

not. We have verified this experimentally (Ref. 9) in several samples of pure zinc and it is also consistent with our theoretical analysis. Dislocations increase  $X$  through "dephasing" of the electron wave function [A. B. Pippard, Proc. Roy. Soc., Ser. A 287, 165

(1965)] while  $H_0$  only changes with direct scattering. We thus compare  $H_0$  with the *change* in  $X$  due to the solute.

<sup>13</sup>R. G. Chambers, Proc. Phys. Soc., London 88, 701 (1966).

## New Interpretation of the Soft-X-Ray Absorption Spectra of Several Alkali Halides\*

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(Received 23 April 1974)

Theoretical calculations have thus far been used to interpret the soft-x-ray spectra of several alkali halides in terms of band structures alone, excluding the possibility that core excitons are formed below the band edge. By independently determining the threshold for band transitions from x-ray photoemission spectroscopy and optical-gap data, we conclude that these spectra are in fact almost entirely excitonic in nature.

Absorption spectra are well known to contain valuable information about the excited states of a crystal. X-ray spectra are particularly convenient for this purpose since electrons are excited from core states which are flat and thus introduce no structure. By assuming constant transition matrix elements over the range of interest, one expects the observed structure to correlate directly with structure in the density of states (DOS) of the conduction bands. Because of the difficulty of computing absolute transition energies, a common practice has been to freely move the DOS on the energy axis until a reasonable correspondence between theoretical and experimental peaks and valleys is obtained. This approach has led to the interpretation of the soft-x-ray spectra of various alkali halides<sup>1-3</sup> in terms of band structures alone, dismissing the possibility that excitons are formed below the band edge. More recent theoretical work<sup>4,5</sup> has arrived at similar conclusions by using calculated transition energies instead of freely aligning spectra.

Such an interpretation of soft-x-ray spectra may be tested directly by making use of additional experimental information from x-ray photoemission spectroscopy (XPS) and optical-gap data in order to pin down the position of the conduction-band edge with respect to the core levels.<sup>6</sup> In this Letter we will use this powerful technique to show that several soft-x-ray spectra must be reinterpreted in a way that contradicts most of

the previous work on the subject.

We first concentrate on the lithium halides LiF, LiCl, LiBr, and LiI. Haensel, Kunz, and Sonntag<sup>7</sup> first measured their  $\text{Li}^+ K$  spectra (Fig. 1) and suggested that the prominent peak in each spectrum at about 60–62 eV is probably an exciton while the remaining structure may be transitions to  $p$ -like band states. No band edges were identified.

The same spectra were measured and interpreted shortly thereafter by Brown *et al.*<sup>1</sup> These authors, and subsequently Kunz and Lipari,<sup>2</sup> performed Hartree-Fock band calculations for LiCl and LiBr and computed the DOS of the conduction bands. By freely shifting the DOS on the energy axis, they aligned theoretical and experimental peaks and valleys and concluded that the observed spectra are entirely due to transitions to conduction-band states with no excitons being formed. By analogy with LiCl and LiBr, Kunz, Devreese, and Collins<sup>8</sup> assumed that the band threshold for LiF lies at 60.5 eV and proceeded to identify a two-electron excitation (core-to-band plus a valence exciton) at about 70 eV. More recently, band calculations for LiF were reported by Menzel *et al.*<sup>4</sup> who used Slater exchange and by Kunz, Mickish, and Collins<sup>5</sup> who used nonlocal Fock exchange. In both cases, the observed structure was identified with similar structure in the computed interband spectra.<sup>9</sup> Both Refs. 4 and 5 predicted a long weak tail to the left of the main

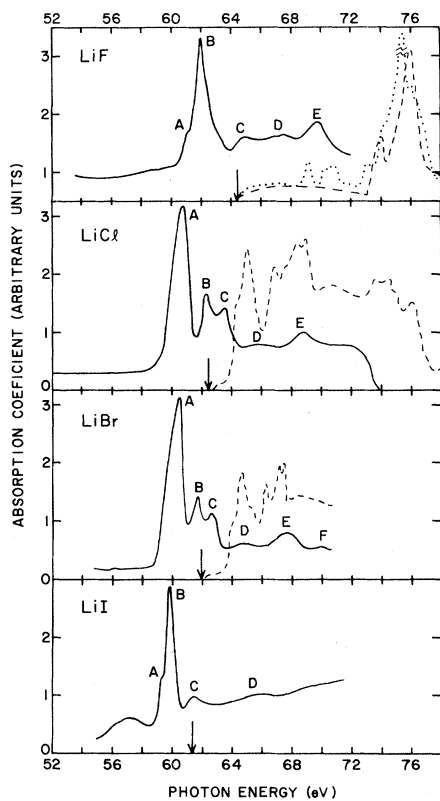


FIG. 1.  $\text{Li}^+$  K spectra of the lithium halides. Solid curves are experimental (Ref. 7; low-energy tail of LiF spectrum from Ref. 10). Dotted curve (from Ref. 4) and dashed curves (from Ref. 5 for LiF, Refs. 1 and 2 for LiCl, LiBr) are theoretical interband spectra positioned on the energy axis according to interband thresholds determined here (vertical arrows).

peak, corresponding to the  $\Gamma_1$  band minimum. Subsequently, Sonntag<sup>10</sup> detected such a weak tail, in apparent support of the band-theoretic predictions. He suggested, nevertheless, that this may not be conclusive evidence for interpreting the spectrum in terms of a one-electron-band model alone.

We now wish to show in a simple way that the prominent peak appearing near the onset of absorption in the lithium halides is purely excitonic and not an interband transition. This is done by combining XPS and optical-gap data. The former measure the binding energies of electrons in the valence bands and in the core levels. The relative difference between a given core level and the top of the valence band is then accurately determined.<sup>11,12</sup> By adding this value to the optical band gap (energy difference between the valence-band top and the conduction-band bottom), the position of the conduction-band edge is unambigu-

TABLE I. Various energies in the Li halides.  $E_v$  is the top of the valence band relative to the  $\text{Li}^+$  1s core level.  $E_{vc}$  is the optical band gap.  $E_c = E_v + E_{vc}$  is the bottom of the conduction band relative to the  $\text{Li}^+$  1s level. "Peak" denotes the position of the dominant peak in the observed spectrum and  $E_B$  is the energy separation between the peak and  $E_c$  (excitonic binding energy). All energies are in eV.

Substance	$E_v$	$E_{vc}$	$E_c$	Peak	$E_B$
LiF	50.8 <sup>a</sup>	13.6 <sup>b</sup>	64.4	61.9 <sup>c</sup>	2.5
LiCl	52.9 <sup>d</sup>	9.4 <sup>b</sup>	62.3	60.8 <sup>c</sup>	1.5
LiBr	54.2 <sup>e</sup>	7.6 <sup>b</sup>	61.8	60.4 <sup>c</sup>	1.4
LiI	55.5 <sup>e</sup>	6.1 <sup>b</sup>	61.6	59.8 <sup>c</sup>	1.8

<sup>a</sup>Ref. 11.

<sup>b</sup>Ref. 15.

<sup>c</sup>Ref. 7.

<sup>d</sup>Ref. 14.

<sup>e</sup>Ref. 17.

ously established.<sup>13</sup> Any structure in the observed spectrum appearing below this threshold can then be conclusively identified as *purely excitonic*.

Accurate XPS data exist for LiF<sup>11</sup> and LiCl.<sup>14</sup> By combining these with optical-gap data, the band thresholds shown in Fig. 1 by vertical arrows are obtained with an accuracy of about 0.5 eV. All the relevant quantities are listed in Table I. The dominant peak is seen to lie 1.5–2.5 eV below the arrow in each case, which clearly demonstrates that it is purely excitonic, contrary to previous band-theoretic interpretations.<sup>1,2,4,5</sup> The binding energy relative to the band edge is not atypical for insulators. However, in view of the fact that the bottom of the conduction band is  $\Gamma_1$ , we must exclude the possibility that the observed exciton derives from that critical point in an effective-mass picture. This is because such an exciton would be *s* to *s* and hence dipole forbidden. Clearly, the observed exciton must derive from higher conduction-band states which are *p*-like in character. In the case of LiF, the computed DOS<sup>4,5</sup> shows that most states lie 10–13 eV above the band edge. This indicates an unusually strong electron-hole interaction which mixes band states over a range of a rydberg. It is in agreement with the strength of electron-hole attraction estimated by Kunz *et al.*<sup>5</sup> ( $\sim 10$  eV) from free-ion calculations. The strength of this interaction in the crystal is not disturbing if we recall that the valence electrons in these ionic crystals are almost entirely on the halogen ions; thus the Coulomb potential of a hole in a core shell of the alkali ion is essentially not screened at all and at-

tracts and binds the electron very strongly. The observation that the  $1s^2 - 1s2p$  transition in the free  $\text{Li}^+$  ion is at 61.3 eV, extremely close to the prominent peaks in the spectra of all the Li halides, lends support to these arguments.

In Fig. 1 we also show the theoretical interband spectra positioned according to the present determination of band thresholds. We observe that there is little or no correspondence between the theoretical interband spectra and experiment. From the positions of the arrows one may identify the upturn leading to peaks C as coinciding with the onset of band transitions. However, such transitions near the band edge are suppressed by symmetry and one must allow for a strong exciton contribution. In short, one may conclude that the observed spectra are almost entirely excitonic in nature.<sup>16</sup> The strong electron-hole interaction simply draws the oscillator strength into an excitonic DOS which accidentally resembles the DOS of Bloch-type conduction-band states.

XPS data for LiBr and LiI are not available. Nevertheless, definite patterns among the binding energies of the Li and Na halides allowed us to estimate by interpolation the corresponding quantities in LiBr and LiI as well.<sup>17</sup> Adding the corresponding band gaps,<sup>15</sup> the band thresholds shown by the arrows in Fig. 1 were obtained. Considerable uncertainties in these numbers do exist, but the similarity of the four spectra and the analogy with the free- $\text{Li}^+$ -ion transition suggests that our conclusions for LiF and LiCl apply to LiBr and LiI as well.

We have seen how by independently pinning down the thresholds for band transitions we were led to revise the interpretation of the soft-x-ray spectra of the Li halides. We have done the same for other alkali halides and results will be published elsewhere.<sup>18</sup> Here we give one more illustration to further our conclusions. We consider the  $\text{Cl}^- L_{2,3}$  spectrum of NaCl reported by Brown *et al.*<sup>15</sup> (Fig. 2, solid line). These authors suggested an interpretation of the first four observed peaks in terms of transitions to critical points in the conduction bands arguing that no significant exciton effects are expected. They also suggested that peaks 5, 6, and 7 might be replicas of 1, 2, and 3, caused by two-electron excitations. Lipari and Kunz<sup>3</sup> subsequently supported this interpretation. They performed a Hartree-Fock band calculation and freely aligned the computed interband spectrum so as to match its first peak with peak 1 of experiment. This is shown in Fig. 2 by the dotted curve. We note that such an

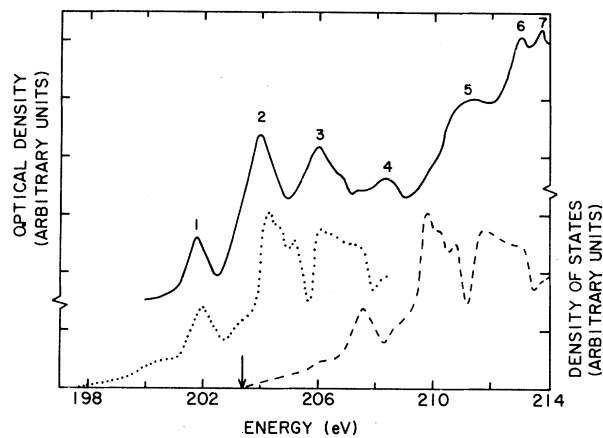


FIG. 2.  $\text{Cl}^- L_{2,3}$  spectrum of NaCl. Solid curve is experimental (Ref. 15). Dotted curve is theory of Ref. 3. Dashed curve is theoretical interband spectrum of Ref. 3 (same as dotted curve) but positioned on the energy axis according to interband threshold (vertical arrow) determined independently. See text.

interpretation would imply a threshold for band transitions below 198 eV. XPS plus optical-gap data, however, place this threshold more than 5 eV higher, at 203.3 eV.<sup>19</sup> The uncertainty in this number is not more than 0.5 eV, which allows us unambiguously to assign the first experimental peak to an exciton below the band edge, with a binding energy of about 1.5 eV. In view of the very low density of states near the band edge, peak 2 is to be identified as an exciton which is at worst metastable, possibly being degenerate with band states. The higher peaks seem to bear a similarity to the band densities, but no definite identification is possible at present. Overall, the electron-hole interaction appears to be weaker in this case as a result of the fact that the hole is in the halogen core and its Coulomb potential is screened by the valence electrons quite effectively.

We conclude that exciton effects are very pronounced near threshold in the soft-x-ray spectra of alkali halides and that band structure alone cannot be used to interpret the observed structure. This is in agreement with interpretations that have been proposed for other soft-x-ray spectra of alkali halides.<sup>20</sup> We conclude further that any attempt to correlate observed spectra with conduction-band DOS must be accompanied by an accurate determination of the threshold energy for band transitions.

We would like to thank Dr. W. A. Harrison, Dr. A. B. Kunz, Dr. D. J. Mickish, Dr. R. M. Martin,

and Dr. P. N. Sen for valuable discussions.

\*Work supported in part by the National Science Foundation through Grant No. GH-39811.

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<sup>6</sup>W. Scheifley, thesis, University of Illinois, 1973 (unpublished).

<sup>7</sup>R. Haensel, C. Kunz, and B. Sonntag, Phys. Rev. Lett. 20, 262 (1968).

<sup>8</sup>A. B. Kunz, J. T. Devreese, and T. C. Collins, J. Phys. C: Proc. Phys. Soc., London 5, 3259 (1972).

<sup>9</sup>In Ref. 4, a straight energy-band calculation yielded an interband spectrum with a peak at 64 eV, which was identified with the prominent peak at 62 eV in the observed spectrum. In Ref. 5, the Hartree-Fock band calculation yielded an interband spectrum with a prominent peak at 85 eV. The authors argued that the experimental peak is not due to excitons below the band edge and thus identified it with the 85-eV peak in the theoretical spectrum. They then included effects beyond band theory, including electron-hole interactions. They argued that these effects shift both bands and excitons rigidly and estimated a net shift of 20 eV for the calculated interband spectrum. The agreement with

the observed spectrum is then reasonable, but the authors suggest that, because of the nature of the approximations, this agreement must be considered accidental.

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<sup>13</sup>The validity of this approach is based on a general theorem that energy bands beyond the Hartree-Fock approximation (i.e., after all correlation and relaxation corrections are included, except for electron-hole attraction) are still "rigid." Electron-hole interactions may introduce additional localized states (excitons), but do not move the band continua. A proof is given in S. T. Pantelides, D. J. Mickish, and A. B. Kunz, Phys. Rev. B (to be published).

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<sup>15</sup>F. C. Brown *et al.*, Phys. Rev. B 2, 2126 (1970).

<sup>16</sup>The tail observed in Ref. 10 in LiF and similar tails in the other compounds may be attributed to "forbidden" s excitons, though other possibilities exist, such as background due to transitions from other shells, etc.

<sup>17</sup>Details will be given elsewhere (S. T. Pantelides, to be published). The values used here are given in Table I.

<sup>18</sup>Pantelides, Ref. 17.

<sup>19</sup>The value of Ref. 12 was corrected by using the more recent optical-gap value of 8.97 eV [D. M. Roessler and W. C. Walker, Phys. Rev. 166, 599 (1968)].

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