lambda}^0+(\mathcal{E}_\lambda-\mathcal{E}_l). \tag{16}$$

The additivity and rigidity of the bands (now known as quasiparticle bands; these are the bands that an empirical pseudopotential calculation[57] reproduces) is retained (Fig. 1), and we have

$$\Delta\epsilon_{l\lambda}=\Delta\epsilon_{ll'}+\Delta\epsilon_{l'\lambda}. \tag{17}$$

We do note, however, that for excitations described by (15) and for which (17) holds, the electron and the hole are not allowed to interact whereby all electron-hole correlations are left out; one electron is removed to infinity and one electron is put into the conduction band, but the two processes are done independently. The validity of (17) *in the absence of electron-hole interactions* is the backbone of the discussion in the remainder of the paper.

C. Hole-electron interactions

The band-theoretical formalism described above does not necessarily represent real excitations in crystals. Nonetheless, as long as electron-hole interactions can be included by perturbation theory, the band picture can be quite useful. Qualitatively, the results are directly obtainable from scattering theory[58,59]: (i) Electrons and holes may scatter elastically from each other; their wave functions are phase-shifted but their energies remain unchanged. Thus, the positions of the interband continua remain unchanged even though the strength of such transitions may be dramatically modified (see subsection E below). (ii) An electron and a hole may form a bound state (an *exciton*) and propagate *together* in the crystal in order to satisfy the symmetry requirement imposed by the periodicity of the lattice of nuclei. For these states, the excitation energies may lie within the forbidden gaps of the band picture.

By writing the total energy of the N-electron system in the presence of an exciton as $E_{\text{ex}}^{(N)}$, the excitation energy is

$$\Delta\epsilon_{\text{ex}} = E_{\text{ex}}^{(N)} - E_0^{(N)}, \tag{18}$$

which can be written

$$\Delta\epsilon_{\text{ex}} = \Delta\epsilon_{l\lambda} - \epsilon_{B,\,l\lambda}, \tag{19}$$

where

$$\epsilon_{B,\,l\lambda} = E_{l\lambda}^{(N)} - E_{\text{ex}}^{(N)} \tag{20}$$

for an *arbitrary* choice of l and λ. If $\Delta\epsilon_{\text{ex}}$ is not degenerate with any $\Delta\epsilon_{l\lambda}$, a meaningful choice of $\Delta\epsilon_{l\lambda}$ in Eqs. (19) and (20) is the lowest one available above $\Delta\epsilon_{\text{ex}}$. This is the case of an exciton lying within a forbidden gap in the energy-band picture, where one *may* choose $\Delta\epsilon_{l\lambda}$ in (19) to be the energy for transitions to the bottom of the band immediately above the exciton. The quantity $\epsilon_{B,\,l\lambda}$ may then reasonably be called the *binding energy* of the exciton. If, however, $\Delta\epsilon_{\text{ex}}$ is degenerate with one or more of the $\Delta\epsilon_{l\lambda}$, which form a continuum, a meaningful choice for $\Delta\epsilon_{l\lambda}$ in (19) may not exist. In the case of semiconductors, excitonic states can be constructed in the effective-mass approximation; they are then unambiguously connected with one or more critical points in the conduction-band continuum so that a definite choice of $\Delta\epsilon_{l\lambda}$ in (19) can be made even for excitons which lie within the continuum. The quantity $\epsilon_{B,\,l\lambda}$ in that case can be thought of as "binding energy" even though the true binding energy is zero. Finally, in the case of insulators, where electron-hole interaction is stronger, excitons lying below the conduction-band minimum may not be associated with that minimum at all because of symmetry incompatibilities, in which case the apparent "binding energy" again does not reflect the true strength of the interaction responsible for the formation of the exciton (see Sec. III).

The computation of the exciton excitation energy $\Delta\epsilon_{\text{ex}}$ directly is a complicated many-body problem. Estimates can be made by starting with a free-atom excitation energy and correcting it with solid state effects, but the uncertainties involved may be several volts even in very tight-binding-like crystals.[31,46] On the other hand, one can arrive at $\Delta\epsilon_{\text{ex}}$ by calculating $\epsilon_{B,\,l\lambda}$ and using Eq. (19). This is possible for semiconductors where electron-hole interaction is screened very effectively by the large dielectric constants and effective masses are small, but not in general for the alkali halides. In the latter case the Koster-Slater difference equations[60] for the calculation of $\epsilon_{B,\,l\lambda}$ might be more appropriate but the problem of constructing a potential beyond the linear dielectric theory limit and including many bands and sites is still to be solved.

D. Connection with experiments

In this section thus far we have given the theoretical framework via which one can, in principle, either predict or interpret observed spectra. Direct theoretical calculations have not been done in general due to the difficulty of including the electron-hole interaction properly. Our purpose here is not to give such a theory. Instead we will use available experimental data to establish the energies of interband excitations from which, using Eq. (20) we can deduce information about the binding energies of excitons lying within the forbidden band gaps. Since we will concentrate on the spectra arising from excitations of core electrons, the most important quantity needed for conclusive interpretation is, as pointed out in the introduction, the threshold for transitions to the conduction bands. In the notation of this section, this quantity is simply $\Delta\epsilon_{l\lambda}$ where l is the core band of interest and λ is the bottom of the conduction band (Fig. 1). As we saw, *ab initio* theory alone can predict this quantity with an uncertainty of at least 2–3 eV at the present time.

The quantity $\Delta\epsilon_{l\lambda}$ can, however, be obtained from independent experiments if one makes use of Eq. (17) and takes l' to be the top of the valence band (Fig. 1). Then, $\Delta\epsilon_{l'\lambda}$ is simply the optical band gap, namely, the energy difference between the top of the valence band and the bottom of the conduction band. This is generally extracted from reflectance or optical-absorption spectra with an accuracy of 0.2 eV or less.[61,1] The quantity $\Delta\epsilon_{ll'}$ represents the difference between the top of the valence band

and the core level of interest:

$$\Delta\epsilon_{ll'} = \epsilon_l - \epsilon_{l'} . \tag{21}$$

This energy difference could be obtained from x-ray emission data[18,19,31,42,43] which represent transitions from the valence band into the core level. In these transitions, however, electron-hole interaction effects are inextricably present so that doubt about such a determination of $\Delta\epsilon_{ll'}$ could be raised.

Alternatively, $\Delta\epsilon_{ll'}$ can be obtained if each of the energies ϵ_l and $\epsilon_{l'}$ in (21) can be obtained separately. This can be done directly from XPS data. In such experiments one measures the binding energy of an electron relative to an arbitrary energy (usually the Fermi level). The electron absorbs a photon of more than a keV of energy, makes a transition into way up in the continuum, and gets out of the crystal, to "infinity." Note that this is exactly the definition for the quantities ϵ_l and $\epsilon_{l'}$ [Eq. (9)]. Each is given by an equation of the form (11) which shows that all correlation and relaxation effects are built in the theory through $\mathcal{E}_l$ and $\mathcal{E}_{l'}$ just as they are present in the experiment. Care must be taken, nevertheless, in extracting information from XPS data. The task is made easier by the fact that we need only the *difference* of ϵ_l and $\epsilon_{l'}$ [Eq. (21)] but this requires that the two quantities be measured during the same run, on the same sample, because of charge accumulation on the surfaces. The way experiments are done now, a single photon energy is used (the Mg *K* or Al *K* line) whereby the final state in the continuum is different for the various initial states. Experiments show, however, that the resultant ϵ_l's and $\epsilon_{l'}$'s (or at least their relative positions) do not depend on the photon energy, as long as the latter is above the "x-ray limit."[62] On the alkali halides, recent accurate measurements by Kowalczyk *et al.*[47] claim an accuracy of 0.1 eV for the energy $\Delta\epsilon_{ll'}$ (Fig. 1). A more conservative estimate, in view of some arbitrariness in treating the tail observed at the top of the valence band, would set the total uncertainty for the interband thresholds $\Delta\epsilon_{l\lambda}$ at about 0.5 eV, far better than present theoretical calculations can do.

E. Shape of absorption spectra

In the above we discussed the absolute magnitudes of transition energies. The probability that a transition occurs is of course proportional to the density of final states and to a matrix element, according to Fermi's Golden Rule. In the case of interband transitions and in the absence of electron-hole interactions this leads to the usual expression for the absorption coefficient for transitions from band l to band λ:

$$\alpha(E) = \frac{4\pi^2 e^2 \hbar}{m^2 n c E} \int_{\mathrm{BZ}} \frac{2 d^3 k}{(2\pi)^3} \left| M_{\lambda l}(\vec{k}) \right|^2 \delta(\epsilon_\lambda - \epsilon_l - E) , \tag{22}$$

where the matrix element $M_{\lambda l}(\vec{k})$ in the HF approximation is given by

$$M_{\lambda l}(\vec{k}) = \langle \psi_{l\vec{k}} | \vec{p} | \psi_{\lambda\vec{k}} \rangle , \tag{23}$$

where $\vec{p}$ is the momentum operator (dipole approximation). Beyond Hartree-Fock, one ought to use correlated wave functions[40] in (23) which becomes a more involved task. If one takes $|M_{\lambda l}(\vec{k})|^2$ to be approximately a constant $\bar{P}$ the result is

$$\alpha(E) = \frac{4\pi^2 e^2 \hbar}{m^2 n c E} |\bar{P}|^2 J_{\lambda l}(E) , \tag{24}$$

where $J_{\lambda l}(E)$ is the joint density of states between bands l and λ. In the case of excitations from core states for which ϵ_l is constant (no dispersion) $J_{\lambda l}(E)$ reduces to the DOS of the conduction bands. Thus, *assuming* that nonconstant matrix elements might alter the *heights* of peaks and valleys in a computed DOS but *not shift* them, one might expect the structure in the DOS to have a one-to-one correspondence with the observed spectrum. The presence of excitons both below and within the conduction band continuum and modification of the matrix elements due to electron-hole scattering may alter the DOS dramatically so that interpretation of the observed spectrum becomes a more complicated task. Trying to untangle exciton and band effects will be the task we will pursue in the rest of this paper for a number of insulators.

III. Li$^+$ SPECTRA OF THE LITHIUM HALIDES

The lithium halides, particularly LiF, are perhaps the most controversial. In this section we concentrate on the soft-x-ray absorption spectra of LiF, LiCl, LiBr, and LiI near the Li$^+$ *K* edge. These were first measured with high resolution by Haensel, Kunz, and Sonntag.[13] The spectra for all four of these materials were found to be similar with a very pronounced peak at about 60–62 eV. This peak was followed by a weaker but quite rich structure at higher energies (Fig. 2, solid lines). Haensel *et al.*[13] speculated that the main peaks are due to the formation of excitons and that the subsequent structure is due to transitions to *p*-like states in the conduction bands. They were not able to identify any band edges.

Shortly afterwards, these spectra were measured and interpreted by Brown, Gähwiller, Kunz, and Lipari.[3] They carried out the measurements to much higher energies than previously; the results in the region 55–70 eV were essentially the same as those of Haensel *et al.*[13] Their interpretation of the spectra was quite different, however. They performed energy-band calculations in the Hartree-Fock limit and computed the DOS for transitions

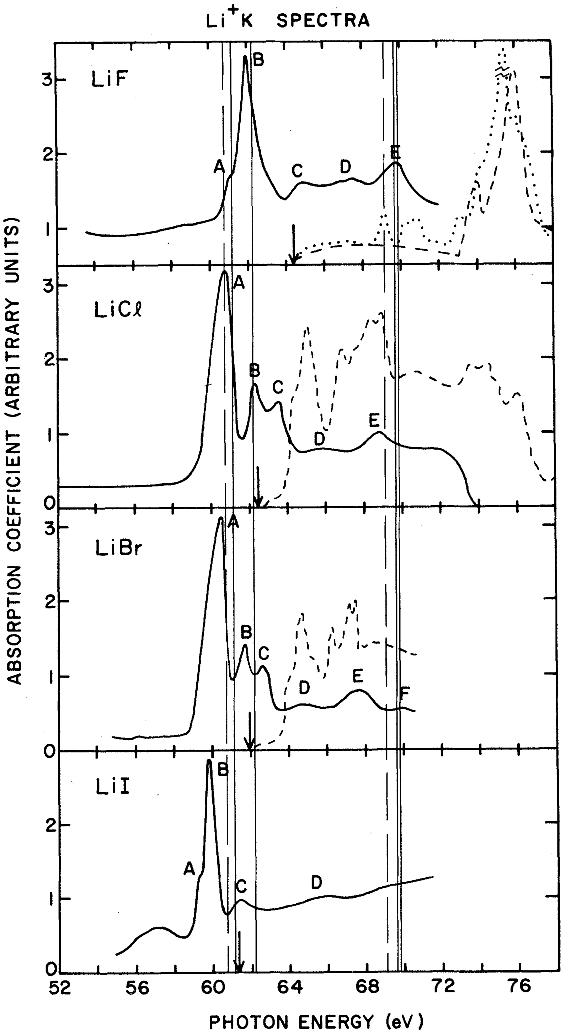

FIG. 2. Li^+ K spectra of the lithium halides. Solid curves are experimental. (Reference 13; low-energy tail of LiF spectrum from Ref. 64). Dotted curve (from Ref. 11) and dashed curves (from Ref. 12 for LiF, Ref. 3–6 for LiCl, LiBr) are theoretical interband spectra positioned on the energy axis according to interband thresholds determined here (vertical arrows). The thin vertical lines mark the positions of transitions in the free Li^+ ion (Ref. 66).

from the Li^+ core levels to the conduction bands. By freely shifting the DOS on the energy axis they interpreted the observed spectra in terms of band-to-band transitions alone, *excluding* the possibility that excitons are formed below the band edge. This point of view was maintained in a series of papers by Kunz[4] and Kunz and Lipari.[6] The Li^+ K spectra of LiCl and LiBr were interpreted by aligning the first peak in the theoretical DOS with the main peak in the observed spectra. Thus it was implicitly predicted that the band threshold lies slightly to the left of the main peak, at 58 eV for LiCl and 58.5 eV for LiBr. By analogy with these identifications, Kunz, Devreese, and Collins[63] assumed the band threshold for LiF lies at about 60.5 eV and proceeded to identify peak E as an electronic-polaron resonance which ought to lie above the band threshold by an amount somewhat less than a valence exciton (12.6 eV in LiF). Similar identifications were made in the LiCl and LiBr spectra.[63]

Theoretical calculations on LiF were reported by Menzel *et al.*[11] and by Kunz, Mickish, and Collins.[12] Menzel *et al.*[11] did a tight-binding band-structure calculation for LiF employing the Slater free-electron local approximation to the exchange. They computed a theoretical absorption spectrum for band-to-band transitions from the Li $1s$ levels and found the onset of such transitions at about 55 eV, followed by a pronounced peak at 64 eV. They identified this peak with the dominant peak in the observed spectrum and thus suggested that the observed spectrum is due *entirely to interband transitions and no excitons.*

Kunz *et al.*[12] also did a tight-binding band structure calculation for LiF but in the rigorous Hartree-Fock limit with nonlocal exchange. The computed absorption spectrum for interband transitions showed remarkable similarity with that of Menzel *et al.*[11] and with the observed one, but was found to lie about 23 eV higher on the energy axis. The authors argued that the experimental absorption is not expected to be due to excitons below the band edge since the exciton transition is s to s and hence not allowed. Then they proceeded to estimate corrections to the interband Hartree-Fock energies and approximately accounted for a rigid shift of the computed spectrum by about 20 eV. The corrected spectrum exhibits the pronounced peak at 65 eV and, like the spectrum of Ref. 11 predicts a weak tail on the low-energy side with the onset at about 54 eV.

In view of these theoretical papers, Sonntag[64] measured the Li^+ K shell spectrum of LiF and detected a slow rise in absorption beginning at about 54 eV, in qualitative agreement with the theoretical predictions. He pointed out, however, that this does not necessarily unambiguously support the interpretation of the observed spectrum in terms of interband transitions alone.

All this controversy can be resolved conclusively by determining the interband threshold from independent experiments as discussed in Sec. II. Accurate XPS data for LiF were reported by Kowalczyk *et al.*[47] According to these data, the top of the valence band lies 50.8 eV above the Li $1s$ level. Combining this with the optical band gap of 13.6 eV (Ref. 1) we get 64.4 eV for the threshold for interband transitions. Since the main peak in the observed spectrum is at 61.9 eV, this establishes

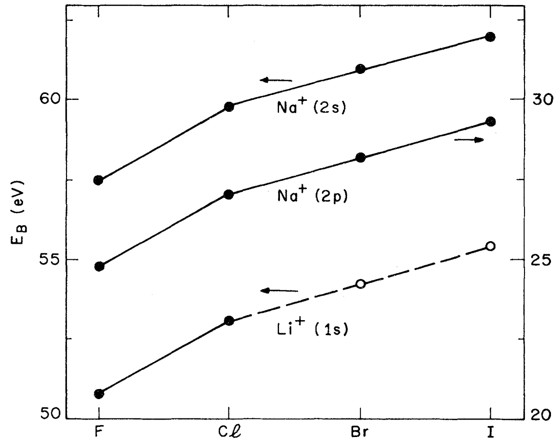

FIG. 3. Comparison of binding energies of the Na$^+$ $2s$, Na$^+$ $2p$, and Li$^+$ $1s$ levels in the four halides which allows us to deduce binding energies for the Li$^+$ $1s$ level in LiBr and LiI. See discussion in text.

TABLE II. Dominant experimental peak (Ref. 13) and the predicted band thresholds for excitations from the Li$^+$ is shells in the lithium halides. All quantities are in eV. E_B are the exciton binding energies relative to thresholds (a).

Substance	Dominant peak (experimental)	Band thresholds a	b	c	E_B
LiF	61.9	64.4	66.0	60.5	2.5
LiCl	60.8	62.3	62.9	58.0	1.5
LiBr	60.4	61.8	63.4	58.5	1.4
LiI	59.8	61.6	···	···	1.8

[a] Determined from XPS and optical-gap data. See text.

[b] From Hartree-Fock–plus–correlation theory. See text.

[c] From Refs. 3, 4, 6, and 63.

conclusively that *this peak is an exciton below the band edge.*[33,34] We will discuss the nature of this exciton and the rest of the spectrum shortly.

XPS data for LiCl have been reported by several authors.[48] Comparison with data on the Na $2p$ and $2s$ levels of sodium chlorides has allowed us to interpolate and obtain estimates of binding energies relative to the top of the respective valence bands for the other compounds as shown in Fig. 3. Combining these values with optical-gap data,[1] we obtain the band thresholds listed in Table II. We also list the position of the dominant experimental peaks which are now identified as *excitons*. The entry labeled (b) in Table II is theoretical band thresholds which we will discuss later on in this section. In Fig. 4 we plot the exciton energies and the band thresholds for the four halides and observe a similarity of patterns. We note that this similarity is expected because for both transitions–excitons, and to the bottom of the band–the electron is mostly on the lithium sublattice (see below). The different halide in the environment causes the shift of about 0.5 eV from one compound to the next. We will see similar patterns for the sodium halides in Sec. IV.

Having identified the prominent peak in the observed spectrum of each lithium halide as an exciton, we now proceed to interpret the remainder of the structure. In Fig. 2 we display the theoretical interband spectra, where available, positioned on the energy axis according to the present determination of the band thresholds (solid arrows).

First we note that in each case the main exciton peak lies about 2.0 eV below the band edge. If we measure binding energies from the band edge, such a value may not be atypical for excitons in insulators. However, in view of the fact that the bottom of the conduction band is Γ_1, we must exclude the possibility that it derives from that critical point in an effective-mass picture. This is because an exciton deriving from the Γ_1 minimum would be s to s and hence dipole forbidden.[12] Clearly, the observed exciton must derive from higher conduction bands which are p-like in character. In the case of LiF, both theoretical calculations in the literature (Refs. 11 and 12; see Fig. 2) show a high density of p-like states about 10–13 eV above the Γ_1 minimum which leads us to infer that electron-hole interaction is extremely strong, *capable of MIXING band states over the range of a rydberg.* This should not be disturbing if we recall that the va-

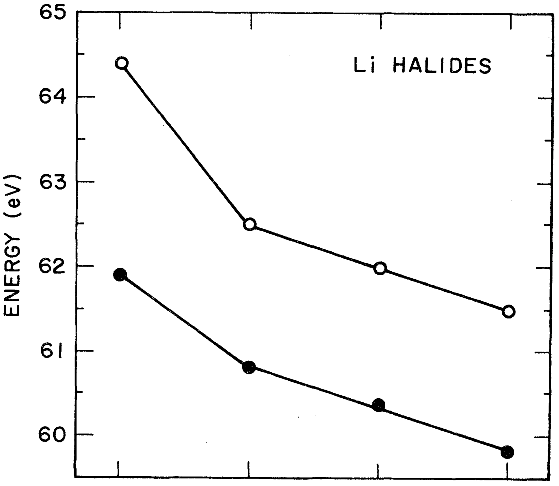

FIG. 4. Positions of the experimental dominant peaks (solid points) in the Li$^+$ K spectra of the lithium halides are compared with the positions of the band thresholds (open points) determined in this work. Note the similarity of patterns with Fig. 3.

lence electrons in LiF are almost entirely on the F^- ions; thus the Coulomb potential of a hole in the Li^+ shell is essentially *not screened at all* and attracts and binds the electron very strongly. Granting this large electron-hole interaction, one may expect that weak excitonic structure may lie as much as a rydberg below the band edge. Such structure may be partly responsible for the low-energy tail observed recently in the LiF spectrum by Sonntag[64] and similar tails present in the original data of Haensel *et al.*[13] In fact, a scarcely discernible bump in these tails may be what can be termed the "forbidden" Γ_1 exciton. Both this "forbidden" exciton and the main exciton have been reproduced by a model calculation by Pantelides, Martin, and Sen.[65]

Examining Fig. 2 further, we note that in each spectrum the rise leading to peak C coincides with the position of the band threshold. In fact, however, transitions near the band threshold are suppressed both by lack of high density of states and by symmetry, so that excitonic enhancement, or, perhaps a superposed metastable exciton must be invoked to account for the observed strength. Indeed, from Fig. 2, we can conclude that the observed spectrum is almost *entirely excitonic* with band transitions in the background retaining little or no oscillator strength.[65] Further, in view of the observation that electron-hole interaction may mix bands over a range of as much as a rydberg, no identification of the excitons with critical points in the band continuum can be supported, and we pursue no such thing. In fact, an energy-band calculation may not be the most appropriate starting point for the computation of such dominantly excitonic spectra.[33,34]

The fairly pronounced peaks marked E are the only peaks which may have strong contributions from interband transitions. These peaks are particularly interesting in that they were identified by Kunz *et al.*[63] as electronic polaron resonances. For LiF and LiCl they were identified as bound electronic-polaron resonances which physically corresponds to the creation of two excitons. Even though in their analysis they assumed the band edges to be at 60.5 and 58.0 eV respectively, such an identification cannot completely be ruled out. For LiBr, peak E was identified in Ref. 63 as due to a "free-electronic-polaron complex" which physically corresponds to an interband transition plus a valence exciton. Such an identification requires that the band edge lies at 58.5 eV.[63] The present determination of the band edge at 61.8 eV implies that a free-electronic-polaron resonance would lie about 4 eV higher than the observed peak E. The possibility remains, however, that peak E is in fact a bound-electronic-polaron complex (a two-exciton excitation), as is probable for LiF and LiCl.

It is possible to shed some light on the nature of some of the peaks in Fig. 2 by comparing with the x-ray transitions in the free Li^+ ion.[66] The positions of these transitions are marked by the thin vertical lines in Fig. 2. (The dashed lines mark the $1s \rightarrow 2s$ and $1s \rightarrow 3s$ transitions and the solid lines mark the $1s \rightarrow 2p$ and $1s \rightarrow 3p$ transitions.) This strongly suggests that the main excitonic peak in each spectrum is essentially a $1s^2 \rightarrow 1s2p$ transition occurring in a Li^+ ion with small corrections due to the halogen neighbors.[32] Peaks E seem to follow a similar pattern, which suggests that $(1s^2 \rightarrow 1s3p)$-like transitions in Li^+ ions contribute strongly. Clearly, however, the spectra of Fig. 2 show rich structure between 62 and 69 eV, which does not correspond to transitions in the free Li^+ ion. This structure probably arises from transitions to states which are mainly constructed from virtual states of the halogen ions.

This completes what can at present be said about the nature of the Li^+ K spectra of the lithium halides, but before we close this section it is worthwhile to check how well theory alone could have done for the determination of the band thresholds. First we note the Hartree-Fock-Slater calculation of Ref. 11 gives a band threshold at 55 eV which is indeed off by about 10 eV. Hartree-Fock calculations are available in the literature for LiF, LiCl, and LiBr. In the case of LiF, the Hartree-Fock band threshold was found to be at 73 eV (Fig. 2 of Ref. 12). The authors estimated that this is shifted by 10 eV due to independent electron and hole correlations and by 10 eV due to hole-electron attraction. This total 20-eV shift brought the dominant peak in the theoretical interband spectrum in reasonable alignment with the main experimental peak but also set the threshold at about 53 eV. We take exception with the suggestion[12] that hole-electron attraction shifts both bands and excitons[67] and note that if one applies only the 10-eV correlation correction to the 73-eV Hartree-Fock threshold, the result is a band threshold at 63 eV, in reasonable agreement with the 64.4 eV determined here from independent experiments. By applying the analysis of Ref. 40 and Sec. II, however, we find that the correlation corrections should be only 7 eV.[68] Thus Hartree-Fock energy-band theory plus correlation predict a band threshold at 66 eV. This number is only 1.5 eV off from 64.4 eV. It is also uncertain by about 1–2 eV. The agreement is overall good and such a theoretical determination of the band threshold would at least suggest that the prominent experimental peak at 61.9 eV is an exciton below the band edge.

The situation in LiCl is similar. Hartree-Fock energy bands reported in Ref. 6 result in a band threshold at 70.2 eV. The electron self-energy is

2.4 eV (Ref. 37) and the hole self-energy is 4.9 eV (3.4 eV from the electronic polaron,[37] 1.5 eV from local correlations). Total correction is 7.3 eV, lowering the threshold to 62.9 eV in excellent agreement with the 62.3 eV determined here. For LiBr a similar analysis yields a band threshold at 63.4 which compares well with the 61.8 determined here. (All these numbers are listed in Table II.) Clearly, Hartree-Fock theory, when properly corrected, can do very well in predicting interband threshold and further applications ought to be encouraged.

IV. Na$^+$ SPECTRA OF THE SODIUM HALIDES

The sodium halides, NaF, NaCl, NaBr, and NaI, have a total of three absorption spectra which result from excitations of sodium core electrons. Excitations of the Na$^+$ 1s electrons (the Na$^+$ K spectra) lie in a range of photon energies which may more appropriately be termed hard x rays. These spectra are, in general, broadened considerably by short lifetimes. XPS data are not available for them and we will not consider them further in this paper. Excitations of the Na$^+$ 2s electrons (the Na$^+$ L_1 spectra) are in the range of interest. Combining XPS data from Ref. 47 and optical-gap data from Ref. 1,[69] the band thresholds for these spectra are predicted to lie at 69.0, 68.8, 68.5, and 67.9 eV for NaF, NaCl, NaBr, and NaI, respectively. No high-resolution data have been reported for that region of the spectrum. The data of Ref. 70 show some structure in the region 67–71 eV, which can be attributed to transitions from the Na$^+$ 2s levels; further detailed measurements are needed [such measurements have been reported for NaBr (Refs. 8 and 46(b)) and will be discussed in Sec. VIII in a more appropriate context].

Excitations of the Na$^+$ 2p electrons, however, give rise to very prominent structures, known as the Na$^+$ $L_{2,3}$ spectra. These spectra have been measured by a number of groups. The earliest measurements were by O'Bryan[71] in 1940. In more recent years, high resolution measurements were reported by Haensel, Kunz, Sasaki, and Sonntag[70] and by Nakai and Sagawa.[22] The two sets of spectra differ considerably in the heights of peaks but the basic structure observed is the same. The solid curves in Fig. 5 are the experimental spectra from Ref. 70.

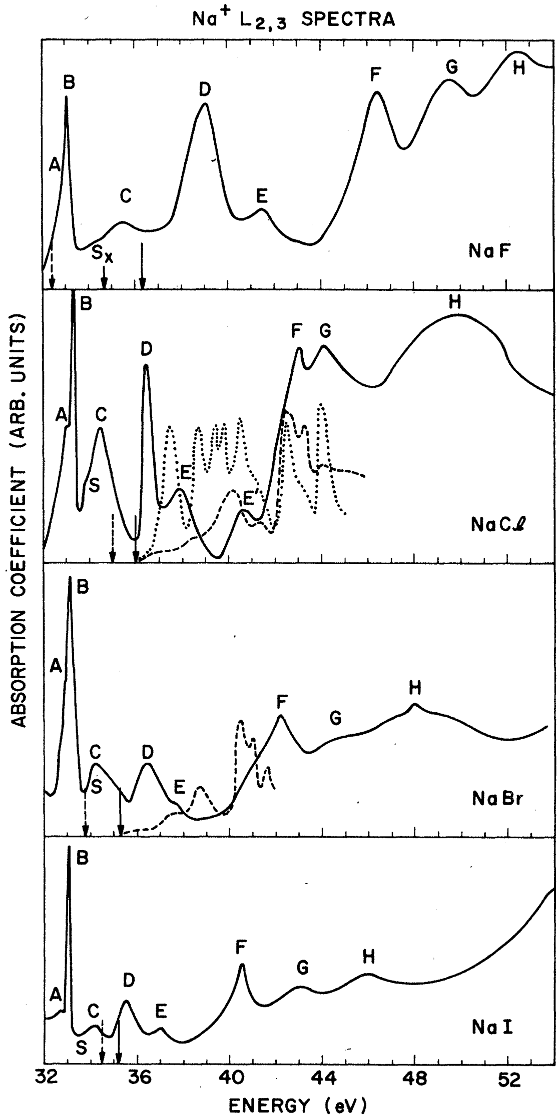

FIG. 5. Na$^+$$L_{2,3}$ spectra of the sodium halides. Solid curves are experimental (Refs. 22 and 23). Dotted and dashed curves are theoretical interband spectra (dotted curve from Ref. 72, dashed curves from Refs. 7 and 8) positioned on the energy axis according to the present determination of band thresholds (solid arrows). The dashed arrows are the band thresholds estimated in Ref. 31. The arrow marked x in the NaF spectrum marks the band threshold for transitions from the F$^-$ 2s level (F$^-$ L_1 spectrum). See text.

As far as interpretation is concerned, Haensel *et al.*[70] only speculated that the AB doublets may be excitons. Nagai and Sagawa[22] studied the temperature dependence of peaks A and B and concluded that they are the two members of a spin-orbit-split exciton associated with the Γ_1 conduction-band minimum. By comparison with other soft-x-ray spectra they assigned the shoulders marked S in Fig. 5 as the onset of interband transitions. The resulting binding energies for the AB exciton were thus of the order of 1 eV. They also suggested that peak D may be an exciton at a point other than Γ and the structure following the rise leading to peak F may be a replica of peaks A–E via a two-exciton process. This last aspect of the interpretation was disputed by Haensel *et al.*[14] who

TABLE III. Dominant experimental peak (Ref. 66) and the predicted band thresholds for excitations from the Na^+ $2p$ shells in the sodium halides. Comparison is made with the band thresholds estimated by Aberg and Dehmer, Ref. 31. All quantities are in eV.

Substance	Dominant peak (experimental)	Band threshold (present work)	Exciton binding energy	Band threshold (Ref. 31)
NaF	33.1	36.3	3.2	32.3
NaCl	33.4	36.0	3.4	35.0
NaBr	33.2	35.7	2.5	33.7
NaI	33.1	35.2	2.1	34.4

carried out photoemission measurements at different retarded potentials and found that peaks *A–E′* behave more like excitons and peak *F* behaves like a continuum transition. Nakai *et al.*[23] identified peak *D* as an exciton associated with an *X* minimum in the conduction bands.

From a band-theoretic point of view, Fong and Cohen[72] computed a density of states for the conduction band of NaCl in the empirical pseudopotential scheme. Because the core levels are not accessible in that scheme, in order to compare with the observed soft-x-ray spectra they had to make an assumption for the position of the band edge. Their suggestion was that peaks *AB* are $1s$ excitons at Γ_1 and peak *C* is the $n = 2$ state of the same exciton. Peaks *D–G* were identified with corresponding peaks in the *DOS*. A Hartree-Fock calculation for NaCl was subsequently reported by Lipari and Kunz.[7] They disagreed with Fong and Cohen[72] and suggested that one need not postulate the existence of excitons below the band edge. They used the computed DOS to interpret the Cl^- $L_{2,3}$ spectrum in this manner (see Sec. VII).

Recently, Aberg and Dehmer[31] approached the interpretation of these spectra from an atomic point of view. They estimated crystal-field corrections to atomic-transition energies and identified peaks *AB* with mostly $2p \rightarrow 3s$ excitations, peak *E* with mostly $2p \rightarrow 3p$ excitations, and peaks *C* and *D* with mostly $2p \rightarrow 3d$ excitations (at least for NaCl). They also made estimates of the band thresholds, shown in Fig. 5 by the dashed arrows; they did attribute considerable structure to interband transitions, however.

The above brief review shows that contradictory interpretations have been advanced which essentially span the whole range of possibilities. A lot of this controversy can again be resolved unambiguously by making use of XPS and optical-gap data. Very accurate measurements exist for all four compounds. Kowalczyk *et al.*[47] give values for the position of the top of the valence band with respect to the Na^+ $2p$ level; band gaps are listed in Ref. 1.[69] The resulting band thresholds for the Na^+ $L_{2,3}$ spectra are listed in Table III and marked in Fig. 5 by solid arrows. In the same figure we display available theoretical densities-of-states positioned on the energy axis according to the present determination of band thresholds. Examination of Fig. 5 leads to the following discussion:

(a) We first note that, as in the case of the Li^+ *K* spectra considerable structure appears below the band edge and this structure is unequivocably purely excitonic. In addition to the sharp peaks *AB*, the shoulders *S* (identified by Nakai and Sagawa[22] as the band thresholds) and the broad peaks *C* also lie below the band edge. Such complicated structure (the data of Ref. 22 show more fine structure than those of Ref. 70 shown in Fig. 5) is quite uncharacteristic of discrete, broadened δ-function-like excitons and indicates some sort of excitonic density of states.

(b) The binding energy of the *AB* doublet exciton relative to the band edge is about 2–3.5 eV, considerably *larger* than suggested by the analysis of Nakai and Sagawa.[22] We also note that the position

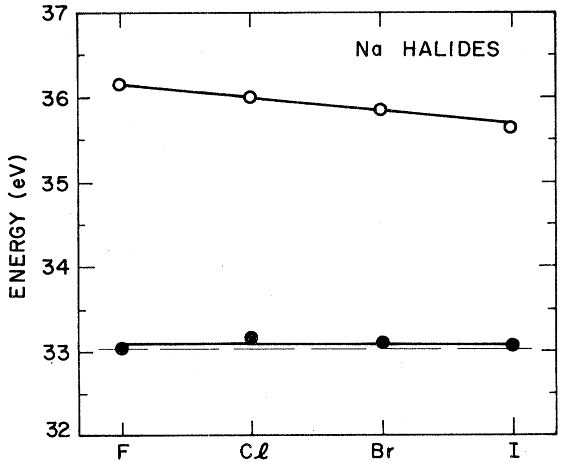

FIG. 6. Positions of the experimental dominant peaks (solid points) in the Na^+ $L_{2,3}$ spectra of the lithium halides are compared with the positions of the band thresholds (open points) determined in this work. The dashed line is the position of the $1s^22s^22p^6 \rightarrow 1s^22s^22p^53s$ in the free Na^+ ion (Ref. 66).

of the *AB* exciton is approximately the same in all four compounds. On the other hand the band edges (solid arrows) shift linearly from the fluoride to the iodide. (Fig. 6)

(c) The rise leading to peak *D* coincides with the onset of band transitions. As the density-of-states calculations show, however, there are not enough states near the edge to account for the height of peak *D*. A similar situation was seen in the Li^+ *K* spectra for peak *C* (Fig. 2). Even though symmetry does not suppress interband transitions near the edge, as it did in the Li^+ *K* spectra, the strength of peak *D* suggests that it is probably due to a metastable exciton superposed on a background of interband transitions. This interpretation is certainly supported by the experiments of Refs. 14 and 23.

(d) We see that there is very little or no correspondence between the densities of states and the observed spectra. In fact most of the density of states appears to lie in a region (37–42 eV) which is depleted of transition strength. Most of the strength seems to have been drawn into the excitonic peaks appearing between 33 and 37 eV.

(e) Comments (a)–(d) above clearly suggest the existence of an extremely strong electron-hole interaction which makes the observed spectrum *almost entirely excitonic*. As in the case of LiF, this interaction seems to mix band states over a range of 9–10 eV and gives rise to a structured excitonic density of states. No identification of exciton peaks with critical points can thus be supported, in contrast to the suggestions of Refs. 22 and 23.

One last comment applies to NaF. As noted by Aberg and Dehmer,[31] the F^- L_1 spectrum overlaps the Na^+ $L_{2,3}$ spectrum and thus particular care should be excercised. By using the XPS data of Kowalczyk *et al.*,[47] we deduce that the F^- 2*s* level lies 1.6 eV higher in energy than the Na^+ 2*p* level. Thus the band threshold for the F^- L_1 spectrum lies 1.6 eV lower than that of the Na^+ $L_{2,3}$. It is shown in Fig. 5 by the short arrow labeled *X*. The F^- L_1 spectrum does not appear to introduce any structure. The reason for this will be discussed in Sec. VI.

V. K^+ SPECTRA OF THE POTASSIUM HALIDES

Potassium, being a larger element than either lithium or sodium, has more core states and thus more x-ray spectra. From among them, the K^+ *K* and *L* spectra lie at high energies, beyond the scope of this study. In the soft-x-ray region, the K^+ M_1 spectra should lie around 38 eV, but to our knowledge, no detailed measurements in that region have been reported.[73] Thus, the interesting spectra are the K^+ $M_{2,3}$ which arise from excitations of electrons in the 3*p* shell of the potassium ion. High resolution data have been published by Saito *et al.*,[20] Blechschmidt *et al.*,[16] and Rubloff *et al.*[17] These are shown in Fig. 7 over the range of energies 15–33 eV. Structure arising from excitations of K^+ 3*p* electrons follows and overlaps structure arising from excitations of valence electrons. The consensus of Refs. 16, 17, and 20 is

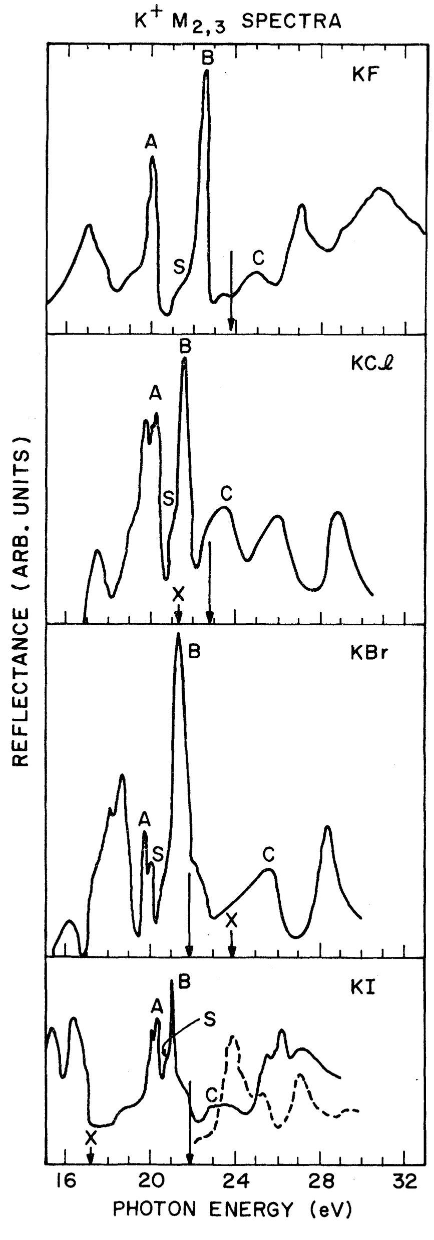

FIG. 7. K^+ $M_{2,3}$ spectra of the potassium halides. Solid curves are experimental (Ref. 16). Dashed curve is theoretical interband spectrum (Ref. 5) positioned on the energy axis according to the present determination of band thresholds (solid arrows). The short arrows labeled × mark the band threshold for the Cl^- M_1 spectrum in the case of KCl, the Br^- N_1 spectrum in the case of KBr, and the I^- O_1 spectrum in the case of KI.

TABLE IV. Dominant experimental peaks *A* and *B* (see Fig. 6) and the predicted band thresholds for excitations from the $K^+ 3p$ shells in the potassium halides. The binding energy of excitation *A* relative to the band edge is also listed. All quantities are in eV.

Substance	Peak *A* (doublet)	Peak *B*	Band threshold (present work)	Binding energy of excition *A*
KF	19.7/20.0	22.1	23.9	4.2
KCl	20.1/20.3	21.5	22.8	2.7
KBr	19.8/20.0	21.3	21.8	2.0
KI	20.1/20.3	21.1	21.9	1.8

that the peaks labeled *A* and *B* are a Γ exciton and an *X* exciton, respectively. The Γ exciton is a doublet (splitting ~0.2 eV) reflecting the spin-orbit splitting of the K^+ $3p$ level. Blechschmidt *et al.*[16] also suggested that the shoulder labeled *S* between the peaks *A* and *B* is the band edge so that the binding energies of the Γ excitons range from 0.5 to 1.3 in the four compounds; the *X* excitons overlap the band continuum and are thus metastable.

Using the XPS data of Kowalczyk *et al.*[47] and optical-gap data[1] we obtain the band thresholds listed in Table IV. These thresholds are indicated in Fig. 6 by the solid arrows. Table IV also lists the energies of peaks *A* and *B*. The net result is that peaks *A* lie below the band edge by 4.0 eV in KF and 2–3 eV for the other compounds. Such binding energies are far larger than those suggested by the analysis of Blechschmidt *et al.*[16] (0.5–1.3 eV). Furthermore, peak *B*, which had been identified as an *X* exciton within the band continuum in Refs. 16, 17, and 20, is now seen to lie below the band edge by about 1 eV. Such binding energies suggest that it might not be appropriate to associate the observed excitons with particular critical points in the energy bands. Instead, the nature of the excitonic peaks labeled *A* can best be understood by noting that the $3p \rightarrow 3s$ transition in the free K^+ ($1s^2 2s^2 2p^6 3s^2 3p^6$) ion gives rise to four peaks at 20.1, 20.2, 20.4, and 20.6 eV.[66] These coincide in energy with the peaks labeled *A* in Fig. 7, which appear to show comparable structure. The halogen neighbors seem to have negligible effect on them. Peaks *B* can be seen to correspond to $3p \rightarrow 3d$ transitions. In the free K^+ ion these transitions give rise to several peaks between 20.3 and 21.3 eV.[66] The shifts to different energies in the various potassium halides is to be attributed to crystal fields.

Density-of-states calculations are not available in the literature except for KI.[5] It is shown as a dashed curve in Fig. 7 positioned at the appropriate point on the energy axis. The agreement between this theoretical interband spectrum and the experimental spectrum is seen to be quite poor. Overall, the conclusions seem to be the same as for the Li^+ and the Na^+ spectra described in the previous spectrum: The hole-electron attraction is very strong; it mixes bands over a wide range of energy and introduces strong and excitonic structure several eV below the band edge; no identification of excitons with critical points in the band continuum can be supported, and the structure above the band edge bears little resemblance with computed interband spectra.

As a final note in this section, we observe that the Cl^- M_1 spectrum overlaps the K^+ $M_{2,3}$ spectrum of KCl, the Br^- N_1 spectrum overlaps the K^+ $M_{2,3}$ spectrum of KBr and the I^- O_1 spectrum overlaps the K^+ $M_{2,3}$ spectrum of KI. The band thresholds for these spectra are determined from the data of 47 and 1 to lie at the positions of the short arrows

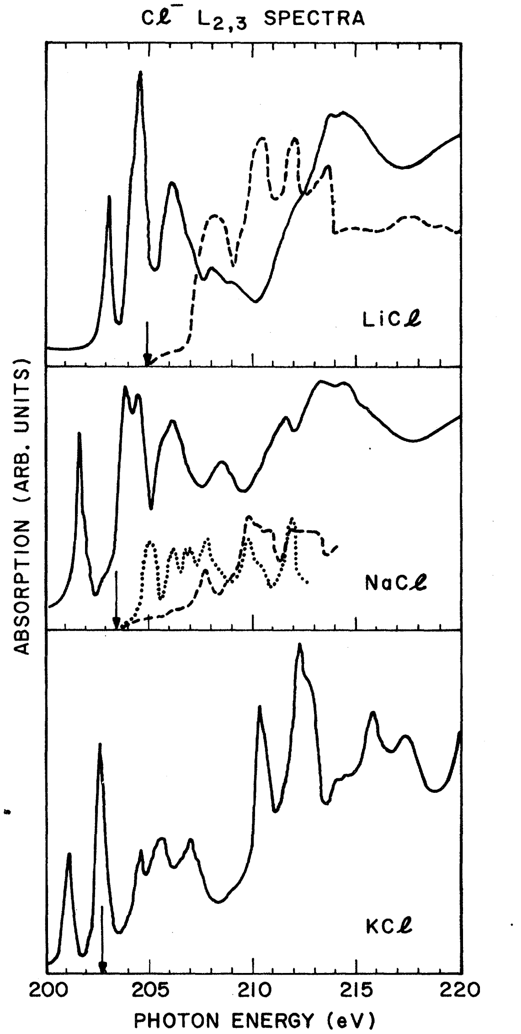

FIG. 8. Cl^- $L_{2,3}$ spectra of alkali chlorides. Solid curves are experimental (Ref. 20). Dotted and dashed curves are theoretical interband spectra (Refs. 67 and 7, respectively) positioned on the energy axis according to the present determination of band thresholds (solid arrows).

labeled × in Fig. 7. No structure is attributable to these spectra. (See discussion in Sec. VI.)

VI. F$^-$ SPECTRA OF ALKALI FLUORIDES

Fluorine is the smallest halogen and has only a 1*s* and a 2*s* core states. The F$^-$ 2*p* states form the valence bands, so that in all fluorides the F$^-$ K and F$^-$ L_1 are the only possible spectra. The K spectra lie outside the realm of soft x rays and we do not discuss them further.

In the case of LiF, the XPS data of Ref. 47 together with optical-gap data place the band threshold for the F$^-$ L_1 spectrum at 38.5 eV. Measurements in that region by Milgram and Givens[74] reveal no structure at all in that region. We note further that the tail with weak bumps seen by Sonntag[64] starts at about 54 eV which is 15.5 eV higher than the F$^-$ L_1 band threshold. It is thus unlikely that transitions from the F$^-$ 2*s* level may contribute to that structure.

In the case of NaF we remarked already in Sec. IV that the band threshold for the F$^-$ L_1 spectrum lies 1.5 eV below the band threshold for the Na$^+$ $L_{2,3}$ spectrum, and that it does not appear to contribute discernible structure. For KF, the band threshold for the F$^-$ L_1 spectrum lies at 33 eV. Energy-loss data by Creuzburg[69] indicate a peak at 31.3 eV and a shoulder with negative slope at 34.3 eV. No positive identification can be made though.

We saw in Sec. V that no structure was attributable to the Cl$^-$ M_1, the Br$^-$ N_1, and the I$^-$ O_1 spectra of potassium halides and this will be seen in the following sections to be a more general trend for L_1, M_1, N_1, and O_1 spectra of the halogen *anions*. Such a lack of oscillator strength in these spectra can be understood as follows[46b]: (a) Transitions to the neighborhood of the bottom of the conduction band are symmetry suppressed since such transitions would be *s* to *s*. (b) Such transitions would involve a jump to the other sublattice since the bottom of the conduction band is mostly made up of alkali virtual orbitals. This makes the transition matrix element smaller. (c) The hole in the *halogen* core shell is screened effectively by the valence electron cloud which also sits on the halogens. Thus hole-electron attraction is not as strong as in the case of holes in the alkali ions (Sec. III–V) and thus not capable of pulling *p*-like states down. (d) Lifetimes of 2*s*, 3*s*, 4*s*, and 5*s* holes are very short due to the presence of the 2*p*, 3*p*, 4*p*, and 5*p* electrons, respectively, at very nearby higher energies; this tends to wash out any structure. This last reason may also account for the fact that no sharp L_1, M_1, and N_1 spectra of the alkali ions have been reported either. (See however, the discussion in Sec. VIII on the Na$^+$ L_1 spectrum of NaBr.)

VII. Cl$^-$ SPECTRA OF THE ALKALI CHLORIDES

Cl$^-$ has 1*s*, 2*s*, 2*p*, and 3*s* core electrons. The 3*p* electrons form the valence bands. From the corresponding spectra, the Cl$^-$ K spectrum is in the region of hard x rays and will not be discussed here; the Cl$^-$ L_1 spectrum gives rise to weak structure in the region of 272–278 eV (Ref. 19); the rules discussed in Sec. VI seem to be followed but a more detailed scan in that region of the spectrum might be worthwhile. The Cl$^-$ M_1 spectra seem to follow the same rules: From XPS (Ref. 47) and optical-gap[1] data we determine the band edges for Cl$^-$ M_1 excitations to lie at 22.0, 21.6, and 21.3 eV for LiCl, NaCl, and KCl, respectively. We already saw that the Cl$^-$ M_1 spectrum in KCl overlaps the K$^+$ $M_{2,3}$ spectrum (Fig. 7) and does not seem to contribute structure. Data on NaCl (Ref. 21) show that, if anything, the absorption coefficient smoothly turns downward at 21.6 eV.

Turning to the Cl$^-$ $L_{2,3}$ spectra, we find that they are both interesting and controversial. They have been measured by a number of groups[18,19,5,24] with very similar results. In Fig. 8 we show the experimental spectra (solid curves) for LiCl, NaCl, and KCl. The Cl$^-$ $L_{2,3}$ spectra of alloys of alkali halides have also been studied experimentally[24] but we will not discuss them here.

Sagawa *et al.*[18] discussed the Cl$^-$ $L_{2,3}$ spectra of KCl and NaCl. By using a variety of x-ray emission experimental data they constructed energy-level diagrams for these materials and thus estimated the band thresholds to be at 201.9 eV for KCl and 202.9 eV for NaCl. They identified the first peak as an exciton and suggested that the second peak is a metastable exciton. They also suggested that the rise at about 209 eV is a replica of the lower structure due to two-electron excitations. The same interpretation was maintained by Iguchi *et al.*[19] They went further to identify the first peak as an exciton deriving from the Γ_1 minimum (binding energy ~0.7–0.9 eV) and the second peak as a metastable exciton deriving from a *d*-like minimum at X. Subsequently, Brown *et al.*[5] measured these and other spectra and proposed an alternative interpretation: They suggested that exciton effects are small and identified all the structure, including the first peak, with interband transitions. The interpretation of structure above 209 eV as due to two-electron excitations was retained however. In two subsequent papers, Kunz[4] and Lipari and Kunz[7] reported Hartree-Fock energy-band calculations for LiCl and NaCl in which they also computed the joint densities of states for transitions from the Cl$^-$ 2*p* core bands to the conduction bands. By freely positioning these interband spectra on the energy axis they obtained a reasonably good one-to-one correspondence between theoretical and ex-

TABLE V. First two experimental peaks and the predicted band thresholds from the Cl$^-$ $2p$ shells in the alkali chlorides. All quantities are in eV.

			Band thresholds		
Substance	First expt. peak	Second expt. peak	Present work	Ref. 18	Ref. 4
LiCl	203.0	204.5	204.9[a]	···	200.0
NaCl	201.6	203.8	203.3	202.9	197.8
KCl	201.2	202.6	202.6	201.9	···
RbCl	200.3[b]	201.7[b]	201.6[b]	···	···

[a] From the extrapolation of Fig. 9.

[b] From Ref. 44.

perimental peaks and valleys. No excitons were thus needed to account for the observed spectra. Recently, on the other hand, Watanabe[24] reported and discussed the Cl$^-$ $L_{2,3}$ spectra of alloys of sodium clorides and offered an analysis in terms of excitons deriving from particular critical points in the conduction bands.

The controversy can again be resolved by using XPS data. Such data are available for NaCl and KCl in Ref. 75. By using optical-gap data from Ref. 1, the Cl$^-L_{2,3}$ band thresholds for these two materials are deduced to lie at 203.3 (Ref. 33) and 202.6 eV, respectively (Table V; the value listed for LiCl is from an extrapolation, as shown in Fig. 9.). These thresholds are marked by solid arrows in Fig. 8. These numbers may be uncertain by as much as 1 eV but we believe they demonstrate conclusively that at least the first peak in the spectra is a pure exciton. That band structure alone cannot explain the observed spectrum is further demonstrated in Fig. 10: The dotted curve is the theoretical interband spectrum as given in Ref. 7, positioned on the energy axis for best alignment of peaks. The one-to-one correspondence is indeed very good except that such a positioning of the interband spectrum implies a band threshold below 198 eV, about 5.5 eV lower than the threshold determined here from independent experiments (solid arrow). Figure 10 also shows that when the interband spectrum is positioned at the appropriate point on the energy axis, very little similarity with the experimental spectrum remains.

Our conclusions about the Cl$^-$ $L_{2,3}$ spectra are thus in support of the interpretations advanced by the authors of Refs. 18 and 19. Our determination of band thresholds, however, suggests binding energies of the lowest exciton which are slightly larger (1 – 2 eV).[76] Such binding energies are, nevertheless, considerably smaller than those obtained from our analysis of cation spectra in Secs. III-V. In that case we noted that the Coulomb potential of a hole

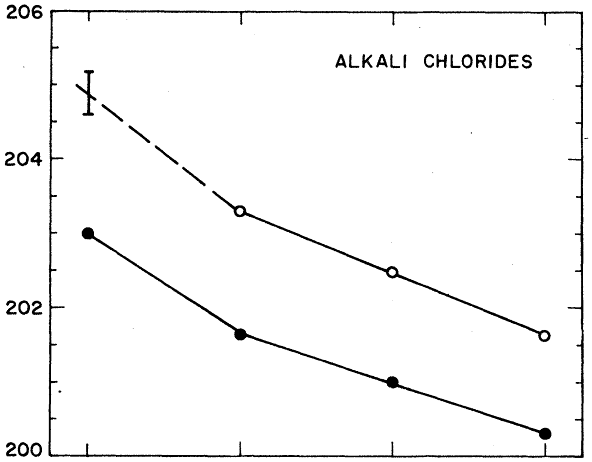

FIG. 9. Positions of the first peaks in the experimental Cl$^-$ $L_{2,3}$ spectra of alkali chlorides (solid points) and the positions of the band thresholds determined here (open points). The error bar is an extrapolated prediction for LiCl.

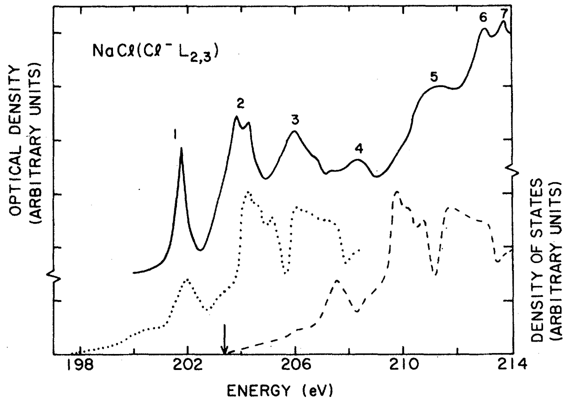

FIG. 10. Cl$^-L_{2,3}$ spectrum of NaCl. Solid curve is experimental (Ref. 19). Dotted curve is theory of Ref. 7. Dashed curve is theoretical interband spectrum of Ref. 7 (same as dotted curve) but positioned on the energy axis according to interband threshold (vertical arrow) determined here.

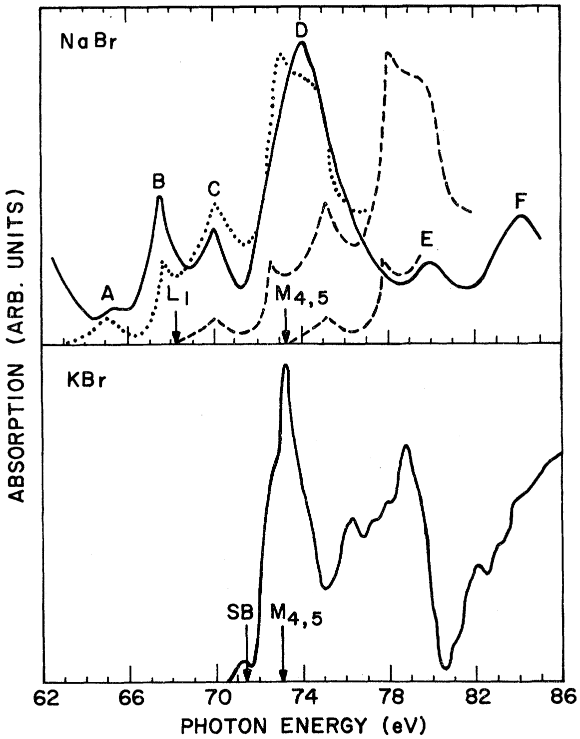

FIG. 11. Br⁻ $M_{4,5}$ spectra of NaBr and KBr. Solid curves are experimental (Refs. 7 and 44). Dotted curve is theoretical spectrum of Ref. 7 for Na⁺ L_1 and Br⁻ $M_{4,5}$ which overlap. Dashed line is same spectrum positioned 5.3 eV higher in energy according to the present determination of band thresholds. In KBr, the solid arrow marks the band threshold for $M_{4,5}$ spectrum determined here. The arrow marked S is band threshold determined in Ref. 44.

in a cation core shell is not screened effectively by the valence electrons which lie mostly on the anions. In the present case of anion excitations, the opposite happens: the hole is in the anion and the valence electron cloud screens the hole-electron attractive potential more effectively.

Because of weaker electron-hole interaction, it is possible that x-ray spectra of anion core shells do contain considerable structure arising from transitions to the conduction bands. Such an interpretation has been proposed by Scheifley and Brown[44] for RbCl. In general, however, reliable density-of-states calculations are not available. In the case of NaCl, three band-structure calculations[7,72,77] do not agree with each other even qualitatively. Two densities of states exist and are shown in Fig. 8. The low density of states near the band edge, characteristic of all alkali halides, suggests that the second peak in each spectrum is also an exciton in accordance with the interpretations of Refs. 19 and 24. In fact, Fig. 8 reveals that electron-hole interaction probably mixes band states over a range of 3–4 eV. More detailed analysis of the remainder of each spectrum cannot be conclusive at this time.

VIII. Br⁻ SPECTRA OF ALKALI BROMIDES

From the many core spectra of the bromine ion in the bromides, only the Br⁻ N_1 and Br⁻ $M_{4,5}$ lie in the region of soft x-rays of interest to the present work. As in the cases of the F⁻ L_1 spectra in the fluorides (Sec. VI) and the Cl⁻ M_1 spectra in the chlorides (Sec. VII), the Br⁻ N_1 spectra are not observed in the bromides. From XPS (Ref. 47) and optical-gap[1] data for NaBr and KBr we deduce band thresholds for the N_1 spectra to lie at 19.9 and 23.6 eV, respectively. No structure is seen in that region for NaBr, whereas for KBr the N_1 spectrum would overlap the sharp K⁺ $M_{2,3}$ spectrum discussed in Sec. V (Fig. 7). No structure is attributed to it.

The Br⁻ $M_{2,3}$ spectra are very sharp, however, and have been considered in the literature. Brown *et al.*[5] reported the Br⁻ $M_{2,3}$ spectrum of KBr (solid curve in Fig. 11) and interpreted it in terms of transitions to the conduction bands. Kunz and Lipari[8] later reported a Hartree-Fock energy-band calculation for NaBr. They noticed that excitations from the Na⁺ $2s$ and the Br⁻ $3p$ core levels overlap on the energy axis and thus computed a joint density of states for transitions from both levels. By freely positioning this curve on the energy axis they were able to account for all the observed structure (unpublished data of Scheifley and Brown quoted in Ref. 8) without need to postulate the existence of excitons (dotted curve in Fig. 11). Scheifley and Brown,[44] on the other hand, considered the KBr spectrum in more detail and combined XPS and optical-gap data to determine the threshold for interband transitions from the Br⁻ $3p$ level. (This is marked by the arrow labeled *SB* in Fig. 11.) They found that a weak excitonic bump appears below this band edge and made a detailed analysis of the remainder of the spectrum in terms of both metastable excitons superposed on the continuum and band states.

From the XPS data of Ref. 47 and optical-gap data[1] we determined the thresholds marked by solid arrows in Fig. 11. For NaBr we find that the Na⁺ L_1 band threshold lies 5.3 eV above the band threshold implicitly predicted by the theory of Ref. 8. Since this discrepancy is far larger than the uncertainty in the present determination of band thresholds, we conclude that band transitions alone cannot explain the observed spectrum. This is illustrated further in Fig. 11 where the theoretical curve of Ref. 8 is positioned at the appropriate point on the energy axis (shown as dashed curve). Some correspondence between peaks and valleys is still

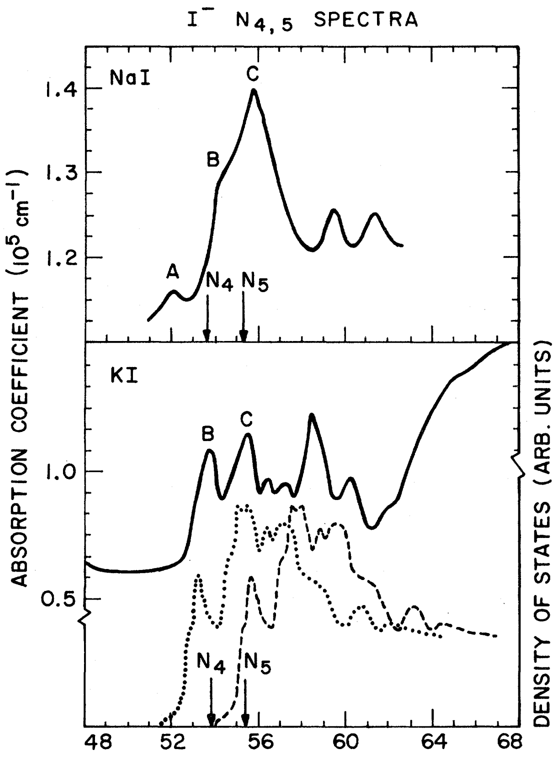

FIG. 12. I⁻ $N_{4,5}$ spectra of NaI and KI. Solid curves are experimental (Refs. 5 and 78). Dotted curve is theoretical spectrum of Ref. 5. Dashed curve is same theoretical spectrum positioned according to present determination of band thresholds (solid arrows).

maintained though.

We proceed now to a more detailed interpretation of the observed spectrum of NaBr. Peaks labeled *A* and *B* in Fig. 11 are most interesting. They definitely cannot be due to transitions from the Br⁻ 3*d* core levels. The band threshold (solid arrow labeled $M_{4,5}$ in Fig. 11) lies much higher in energies and transitions to it are symmetry suppressed. Any excitons of the Br⁻ $M_{2,3}$ spectrum would have to pull down *p*-like states from higher energies. However electron-hole interaction is not strong enough to bring them all the way down to where peaks *A* and *B* are; this fact is established by the KBr spectrum (Fig. 11) in which one weak excitonic peak appears with very small binding energy relative to the band edge. We therefore conclude that peaks *A* and *B* are solely associated with transitions from the Na⁺ 2*s* core levels. This result is particularly interesting because this structure is a rare case in which an L_1 spectrum is seen to give rise to sharp structure.[46(b)]

In view of the L_1 band threshold (arrow labeled L_1 in Fig. 11), the conclusion is that peaks *A* and *B* are excitons. The binding energies relative to the band edge are 3.0 and 0.8 eV, respectively. As in the case of the Li⁺ *K* spectra discussed in Sec. III, these excitons cannot be associated with the Γ_1 band minimum because of symmetry requirements. The excitons are instead formed from *p*-like states at higher energies. A look at the conduction band density of states of Ref. 8 reveals that the presence of excitons 3.0 eV below the band edge implies that electron-hole interaction *mixes* energy bands over a range of about 8 eV. This is in agreement with the conclusion reached in Sec. IV in connection with the Na⁺ $L_{2,3}$ spectra of the sodium halides.

Peak *C* is partly the weak exciton of the Br⁻ $M_{4,5}$ spectrum, analogous to the one seen in KBr, and partly an exciton or band transition of the L_1 spectrum. The remaining structure is a mixture of many things which cannot easily be untangled. The influence of the L_1 spectrum or the $M_{3,4}$ spectrum is clear, however, from the many dissimilarities in the NaBr and KBr spectra. We might also suggest from the general trends established thus far, that peak *D* has strong excitonic contributions.

Detailed analysis of the KBr spectrum (and also RbBr) has been given by Scheifley and Brown.[44] Our result for the interband threshold simply confirms their assignment of both the weak peak and the first prominent peak as excitons.

IX. I⁻ SPECTRA OF ALKALI IODIDES

The core spectra of the iodine ion in the iodides have not been studied extensively in the literature. We have been able to find spectra for NaI, KI, and CsI in the range 50–170 eV reported by Fujita, Gähwiller, and Brown.[78] The dominant feature of these spectra is a broad resonance caused by *d*- to *f*-like transitions. This is understood in terms of the $l(l+1)/r^2$ potential barrier present in an atomic-like Hamiltonian.[79,28] The fine structure in the range 50–65 eV is of more direct interest here and we concentrate on that. This region of the spectrum for KI was reported and discussed in detail by Brown *et al.*[5]

In Fig. 12 we show the experimental spectra for NaI and KI in the range 50–68 eV (Refs. 5 and 78) (solid curves). In Ref. 78 no clear-cut conclusion was given about the nature of the transitions giving rise to the observed structure other than the identification of the initial states as I⁻ 4*d* and of the final states as *p*-like in character, at least associated with the conduction bands. In Ref. 5, the results of an orthogonalized-plane-wave band calculation were employed to construct a joint density of states for transitions from the I⁻ 4*d* states to the conduction bands. This theoretical spectrum was freely aligned on the energy axis. Positioned[5] as shown by the dotted line in Fig. 12 it was found to account for all the observed structure.

TABLE VI. Summary of all the interband thresholds discussed in this paper. Spectroscopic notation (see Table I) is used for the occupied shells. The "shells" designated by "opt" correspond to the top of the highest valence band, so that the accompanying entries are the optical band gaps. All quantities are in eV.

Cation	Shell \ Anion	F	Cl	Br	I
Li	K	64.4	62.3	61.8	61.6
Na	$L_{2,3}$	36.3	36.0	35.7	35.2
	L_1	69.0	68.8	68.5	67.9
K	$M_{2,3}$	23.9	22.8	21.8	21.9
	M_1	38.7	38.8	37.8	37.9
Anion	**Shell \ Cation**	**Li**	**Na**	**K**	
F	$L_{2,3}$ (opt)	13.6	11.5	10.9	
	L_1	38.5	34.7	33.1	
Cl	$M_{2,3}$ (opt)	9.4	9.0	8.7	
	M_1	22.0	21.6	21.3	
	$L_{2,3}$	204.9	203.3	202.6	
Br	$N_{2,3}$ (opt)	7.6	7.5	7.6	
	N_1		20.3	23.8	
	$M_{4,5}$		73.7	73.3	
I	$O_{2,3}$ (opt)	6.1	5.9	6.3	
	O_1		17.1	17.1	
	N_5		53.6	53.8	
	N_4		55.3	55.4	

With XPS data from Ref. 47 and optical-gap data[1] the band thresholds for the N_4 and N_5 spectra were determined as shown by the vertical arrows in Fig. 12. The dashed curve in the case of KI is the theoretical interband spectrum given in Ref. 5 positioned according to the present determination of thresholds. We see once more that band structure alone cannot account for all the observed structure and that excitons dominate the onset of absorption from a given shell. We identify peaks B and C as excitons for which the hole is in the $I^- \, 4d_{5/2}$ and $I^- \, 4d_{3/2}$ core levels, respectively, and the electron is in a localized wavefunction composed of p-like Bloch functions. Note that binding energies relative to the band edge are small in accordance with the observations made in the previous sections about transitions from d core levels. The remaining structure may be partly due to transitions to band states as the comparison between experiment and the dashed curve in Fig. 12 indicates.

X. SUMMARY AND CONCLUSIONS

We have presented a systematic analysis of the observed soft-x-ray absorption spectra of twelve alkali halides. The crucial step in the interpretation of each spectrum was to determine the threshold for transitions to the conduction bands. In most cases this was done by using the recent accurate XPS data of Kowalczyk, McFeely, Ley, Pollak, and Shirley[47] and optical-gap data from the literature.[1] (All the band thresholds discussed in this paper are summarized in Table VI.) Once the band threshold in determined in this fashion, any structure appearing at lower energies was unambiguously identified as pure excitons, namely bound states of the electron and hole. The structure at higher energies might be related to the density of states of the conduction bands, but careful checks were needed each time. The main conclusions of this study were as follows:

(a) For spectra arising from excitations of the core electrons of the *alkali cation*, the electron-hole interaction is so overwhelmingly large that the observed spectra are essentially entirely excitonic in nature. Little or no structure can be associated with transitions to band states. If the electron-hole interaction is thought of as a perturbation to the energy-band picture, the net result is that this interaction *mixes* band states over a range of as much as a rydberg. Thus binding energies are large and no association of the observed excitonic structure with critical points in the conduction-band continuum can be supported. The extraordinary magnitude of the electron-hole interaction in these cases can be understood by noting that the Coulomb potential of a hole in the alkali cation is essentially not screened at all due to the fact that the valence electron cloud is localized mostly on the halogen anions.

(b) For spectra arising from excitations of the core electrons of the *halogen anion*, the electron-hole interaction is weaker due to the fact that the Coulomb potential of the hole in the halogen is effectively screened by the valence electrons, which also reside on the halogen sublattice. Excitons appear below band edges in all cases and binding energies are still large (1–3 eV), larger than obtained from previous analyses. In the case of anion excitations,

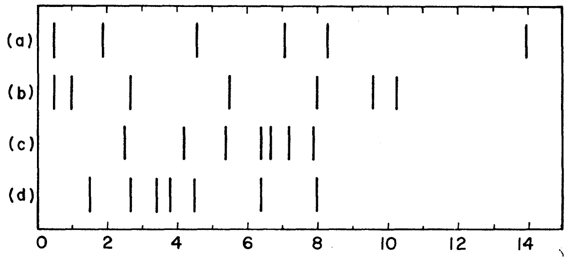

FIG. 13. Positions of peaks in (a) experimental Na^+ $L_{2,3}$ spectrum of NaCl, (b) experimental Cl^- $L_{2,3}$ spectrum of NaCl, (c) density of conduction-band states of NaCl from Ref. 7, and (d) density of conduction-band states of NaCl from Ref. 72. The zero of energy is the respective band edge.

transitions to conduction bands may in fact give rise to some structure above the interband threshold; their identification is difficult partly due to the lack of accurate density-of-states calculations.

(c) Conclusions (a) and (b) above are in direct contradiction to published theoretical interpretations in terms of transitions to conduction-band states alone, excluding the possibility that excitons are formed below the band edge. They are in partial agreement with other published interpretations which were in terms of excitons associated with critical points in the conduction bands and having small binding energies.

(d) The conclusions discussed above have a direct bearing on the interpretations of soft-x-ray absorption spectra in other materials such as alkaline-earth compounds, etc. In particular, the interpretations proposed for the x-ray spectra of rare-gas solids[9,10] in terms of band transitions ought to be reevaluated. XPS data are not available for those solids, but theoretical studies can show that those spectra are also mostly excitonic as well.[80] This would be in agreement with the suggestions of Haensel *et al.*[15] and in accordance with the observation that there is a very close similarity between the spectra of the gas and solid phases of these substances[15,81] A call for accurate XPS data for these and other solids is clearly in order.

(e) Finally, a word about the band versus atomic point of view is in order. If transitions to the conduction bands played an important role, at least above the band threshold, there should be a reasonable one-to-one correspondence between observed structures in different spectra of the same substance and between those and theoretical calculations of the density of states of the conduction bands. The almost extreme opposite is, however, seen to be the case. This is clearly illustrated in Fig. 13 where the vertical bars indicate the positions of the peaks above the band threshold for various spectra in NaCl. The utter disagreement between the two experimental spectra (Na^+, $L_{2,3}$) and Cl^- $L_{2,3}$) is in agreement with the present conclusions about the importance of electron-hole effects and their different strengths for excitations of the two sublattices. It is also conclusive evidence that structure in the density of states of the conduction bands *cannot* be expected to correlate directly with structure in observed spectra. The disagreement between the two theoretical sets simply reflects the state of the art of theoretical calculations.

The atomic point of view on the other hand has not done considerably better. Soft-x-ray spectra of solids can perhaps be *understood* by comparison with atomic spectra and shifts of peaks may be *accounted for* in terms of crystal fields, but this is a far cry from a theory which can *predict* the clearly much richer structure present in solid-state spectra.

ACKNOWLEDGMENTS

The author would like to express sincere thanks for valuable discussions to Dr. F. C. Brown, Dr. W. A. Harrison, Dr. A. B. Kunz, Dr. D. J. Mickish, and Dr. T. C. Collins and also thank Dr. Roger A. Pollak for supplying a preprint of Ref. 47.

Note added in proof. Dr. E. O. Kane has brought to my attention a series of papers by Jossem and Parratt, published in the 1950's, in which they interpreted some x-ray spectra, particularly of KCl, in terms of excitons. The review paper by Parratt [L. G. Parratt, Rev. Mod. Phys. 31, 616 (1959); see other references therein] contains a lot of the physics of x-ray excitations (it employs a jargon slightly different from that currently in use). Unfortunately, these papers were all but ignored in the papers of the last decade referred to in this paper. I am thankful to Dr. Kane.

The Li^+ K spectra of LiF, LiCl, and LiBr have been interpreted as mostly excitronic in nature independently by M. Elango, A. Maiste, and A. Saar, reported in Ref. 44(c). Other papers relevant to the present work were also presented at that conference.

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[*] Work supported by the National Science Foundation Grant No. GH-39811.

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another way of seeing that electron-hole attraction will inevitably scramble the interband spectrum. (See also Ref. 65 where electron-hole interaction is applied to a model interband spectrum resembling that calculated in Refs. 11 and 12.) As noted in Ref. 12, the agreement with experiment produced by the rigid shift must be accidental. The rigid-shift procedure has also been criticized in Ref. 34.

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