PHYSICAL REVIEW B VOLUME 9, NUMBER 8 15 APRIL 1974

X-ray photoemission studies of the alkali halides*

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(Received 8 November 1973)

High resolution x-ray photoemission spectra of the alkali halides LiF, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, and KI are reported. The valence-band spectra are compared with previous spectra of group-IV,-III-V, and -II-VI crystals. It is shown that features of the spectra evolve systematically in proceeding from the group-IV elements to the I-VII crystals. Analysis of this evolution leads to the interpretation of the structure of the outermost halogen *p* band in the less ionic cases as being due to band effects rather than spin-orbit splitting. The outermost-core-level binding energies are tabulated. Intrinsic and extrinsic satellite structure associated with the core levels is discussed.

I. INTRODUCTION

The alkali halides have been the subject of intense research for many years. Part of the reason for this is that the alkali halides almost comprise a class of compounds by themselves. They are the prototype of the ionic insulator and as such may be considered the simplest of binary crystals, being composed of positive and negative ions bound together by Coulomb attraction. In this paper x-ray photoemission spectroscopy (XPS) is used to determine the valence-band densities of states and core-level binding energies for LiF, NaF, NaCl, NaBr, NaI, KF, KCl, KBr, and KI, all of which crystallize in the rock-salt structure. The spectra of these salts show that, far from being anomalous cases, the alkali halides demonstrate features in their valence-band densities of states which bear a qualitative relation to features found in the spectra of II-VI and III-V compounds, and even group-IV elements. Extrinsic loss structure and photoemission satellite peaks in the spectra are also examined.

Experimental procedures are given in Sec. II. The valence-band structure and core-level energies are presented and discussed in Sec. III. Loss structure is treated in Sec. IV.

II. EXPERIMENTAL

The samples used for these experiments were all high-purity single crystals. In order to minimize the contamination of the samples by the adsorption of hydrocarbons and/or oxygen, the samples were cleaved in a glove bag under a dry nitrogen atmosphere and placed in a Hewlett-Packard 5950A electron spectrometer at pressures $< 1.0 \times 10^{-8}$ Torr without exposure to the room atmosphere. They were then irradiated with monochromatized Al $K\alpha_{1,2}$ radiation (1486.6 eV) and the ejected photoelectrons were energy analyzed. The use of monochromatized x rays reduces the minimum peak full width at half-maximum to ~0.6 eV and eliminates unwanted bremsstrahlung and x-ray satellite lines.

In addition to the valence-band regions and the specific core peaks of interest, spectra were taken over a binding energy range of 0–1000 eV in order to detect core-level peaks from any impurities which might be present. Experience has shown that small amounts of impurities (notably oxygen) can give rise to extraneous features in the valence-band region. The only detectable impurities were carbon and oxygen, and they were present in sufficiently small amounts to preclude serious effects on the valence-band spectra.

The use of cleaved single crystals for these experiments is desirable in itself, quite apart from any question of contamination. It has been demonstrated by Ley *et al.*, both for the group-IV elements Si and Ge[1] and for the group-V elements As, Sb, and Bi,[2] that evaporated films can give quite different results for the valence-band density of states than will the corresponding single crystals. This is hardly surprising because the density of states must be sensitive to the local bonding of the atoms, which must in turn be sensitive to the structure. While the alkali halides are more likely to form good crystals than are the aforementioned elements, we note that the degree of imperfection that must be present in order to distort the spectra significantly may be rather small.

Energy conservation gives the photoemission equation

$$\hbar\omega = E_B^F + K + e\phi_{sp} + e\psi ,$$

where K is the kinetic energy of the photoelectron, ϕ_{sp} is the spectrometer work function, E_B^F is the binding energy of the photoelectron with respect to the Fermi energy, and ψ is the potential due to the charging of the sample. This final term in the equation, the charging shift, prevents the assignment of absolute binding energies from our spectra alone.

In order to deal with the charging-shift effect, the following referencing procedure was adopted. The top of the experimental valence bands were determined by linear extrapolation of the segment of

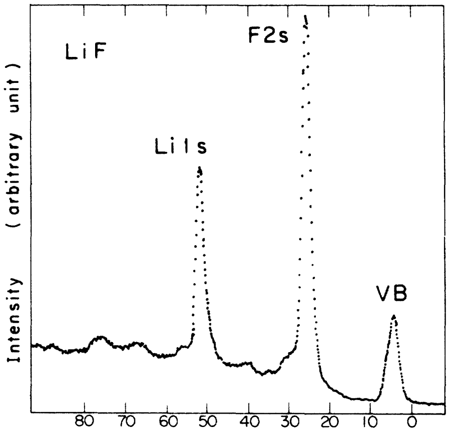

FIG. 1. X-ray photoemission spectrum of the valence-band region of LiF.

maximum negative slope to the background level. This point is taken hereafter as our arbitrary zero of energy.

III. VALENCE BAND AND CORE LEVELS: RESULTS AND DISCUSSION

The spectra obtained for the valence-band regions are shown in Figs. 1–3. In light of the well-known ionic nature of these crystals it is not surprising that the uppermost valence-band peaks strongly resemble core-level peaks. Indeed for many purposes this uppermost valence band may be considered to be the pure-anion *p* level. However, the valence-band peaks of LiF, NaCl, NaBr, NaI, KBr, and KI all show definite structure on the low-energy (high-E_B) side. In this section we show that this structure is similar to that found in III-V and II-VI binary crystals, and that this and other features of the spectrum evolve regularly in proceeding from the covalent group-IV elements to the ionic alkali halides.

In any binary crystals of the form $A^N B^{8-N}$, the outermost principal shells contain eight electrons per *AB* unit, which may be thought of as occupying four valence bands. Of course, the extent to which these bands represent truly delocalized states as opposed to corelike levels is determined by the potential in each individual case. With this in mind, let us examine the evolution of the valence bands in proceeding from the group-IV covalent prototypes to the alkali halides.

In Fig. 4 the theoretical band structures, calculated by Cohen and co-workers[3–6] by the empirical pseudopotential method, of Ge, GaAs, ZnSe, and NaCl are shown along with the valence-band XPS spectra.[7] Ge, GaAs, and ZnSe occur in the zinc-blende structure, for which these calculations were done. The bands are in all cases grouped as would be expected from atomic-structure considerations, in a group of three bands nearest the Fermi level and a single band at lower energy. The lowest level has in all cases Γ_1 symmetry and may be characterized quite unequivocally as an *s*-like level. The other three bands have Γ_{25}' symmetry in the tetrahedral case and Γ_{15} in the octahedral NaCl lattice. It is therefore quite tempting to classify these three bands as *p* like. It is clear, however, that in the case of Ge, where the *s*-like band (band 1) and the lowest *p*-like band (band 2), are degenerate at the *X* point, this artificial categorization of the bands by labels reflecting their supposed atomic parentage is misleading.

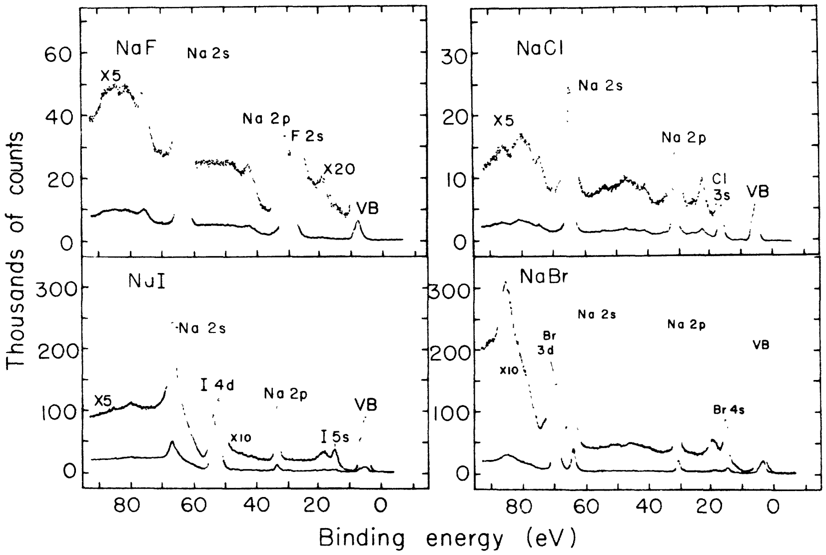

FIG. 2. X-ray photoemission spectra of the valence-band region of the sodium halides.

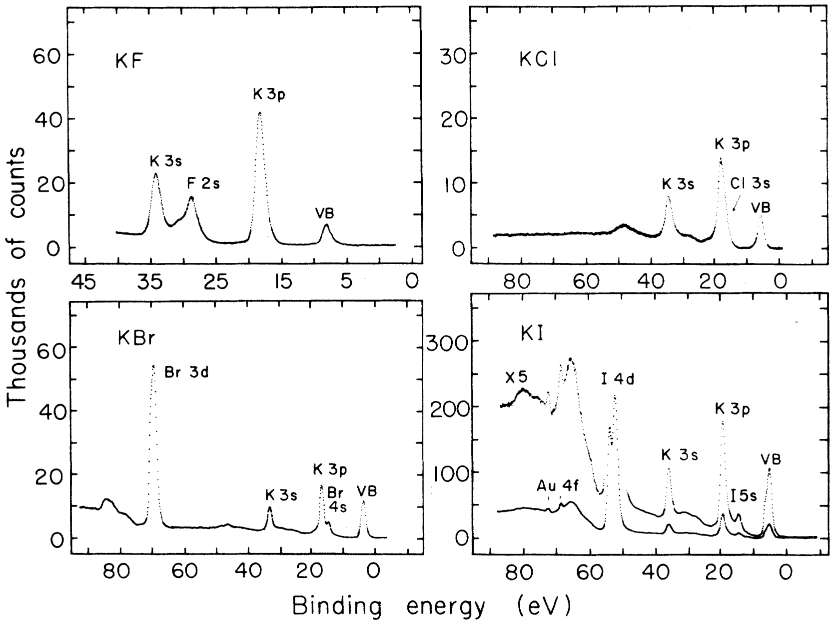

FIG. 3. X-ray photoemission spectra of the valence-band region of the potassium halides.

The similarity of bands 1 and 2 in the group-IV elements is demonstrated by both experimental and theoretical results. Cavell *et al.*[8] studied the variation of the XPS cross sections across the valence bands for diamond, Si, and Ge. These results showed that the XPS cross section of the peaks corresponding to band 2 in each case followed quite closely that of band 1, the *s*-like band, and was very different from that of bands 3 and 4, the *p*-like bands. Charge-density calculations were also performed on each of the four bands of Ge by Walter and Cohen.[9] They showed that the charge distributions of bands 1 and 2 are practically identical, and are very *s* like. Bands 3 and 4 were found to be very similar to each other also, and both very *p* like. By *s* like, we mean that the charge density is concentrated on the atomic sites; and by *p* like, we mean that the charge density is concentrated between the atomic sites in bonding regions.

In progressing along this series to GaAs, definite changes are apparent in both the photoemission spectrum and in the calculated band structure. The primary difference in the photoemission spectrum is that the band 1 peak has split off somewhat from the peaks due to bands 2–4 and has moved to higher binding energy. This is reflected as well in the band structure; i.e., the degeneracy of bands 1 and 2 is lifted at the point X. On the basis of these changes, one would expect that band 1 is becoming more *s* like and band 2 more *p* like. The calculated charge densities bear out this expectation. Band 1 in GaAs is almost completely localized on the As site and is virtually undistorted from spherical symmetry. Band 2 is less profoundly changed from the case of Ge but is definitely more *p* like. These

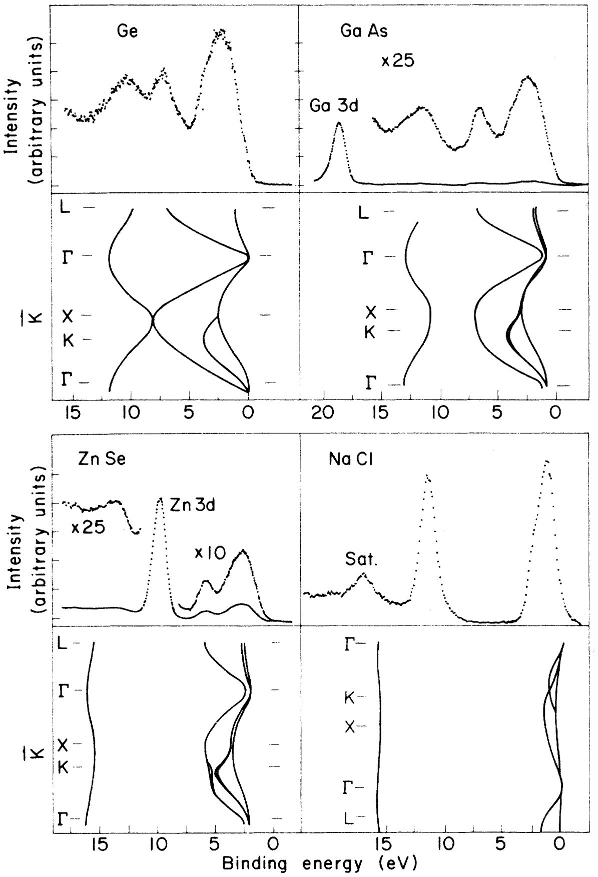

FIG. 4. X-ray photoemission spectra and band structures of Ge, GaAs, ZnSe, and NaCl. The upper row shows the uncorrected experimental spectra. The lower row shows the corresponding band structure of empirical pseudopotential method calculations of Refs. 3–6.

changes in the bands can be readily understood in terms of a simple argument. Imagine a crystal composed of the ion cores As^{5+} and Ga^{3+}. The first electrons added to this lattice would fill band 1, concentrating around the As^{5+} ion due to its higher charge. This explains the increased atomic character of band 1 in GaAs, as well as the shift to higher binding energy due to the +5 as opposed to +4 core charge. Considering this (admittedly crude) model after the first band is filled the lattice consists roughly of Ga^{3+} and As^{3+}. Since the ionic potentials are now roughly equal, the next three bands should roughly resemble those in Ge where the potentials are rigorously equal. Qualitatively, this is indeed the case.

In ZnSe the analogous changes are observed, with band 1 becoming almost completely corelike and band 2 showing a high degree of p character. It is evident that the effect of increasing the antisymmetric part of the potential is to progressively unmix the s-p bands 1 and 2 into purer atomiclike states.

In the alkali halides, the description in terms of a band structure has come under question.[10,11] Band-structure theory operates within the confines of the Hartree-Fock (and usually, in fact, of the Hartree-Fock-Slater) approximation, in which the motions of electrons of opposite spin are completely uncorrelated. In this approximation every electron sees a truly periodic potential. Bloch's theorem therefore holds for each one-electron state and the electronic eigenfunctions may be labeled by $\vec{k}$. If correlation effects are introduced, the symmetry of the Hamiltonian will be broken, which can result in the mixing of states of different $\vec{k}$ such that highly correlated Wannier-like states become the true eigenfunctions of the system. These two possible descriptions of the system may, of course, both describe the same real-space electron density distribution in the crystal. For example, in NaCl one would expect to find the eight valence electrons per primitive cell near the Cl sites. This could be described in the local-orbital picture by four localized orbitals on the Cl site made up of linear combinations of a large number of Bloch states. In the band scheme, the periodic part of each Bloch function $\phi_k(\vec{r})$ would have an equal amplitude on each Cl site in the lattice, and the $\sim 10^{23}$ states thus formed would each contribute to the electron density of the given site. It has been suggested[11] that the local orbital (Heitler-London) description of the alkali halides could be valid since the total calculated bandwidths, and thus the magnitude of the energy gain by delocalization, are smaller in comparison with the correlation energy than in any other case.

The implication of each of these models for the photoemission results is clear. If the localized-state description were valid the XPS spectrum would be that of essentially atomic orbitals in a cubic crystal field. Since p orbitals are not split by a cubic field, the only structure in the alkali-halide "valence bands" would be due to spin-orbit splitting. If the band picture were valid, dispersion in the band structure could give rise to extra structure in the valence-band peaks. The band picture could still be qualitatively valid, however, without giving rise to structure in the photoemission spectrum, provided that the bands are sufficiently flat.

Figures 5 and 6 show expanded drawings of the outermost p bands of each of the nine salts studied in this work. In three of the salts (KF, KCl, NaF) there is only one fairly symmetrical peak nominally corresponding to bands 2–4 as observed in the zinc-blende-structure semiconductors. This indicates, whether the Bloch-state formalism is valid or not, that the p bands retain a good deal of their atomic character in the solid. Band-structure calculations on KCl by Fong and Cohen,[6] Howland,[12] and De Cicco[13] all predict the valence bands to be ~ 1 eV wide. Allowing for the ~ 0.6-eV resolution of our spectrometer, it would be unlikely that we would observe any significant structure in the valence-band peak, even if the Bloch-state limit were rigorously correct.

In contrast to the above cases, the valence bands of LiF, NaCl, NaBr, NaI, KBr, and KI show definite structure on the high-binding-energy side. Since these levels in the solid arise from the outermost p levels of the halogens, one could conceivably attribute this structure to the spin-orbit splitting of localized ionic states. We must reject this interpretation for several reasons. In Table I we compare the atomic spin-orbit splittings[14] of the appropriate halogen levels with the splittings of the two features in the alkali-halide valence bands. In

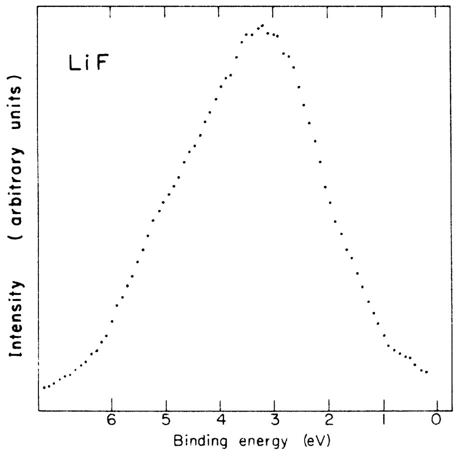

FIG. 5. Outermost p band of LiF.

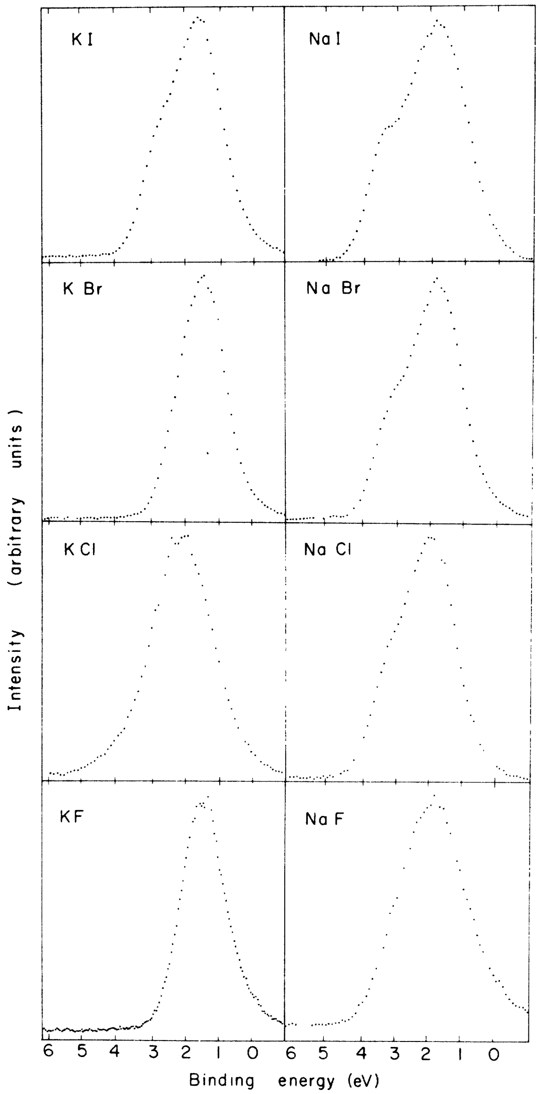

FIG. 6. Outermost *p* band of the sodium and potassium halides.

every case the separation of the features in the solid is larger than that predicted by spin-orbit splitting. In several cases—NaCl, NaBr, NaI, and especially LiF—the features are split much more than could be accounted for by spin-orbit splitting alone. Also, the large effect in the spectra of the change from Na^+ to K^+ in the chlorides argues against the structure being due to localized chlorine states.

A further strong argument in favor of a band picture is provided by the systematics of the variation in the valence-band photoemission spectra and theoretical band-structure calculations in progressing through the Periodic Table. As we have already discussed, there is a systematic progression in the character of the photoemission spectra in progressing from group-IV to III-V to II-VI crystals. In going on to the alkali halides, the crystal structure is changed; therefore, in terms of group-theoretical symmetry designations, the band structure is qualitatively different. However, a comparison of the features in the photoemission spectra is still not unreasonable. In the alkali halides, the analog of "band 1" in germanium is surely a *bona fide* core level, as was the case in ZnSe. In going from Ge to ZnSe the top two peaks merged as bands 2–4 came together to form a partially resolved shoulder on the high-binding-energy side of the valence-band peak. This shoulder arises mainly from band 2, which projects down farthest near the L and X points in the Brillouin zone in all the band-structure calculations for both the rock-salt and the zinc-blende structures.

While it is dangerous to compare different types of band-structure calculations done on different crystals, band structures done by the same method can be compared without too great a risk of systematic errors. Fong and Cohen[6] have calculated the band structures of NaCl and KCl by the empirical pseudopotential method. In our spectra NaCl shows distinct valence-band structure splitting while KCl does not. That this should indeed be the case is at least strongly indicated by these calculations. The calculated band structures are quite similar except for the fact that the valence band of NaCl is wider and shows a branch of the p bands forming a high density-of-states region near $L \sim 1.8$ eV below the top of the valence bands. It is clear from our previous experience that such a feature in the band structure could give rise to just such a feature in the photoemission spectrum as is observed.

Our results therefore indicate strongly that, at least for the less ionic of the alkali halides, a band-structure picture is valid. This agrees with the conclusion reached by Di Stefano and Spicer[15] regarding CsI. The agreement is especially interesting since they made their conclusions on the basis that they saw evidence for direct transitions in their uv photoemission spectra, and also because

TABLE I. Comparison of atomic spin-orbit splitting of outermost halogen level with splitting of observed features in valence bands of the alkali halides of this study.

	Atomic spin-orbit splitting[a]	LiX[b]	NaX[b]	KX[b]
F	0.05	1.68	···	···
Cl	0.11		1.13	···
Br	0.46		1.28	···
I	0.94		1.48	1.08

[a] Reference 14. [b] This work.

TABLE II. Binding energies (eV) of the outer core levels of the sodium and potassium halides. Energies are relative to the top of the valence band and are given to ±0.1 eV. VB stands for valence band.

LiF	
VB(1)	3.54
VB(2)	5.22
F 2*s*	24.90
Li 1*s*	50.77

NaF		NaCl		NaBr		NaI	
VB	2.06	VB(1)	1.47	VB(1)	1.67	VB(1)	1.67
F 2*s*	23.20	VB(2)	2.60	VB(2)	2.95	VB(2)	3.15
Na 2*p*	24.77	Cl 3*s*	12.58	Br 4*s*	12.83	I 5*s*	11.21
Na 2*s*	57.46	Na 2*p*	27.03	Na 2*p*	28.21	Na 2*p*	29.29
		Na 2*s*	59.77	Na 2*s*	61.00	I 4$d_{5/2}$	47.68
				Br 3*d*	66.21	I 4$d_{3/2}$	49.35
						Na 2*s*	61.96

KF		KCl		KBr		KI	
VB	1.38	VB	1.87	VB	1.27	VB(1)	1.48
K 3*p*	13.01	K 3*p*	14.07	K 3*p*	14.17	VB(2)	2.56
F 2*s*	22.24	K 3*s*	30.11	Br 4*s*	16.24	I 5*s*	10.82
K 3*s*	27.75			K 3*s*	30.21	K 3*p*	15.55
				Br 3*d*	65.68	K 3*s*	31.59
						I 4$d_{5/2}$	47.48
						I 4$d_{3/2}$	49.10

their higher resolution made the separation of band-structure and spin-orbit coupling effects even easier and more complete.

Table II lists binding energies of the outer core levels in these salts, both relative to the top of the valence bands. These values agree with the lower-resolution results of Citrin and Thomas.[16,17] Since those authors discussed these binding energies thoroughly, we simply list our values without further comment.

IV. LOSS STRUCTURE AND SATELLITE LINES

In many photoemission spectra of solid samples, peaks appear at energies of roughly 5–50 eV below the primary photoemission peak. These can be of two distinct types: (i) intrinsic satellite lines due to additional final states which may be reached in the photoemission process, and (ii) extrinsic structure due to energy losses suffered by the photoelectron as it escapes the crystal. Both intrinsic and extrinsic losses may have multiple causes. Extrinsic loss peaks may arise from the excitation of bulk or surface plasma oscillations, the ionization of other atoms in the crystal, or the excitation of interband transitions. The intrinsic structure may be due to final states which, although they correspond to two-electron transitions, are mixed with the configuration giving rise to the main peak via configuration interaction. Intrinsic satellite peaks may also arise from the induction of a monopole transition during the photoemission process arriving at a final-state configuration of higher energy than that corresponding to the main peak, but which may be unmixed with that configuration. These are commonly referred to as shake-up processes.

Since the energy-loss spectra of externally produced electron beams passing through the alkali halides have been studied in detail,[18,19] it is in principle a simple matter to distinguish between extrinsic and intrinsic loss structure. At least for photoelectrons with roughly the same kinetic energy, the extrinsic loss structure should be identical for each peak; this could be subtracted out and the intrinsic satellite lines would remain. An examination of the experimental data, however, shows that

TABLE III. Loss structure observed in this work and characteristic energy losses (CEL) reported by Best (Ref. 18).

LiF	
Li 1*s*	4.13, 15.0, 23.91, ~36.0
F 2*s*	2.95, 5.81, 8.46
CEL	14.5, 17.0, 24.9, 43.2

NaF		NaCl		NaBr		NaI	
F 2*p*	11.5	Na 2*p*	9.4, 12.4, 15.4, 21.6	Br 3*d*	14.7, 19.8	Na 2*s*	12.4
CEL	11.6	Na 2*s*	9.5, 12.7, 15.5, 20.8	Br 4*s*	15.1	I 4*p*	14.7, ~30
		Cl 2*p*	18.6	Na 1*s*	8.64, 13.7	I 4*s*	~12
		Cl 2*s*	10.0, 15.3	CEL	7.6, 13.9, 20.8	I 3$p_{1/2}$	~12.6
		Na 1*s*	9.4, 12.6, 15.3, 21.4			Na 2*s*	12.6
		CEL	8.7, 12.7, 15.5, 22.2			I 5*p*	12.8
						CEL	12.3, 17.8, 25.9, 33.1

KF		KCl		KBr		KI	
K 2*s*	11.4, 28.5	K 3*s*	10.6, 13.4, 14.8, 22.7	K 3*s*	10.1, 12.8, 14.9	K 2*s*	10.4
K 2*p*	11.3, 28.9	K 3*p*	~11	Br 3*d*	9.7, 14.1, ~27	CEL	8.0, 11.2
F 1*s*	7.4, 11.7, ~28	K 2*p*	8.1, 11.39, 25.9	CEL	9.2, 12.5, 18.2, 22.0, 25.4, 28.0		
CEL	10.1, 12.4, 17.1, 22.5, 26.9, 31.0	Cl 2*p*	17.1, 26.5				
		CEL	10.2, 13.8, 19.6, 23.0, 26.4				

the separation is not nearly this simple.

As a case in point, let us consider NaCl. The loss structure from the Na 2*p*, Na 2*s*, and Na 1*s* lines in each case consists of four peaks, the energies of which are set out in Table III along with the energies of characteristic energy losses determined by Best.[18] The agreement in the positions of the loss peaks from each of the photoemission lines is excellent, despite the greater than 1000-eV difference in the kinetic energy of the photoelectrons arising from the Na 1*s* and Na 2*s* and 2*p* lines. The agreement with Best's data is also quite good. These are thus extrinsic loss peaks, and one would therefore expect to find them associated with every peak in the photoemission spectrum. This is, however, not the case. The loss structure of the Cl 2*p* and the Na 2*s* are shown plotted together in Fig. 7. Despite the similarity in width of the two main peaks, the loss structure arising from the Cl 2*p*'s is grossly different from that from the Na 2*s*. Instead of the weak four-peak structure, there is one strong peak with a huge tail. This tail, due to diffuse inelastic scattering of the photoelectrons, is over ten times the height of the tail in the losses from the Na 2*s*. Of course, since the total intensity of the loss structure from the Cl 2*p* normalized to the photoemission peak intensity is almost five times that from the Na 2*s*, all the loss peaks for the Na 2*s* could have their analog in the Cl 2*p*, being rendered unobservable by the more intense structure intrinsic to the Cl 2*p*. The loss structure from the Cl 2*s* resembles that from the Cl 2*p*'s very closely. It is not shown as the carbon 1*s* peak due to the presence of impurities on the surface of the crystal partially obscures the comparison. The presence of this loss structure from the Cl 2*s* does seem, however, to preclude the possibility of the 2*p* loss structure being due to an intense final-state photoemission satellite. This change in loss structure further cannot be due to the deterioration of the crystal in the x-ray beam with time since the Cl 2*s* and 2*p* spectra were taken after the Na 2*s* but before the Na 1*s*.

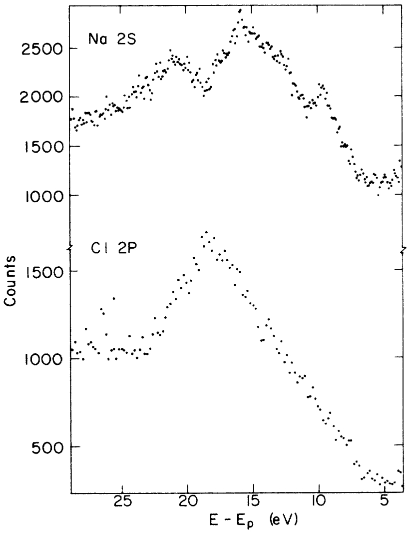

FIG. 7. Loss structure of the Cl 2*p* and Na 2*s* levels of NaCl.

Another interesting feature in the NaCl spectrum is a sharp fairly intense peak located at 5.9 eV below the Cl 3*s* and 16.8 eV below the centroid of the valence band. We have observed loss peaks in spectra from other crystals, e.g., NaF, originating from the valence electron peak. However, in NaF this peak, located at $(E_p - 11.5)$ eV, where E_p is defined as the energy of the primary (loss-free) photoemission peak, can be correlated with the energy loss peaks observed by Creuzberg[19] and Best.[18] Best, in fact, gives the value of 11.6 eV for this peak, attributing it to an ionization process. It is difficult to accept this peak in NaCl as a loss from the valence band for two reasons. First, it does not correspond to the energy of any loss peak, either in the work of Creuzberg[19] or Best[18] or to any loss from any other line in our spectra. Second, it appears to be too narrow to have arisen from the valence-band peak.

If this peak in the NaCl spectrum is a photoemission final-state effect, one would expect to find a similar feature in the KCl spectrum. Unfortunately, in KCl the peaks corresponding to the K 2*p* and the Cl 3*s* overlap to such an extent that the accurate assignment of the positions of either of these two levels is impossible. Nevertheless, a shoulder is observed on the "K 2*p* side" of this feature which could correspond to a satellite 5.9 eV down from the Cl 3*s* level. The interpretation of this peak as a final-state satellite is further reinforced by the observation of a 6-eV satellite from the Cl 3*s* in the spectrum of LiCl by Wertheim and Rosencwaig,[20] as well as in the soft x-ray spectrum of Fischer and Braun.[21] Wertheim and Rosencwaig pointed out that this energy range below the Cl 3*s* in KCl was obscured by the Al $K\alpha_{3,4}$ line from the K 3*s* level; however, they made no mention of observing this satellite in NaCl.

Another particularly interesting case is the loss structure arising from the K 3*s* level in KBr and KCl. Wertheim and Rosencwaig have attributed some of this loss structure to configuration-interaction final-state satellites. The loss structure from each of these crystals is plotted in Fig. 8. The vertical lines give the positions of the $3s^2 3p^4 4s$ and $3s^2 3p^4 3d$ configurations in atomic K(III) given by Moore.[14] To what extent the satellite structure should reflect the position of the atomic levels is of course a moot point. While, within the cores, the electron correlation and hence the configuration in-

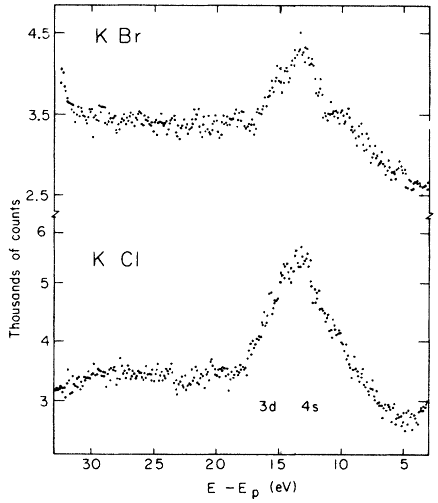

FIG. 8. Loss structure of the K 3*s* levels of KBr and KCl. Vertical lines denote positions of atomic states, as described in the text.

teraction in the gas phase and in the solid should be nearly identical, the 3*d* and 4*s* levels of potassium contribute to the conduction bands in the solid and these bands show considerable dispersion. In the atomic case, the potassium 4*s* level lies lower in energy than the 3*d* level; however, band-structure calculations indicate that while the *s*-like conduction bands form the lowest edge of the conduction bands there are regions in the Brillouin zone where the *d*-like bands are lower. In the final state, however, it is possible that the deeper local potential caused by the K^{++} ion would serve to pull a delocalized state out of the conduction band to form a localized state in a manner described by Friedel.[22] Previous work in this laboratory has shown that this model may be used to estimate extra-atomic relaxation energies.[23] If the model holds in this case the K^{++} ion, which resembles the Sc core, would be more likely to form a localized *d* state than a localized *s* state. Thus the configuration $3s^2\,3p^4\,3d$ would be more similar to the final-state configuration in the solid than would $3s^2\,3p^4\,4s$. The satellite corresponding to the $3s^2\,3p^4\,3d$ atomic state should fall at the energy of the atomic level more than the satellite corresponding to the $3s^2\,3p^4\,4s$ level, as appears to be the case.

Reader[24] has recently reanalyzed the data of Wertheim and Rosencwaig in light of recent optical data and calculations. Based on preliminary calculations he suggests that the $3s^2\,3p^4\,3d$ configuration is much more strongly mixed with the $3s\,3p^6$ state than is $3s^2\,3p^4\,4s$. This is at odds with our spectra, which show two peaks of comparable intensity. This suggests that perhaps the two satellite peaks correspond to two final states of mixed *s* and *d* character which interact with the $3s\,3p^6$ configuration.

The above analysis of course presupposes that these peaks cannot be explained in terms of extrinsic loss processes. Unfortunately, it is not completely clear that this is the case. Leder, Medlowitz, and Martin[25] reported an energy-loss peak of 12.8 eV in KBr which was measured by Best[18] to be at 12.5 eV and by Creuzberg[19] at 13.2 eV. This was ascribed by Best[18] to a valence electron plasma. The energies measured locate these features in the vicinity of the "$3s^2\,3p^4\,4s$ peak" and there is a similar situation in KCl. The only other set of energy losses we measured with reliable statistical accuracy were from the Br 3*d*'s and they located this loss peak at ~14.1 eV. However, in light of our results on NaCl, these losses cannot be relied upon for comparison with the cation loss peaks. In KCl the losses from the K 2*p*'s were measured and they indicated that there should be no interfering loss structure in the Cl satellite region. However, the energies of the loss peaks from the K 2*p*'s did not agree with the energies of the *bona fide* loss peaks from the K 3*s* or with any of the electron energy-loss data, so here, too, the situation must be regarded as somewhat unclear.

In reviewing the results on the loss structure, we can make the following general observations. First, even "extrinsic" loss structure, i.e., that not due to additional photoemission final states, is dependent in some degree upon the atom from which the photoelectron originated. For example, we generally observed substantially higher diffuse inelastic scattering from the halide peaks than from the alkali peaks. This suggests that the collapse of passive orbitals around the hole during the photoemission process enhances the probability of inelastically scattering the photoelectron. This explains the relative intensities of loss structure at least qualitatively since the more polarizable halides should be expected to show more orbital relaxation. The second point is that extreme care must be taken in comparing the energies of photoemission satellite peaks with the energies of gas-phase ionic levels. Within the cores, electron-electron correlation should be similar and thus the configurations should interact similarly. However, when the relevant free ion levels correspond to conduction-band states in the solid, the correlation effects are likely to be very different, and agreement between the two cases should not be expected.

ACKNOWLEDGMENT

We would like to thank Dr. Norman Edelstein for the crystals used in these experiments.

*Work performed under the auspices of the U. S. Atomic Energy Commission.

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