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Photoemission studies of LiCl, NaCl, and KCl[†]

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Photoemission measurements were made on evaporated films of LiCl, NaCl, and KCl at photon energies 12–23 eV. The observed energy distributions of photoemitted electrons show structure that can be identified as high density of states in the valence and conduction bands. The effective widths of the valence bands of LiCl, NaCl, and KCl are found to be 5.0 ± 0.5, 3.1 ± 0.3, and 2.3 ± 0.3 eV, respectively. The experimental results are compared with the recently calculated band structures for these materials.

INTRODUCTION

The electronic energy bands of alkali halides have been investigated extensively in recent years.[1–10] Shockley[1] calculated the band structure of NaCl and found the width of the Cl^- $3p$ band to be about 4 eV. On the other hand, the calculations reported by Casella[2] and Page and Hygh[3] showed a significantly smaller bandwidth, i.e., 1.1 and 0.57 eV. For KCl, the calculations by Howland[4] and DeCicco[5] indicate a valence-band width of 1.5 and 0.82 eV, respectively. More recently, the band structures of LiCl, NaCl, and KCl were calculated from a first-principles point of view by Lipari and Kunz.[8–10] The results of their calculations indicate that the valence-band widths for LiCl, NaCl, and KCl are 8, 4.4, and 2.6 eV, respectively. In view of the conflicting values of the calculated bandwidth, it is particularly desirable to find experimental data for comparison with the theoretical results.

In this paper, we present new experimental information from photoemission measurements for comparison with the results of band-structure calculations. With dispersed uv radiation of energies above 12 eV, we were able to observe photoelectron energy distributions which show peaks that can be identified as relatively high optical densities of states in the valence and conduction bands of alkali chlorides. While the experimental results associated with the band structure of KCl are found to be in good agreement with the calculations of Lipari and Kunz,[10] the observed valence-band widths of LiCl and NaCl are significantly different from the calculated values.

EXPERIMENTAL METHOD

The photoemission experiments were performed with the equipment shown in Fig. 1. Radiation of photon energies above 12 eV was produced by a helium-continuum source.[11] The radiation was dispersed by a 1-m normal-incidence vacuum-uv monochromator. The evaporated films of LiCl, NaCl, and KCl were prepared in a vacuum of base pressures 10^{-7}–10^{-8} Torr, and measurements were made *in situ* immediately after evaporation. The sample was evaporated onto a polished-stainless-steel substrate from a quartz crucible at about 10^{-7} Torr. The thickness of the evaporated film was estimated to be in the range of 500–800 Å. This estimate was obtained by comparing the observed quantum yield of the sample with the saturated yield. The thickness of similar films of saturated yield was found to be about 800 Å. The quantum yield was measured by comparing the photoemission current of the sample with that of a tungsten foil. The absolute yield of the foil was determined with the use of a calibrated thermocouple at wavelength 584 Å. The spectral yield of the foil was obtained by comparison with the response of sodium salicylate.[11] The energy distributions of the photoemitted electrons were measured by the ac method.[12] The results were found to be reproducible by repeating the measurements at various photon energies.

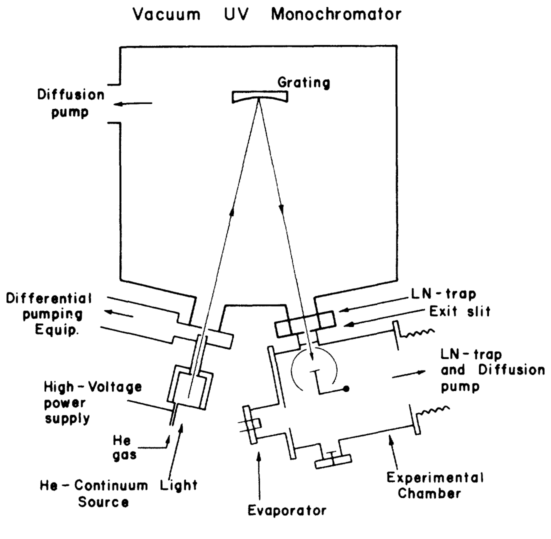

FIG. 1. Vacuum-uv monochromator and vacuum chamber for photoemission measurements at photon energies 12–23 eV.

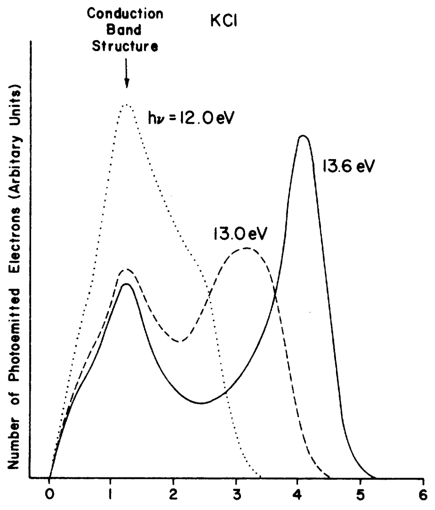

FIG. 2. Energy distributions of photoemitted electrons from KCl films. Zero energy represents the vacuum level. Conduction-band structure is located at 1.3 eV above the vacuum level.

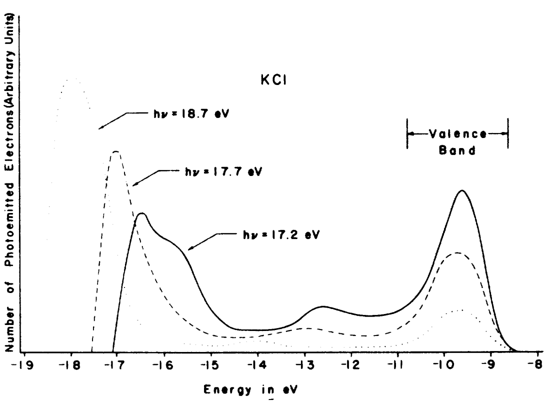

FIG. 4. Energy distributions of photoemitted electrons from KCl films. The energy scale of each distribution curve is shifted according to the difference of photon energy. The highest occupied states are located at −8.6 ± 0.2 eV. Zero energy is the vacuum level. A peak in the density of states of the valence band is located at 1.0 ± 0.2 eV below the highest occupied states. The effective base width of the Cl⁻ $3p$ valence band of KCl is 2.3 ± 0.3 eV.

RESULTS AND INTERPRETATION

The significant features of the photoelectron-energy-distribution curves for KCl are shown in Figs. 2–4. For comparison of peak heights, the areas under the energy distribution curves of different photon energies are normalized according to the quantum yield of the sample. In Fig. 2 zero energy represents the vacuum level, which is located at 8.6 ± 0.2 eV above the top of the valence band. As the photon energy is increased, there is a peak which remains fixed at 1.3 eV above the vacuum level while the high-energy peak is shifted to a higher-energy region. At higher photon energies, it can be seen that there are two stationary structures as shown in Fig. 3. We associate these with the high densities of states in the conduction band of KCl. The appearance of these peaks at high photon energies can be attributed to inelastic scattering of the photoelectrons. Their location above the vacuum level is consistent with the semiempirical analysis of the conduction-band states of KCl by Phillips.[13] The high-energy peaks which shift with increasing photon energy are attributed to electrons optically excited from the valence band.[14] If the distribution curves are plotted with the energy

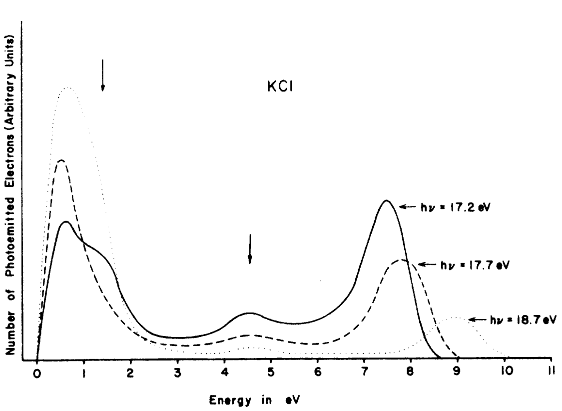

FIG. 3. Energy distributions of photoemitted electrons from KCl films at higher photon energies. Vertical arrows indicate conduction-band structure at 1.3 and 4.5 eV above the vacuum level.

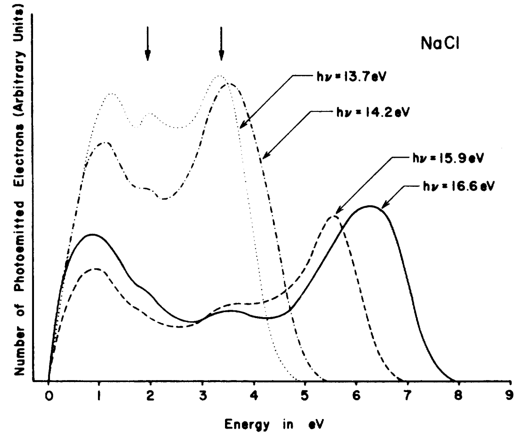

FIG. 5. Energy distributions of photoemitted electrons from NaCl films. Vertical arrows indicate conduction band structure at 2.0 and 3.5 eV above the vacuum level, which is at zero energy.

scale of each distribution shifted according to the difference of photon energy, the high-energy peaks appear at the same energy position. We identify the width of this structure as the width of the Cl^- $3p$ band. This is illustrated in Fig. 4, in which the cutoff on the right represents the highest occupied states below the vacuum level. The width of the valence band is found to be 2.3 ± 0.3 eV for KCl. This is in good agreement with the most recent theoretical value.[10] In contrast, the value obtained from x-ray measurements is of the order of 1–4 eV.[15–17]

The normalized energy distribution curves for NaCl are shown in Figs. 5 and 6. As indicated in Fig. 5, two peaks which can be associated with the conduction band structure appear at 2.0 and 3.5 eV above the vacuum level. The relative position of the peaks is in agreement with that of the first two structures in the calculated density of states.[9] Only the relative positions can be compared for the vacuum level is not shown in the calculations. The structure which is due to electrons excited from the valence band can be seen in Fig. 6. The high densities of states are found at 1.0 ± 0.2 and 2.1 ± 0.2 eV below the highest occupied states. The effective base width of the valence band is 3.1 ± 0.3 eV. This is somewhat smaller than the calculated valence-band width of 4.4 eV.[9]

The normalized energy distribution curves for LiCl are shown in Figs. 7 and 8. The curves in Fig. 7 show three peaks which can be identified as conduction band structure of LiCl. The relative positions of these peaks agree with those of structures labeled *B*, *C*, *D* in the calculated density of states.[8] Again the vacuum level is not shown in the calculations. The valence-band structure is shown in Fig. 8. The high densities of states are located at 1.3 ± 0.2 and 3.0 ± 0.3 eV below the top of the valence band. The width of the valence band is found to be 5.0 ± 0.5 eV, which is not in agreement with the calculated width of 8 eV.[8] It should be noted that the observed width as indicated by the photoelectron energy distribution curves may be some-

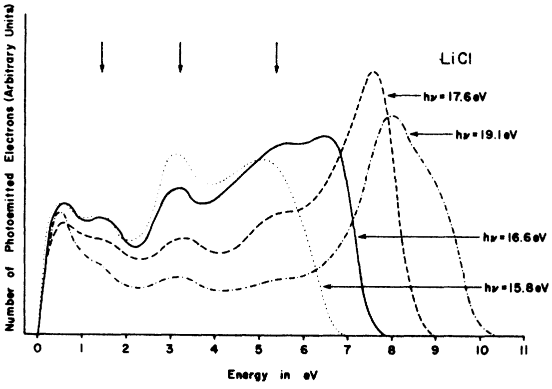

FIG. 7. Energy distributions of photoemitted electrons from LiCl films. Zero energy is the vacuum level. Vertical arrows indicate conduction band structure at 1.5, 3.2, and 5.3 eV above the vacuum level.

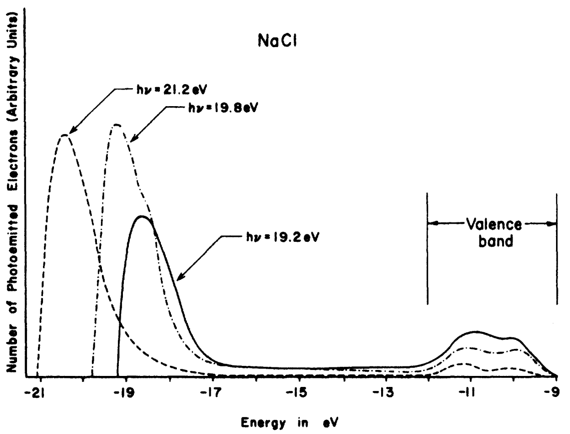

FIG. 6. Energy distributions of photoemitted electrons from NaCl films. The energy scale of each distribution curve is shifted according to the difference of photon energy. Zero energy is the vacuum level. The highest occupied states are located at − 9.0 ± 0.2 eV. Structure in the valence band can be seen at 1.0 ± 0.2 and 2.1 ± 0.2 eV below the highest occupied states. The effective base width of the valence band of NaCl is 3.1 ± 0.3 eV.

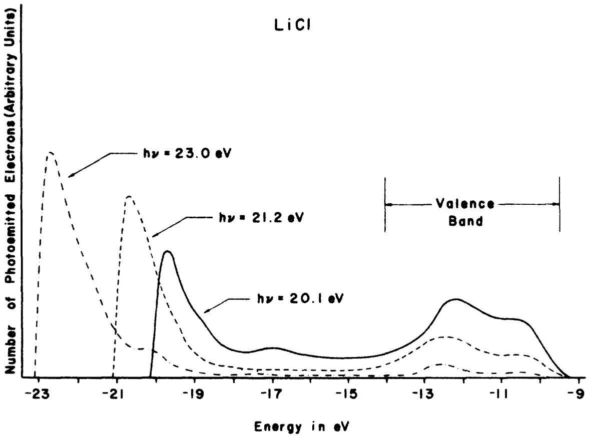

FIG. 8. Energy distributions of photoemitted electrons from LiCl films. The energy scale of each distribution curve is shifted according to the difference of photon energy. Zero energy is the vacuum level. The highest occupied states are located at − 9.3 ± 0.2 eV. Valence-band structure can be seen at 1.3 ± 0.2 and 3.0 ± 0.2 eV below the highest occupied states. The effective base width of the valence band of LiCl is 5.0 ± 0.5 eV.

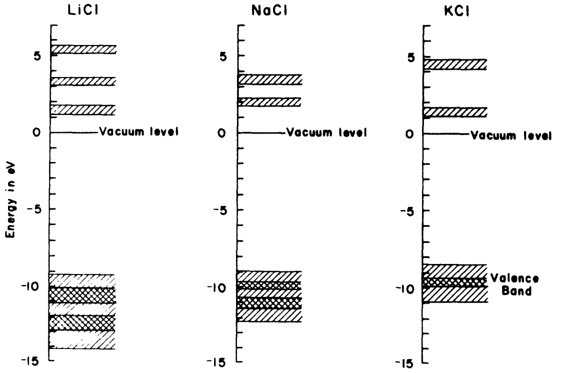

FIG. 9. Conduction- and valence-band structures of LiCl, NaCl, and KCl. Shaded regions in the conduction band represent high densities of states. Regions of double hatching represent high densities of states in the valence band.

what larger than the valence band width because of scattering. This is particularly noticeable in our study of LiCl.

The results of our photoemission measurements are summarized in Fig. 9. The increase in width of the valence band in going from KCl to LiCl is consistent with the corresponding decrease in interionic distance. The values of the valence-band widths are comparable to those obtained in some recent photoemission studies of KI and CsI in the photon-energy region below 12 eV.[18,19] The observed width of the valence band for LiCl is significantly smaller than the calculated width.[8] This discrepancy may not be surprising because the correlation effects were not considered in the recent LiCl calculations. The effects would be expected to narrow the valence-band width as indicated in the calculations for KCl and NaCl.[9,10]

TABLE I. Energies of interband transitions from the high densities of states of the valence band to those of the conduction band as determined by photoemission measurements.

	Transition energies (eV)	
LiCl	NaCl	KCl
12.1	12.0	10.9
13.8	13.1	14.1
15.5	13.5	
15.9	14.6	
17.6		

The observed structure in the densities of states of the valence and conduction bands may help clarify the interpretation of the absorption and reflectance spectra of alkali halides in the ultraviolet and soft-x-ray regions.[20–32] In Table I, the transition energies are listed for the possible transitions from the high densities of states of the valence band to those of the conduction band as determined by our photoemission measurements at 300 °K. Of the six possible transitions for LiCl, two have transition energy of 13.8 eV. Thus, only five values are shown. For KCl and NaCl the values are in agreement with the optical data reported by Roessler and Walker[20] in the region below 14 eV. It is interesting to note that the interband transition at 14.1 eV for KCl is coincident with the observed structure in the energy-loss function, which has been identified as a plasma resonance.[32] This structure does not correspond directly to any intense peak in optical absorption. In view of the relatively high joint density of states at 14 eV, the relatively weak optical absorption at this energy must be due to a small matrix element for excitation by photons.

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