Far-Ultraviolet Reflectance Spectra of Ionic Crystals

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Synchrotron radiation has been used to measure the reflectance spectra of KCl, KBr, RbCl, CsCl, CsBr, CaF₂, SrF₂, and BaF₂ for photon energies $6 < \hbar \nu < 36$ eV at temperatures $90 < T < 400$ K. Excitations of both valence and core electrons show sharp structure and strong $T$ dependence. Analysis of the data in terms of excitonic and interband transitions from core states is made with regard to $T$ dependence, crystal structure, and chemical composition.

Our understanding of the electronic band structure of ionic crystals is not as advanced as for many other solids, even though the alkali halides were among the first materials studied in solid-state physics. This situation arises because the large energy gaps of these crystals place their fundamental absorption spectra in the vacuum ultraviolet, a region not easily accessible for experiments. This paper reports the normal-incidence reflectance spectra of several ionic crystals for photon energies $6 < \hbar \nu < 36$ eV and temperatures $90 < T < 400$ K. Low-$T$ measurements beyond 12 eV, the transmission cutoff of LiF windows, were made possible for the first time by the use (without windows) of synchrotron radiation as a light source. A number of new structures have been observed, particularly at low $T$.

Synchrotron radiation from the 240-MeV electron storage ring at the University of Wisconsin was used. The experimental system employs the rotating-light-pipe scanning-reflectometer technique to obtain detailed reflectance spectra directly. Before measurement, bulk samples are heated to 400 K in the ultrahigh vacuum to remove absorbed gases from the surface.

Figure 1 shows the reflectance spectra of KCl, KBr, RbCl, CsCl, CsBr, CaF₂, SrF₂, and BaF₂. Correction was made for second-order light from the grating. Reflectance shifts separate the spectra at different temperatures, placing the 90-K curves above and the 400-K curves below the 300-K measurements. The wavelength resolution is $\Delta \lambda = 5$ Å.

The spectra have been divided by dashed vertical lines into three regions. Structure in region I arises from electronic excitation of the valence bands, which originate predominately from the filled $p$ states of the negative ions. Region II begins with the onset of excitations from flat core bands which lie below the valence bands and originate from the $p$ states of the positive ions. This core threshold may be determined for K*(3p) and Cs*(5p) at 19.9 and 13.2 eV, respectively, by observing which structures are insensitive to changes of the halide. Atomic x-ray levels help to determine the onset in the other crystals. Region II, several eV wide, is composed of very sharp peaks (width < 0.2 eV) which also characterize the core threshold. Their width is resolution limited. We believe, in agreement with others, that these sharp peaks correspond to core excitons. The present analysis uses this interpretation. It should be noted, however, that the experimental results do not exclude the possibility that the sharp peaks are caused by interband transitions. An abrupt change to much broader momentum at $X$. The $A_1'$ peak may be the first excited state of the $A_1$ exciton. Most likely arises from interband transitions between core and conduction bands.
FIG. 1. Normal-incidence reflectance spectra of several ionic crystals in the far ultraviolet. Reflectance shifts ($R_{\theta}$) separate the 90- and 400-K spectra from the 300-K spectra.

In RbCl, the sharp core-exciton peaks in region II are identified as follows. $A_1$ and $A_2$, as well as $B_1$ and $B_2$, are separated by about 0.8 eV, the spin-orbit (SO) splitting of the Rb(4p) atomic
level, $A_1$ and $A_2$ have a negative temperature shift (a few times $10^{-6}$ eV/K). In contrast $B_1$ and $B_2$ have positive temperature shifts. Thus, $A_1$ and $A_2$ are the SO-split core excitons associated with the minimum at $\Gamma_1$ of the conduction band formed from Rb$^+(5s)$, while $B_1$ and $B_2$ are the corresponding SO split excitons associated with the higher lying Rb$^+(4d)$ conduction-band minima at $X_\nu$. The $A_1'$ peak may be the first excited state of the $A_1$ exciton.\(^{10}\)

In KCl$^{11,12}$ and KB$^{9,13}$ the SO splitting of the K$^+(3p)$ core level (0.27 eV in the atom) induces a corresponding splitting,\(^{5,9,6}\) resolved at low $T$, into two core excitons $A_1$ and $A_2$ associated with the conduction-band minimum at $\Gamma_1$.\(^{4,6,7}\) The observed intensity ratio differs strongly from the ratio 2:1 expected from the statistical weight of the $(j = \frac{3}{2})$ and $(j = \frac{1}{2})$ components. However, exchange interaction\(^{15}\) between electron and hole can greatly suppress the first exciton peak relative to the second for small SO splittings. This may cause the ratio 1:1 in KBr. In KCl an additional effect contributes. The strong valence excitation peak at 18.5 eV in KBr shifts to 19.5 eV in KCl and overlaps $A_1$ considerably, broadening and suppressing it by lifetime effects.

The sharp peak $B_2$ at 21.25 eV in KCl and KBr has been assigned\(^{4,6,7}\) to the core exciton associated with the K$^+(3d)$ conduction-band minimum at $X_\nu$. It shifts to slightly lower energy upon cooling, as do $B_1$ and $B_2$ in RbCl. The lack of a SO splitting of the $X$ exciton has been attributed\(^3\) to a short lifetime which supposedly results from its energy degeneracy with core interband transitions. However, stronger lifetime broadening of $B_2$ than $A_1$ and $A_2$ is not observed; the widths of all three are comparable. Alternatively, we suggest that exchange interaction may suppress $B_1$ so that only $B_2$ is observed. Since $A_1$ is still observed while $B_1$ is not, it appears that exchange effects are smaller at $\Gamma$ than at $X$ in KCl and KBr. The shoulder $A_1'$ cannot be the missing $B_1$ peak because exchange hardly affects the SO splitting of core states.\(^{15}\) We consider $A_1'$ to be the first excited state of the $A_1$ exciton or the interband edge at $\Gamma$.

In the simple cubic Cs halides, the minima of the Cs$^+(6s)$ and Cs$^+(5d)$ conduction bands are at $\Gamma_1$ and $\Gamma_1$, the former slightly (<0.5 eV) below the latter.\(^{15,16}\) The SO splitting of the atomic Cs(5p) level is 1.7 eV. Hence, we consider $(A_1, A_2)$ and $(B_1, B_2)$ to be the SO-split core-exciton pairs associated with $\Gamma_1$ and $\Gamma_1$, respectively. The separation between these minima must be smaller in CsBr than in CsCl, so that in CsBr at low $T$, $B_1$ appears as a narrow shoulder on $A_1$. The $A_1'$ peak may again be an excited state of the $A_1$ exciton.

In the alkaline-earth fluorides, the ordering of the conduction bands is uncertain.\(^{18}\) The SO splitting of the Ba(5p) atomic level is 2.0 eV but for Sr(4p) and Ca(3p) it is negligible. In BaF$_2$, $(A_1, A_2)$ and $(B_1, B_2)$ may be SO-split exciton pairs.

In region III the crystals with the NaCl structure (KCl, KBr, and RbCl) show broad peaks fairly evenly spaced in energy. In contrast, the crystals with the CaF$_2$ structure (CaF$_2$, SrF$_2$, and BaF$_2$) as well as those with the CsCl structure (CsCl and CsBr)\(^{19}\) show a strong doublet about 4 eV wide dominating region III, with a structure between the doublet and weak structures on either shoulder at low $T$. The positive ions in both the CaF$_2$ and CsCl structures have the same eightfold coordination of nearest neighbors (negative ions), in contrast to the sixfold coordination in the NaCl structure. We thus observe a correlation of the core interband absorption spectra with the spatial coordination of the positive ion and not with the shape of the Brillouin zone (which is identical for the NaCl and CaF$_2$ structures but different for the CsCl structure).\(^{20}\)

These spectra show very dramatic $T$ dependence in all parts of the spectrum, for example at 14 eV in KCl, at 6.7 eV in KBr, and at 17 and 26 eV in BaF$_2$. The $T$ dependence is even stronger than the "giant temperature dependence" seen in photoemission from the silver halides.\(^{21}\) There the temperature sensitivity was attributed to a modulation of the valence-state energies by the thermal vibration of the ions. Similar effects on the core states should be small. Thus the strong $T$ dependence of core interband structures suggests that in these crystals the conduction-band states are also sensitive to lattice vibrations. This is plausible because the conduction-band states retain a considerable atomic character and localization of their wave functions on ionic sites.\(^{11,15}\)

The sharp peaks in region II, considered core excitons, have some interesting properties. Their strength increases with heavier positive ions. They are strongest in the crystals with the CsCl structure. The $A_1$ core excitons in CsCl, CsBr, and BaF$_2$ are much larger than even the excitons at the absorption edge. The $T$ dependence of the core excitons is just as striking as that of the valence excitons.

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10Ref. 8 reports that H. Saito et al. have extended their work (Ref. 7) to low T and associate $A_1'$ as well as $B_1$ and $B_2$ with Rb$^+$ $4f^4$ transitions. This assignment of $A_1'$ seems unlikely because the crystal-field splitting of the core states is negligible and only two core excitons related to $X_2$ should be observed.
14The work of Ref. 4, recently extended to low T, also shows this splitting.
19Recently we have found the CsI spectra to be similar to CsCl and CsBr.
20Differences in the soft x-ray spectra of sc and fcc phases of Cs halides have been observed by M. Cardona et al., Phys. Rev. B 2, 1117 (1970). However, both the coordination of the positive ion and the shape of the Brillouin zone are different for these two structures.

Single-Impurity and Interaction Effect on the Host NMR Linewidth of CuFe in the Kondo State*

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The effects of single Fe impurities on the Cu-host NMR in CuFe have been measured over a wide range of Fe concentrations up to 45 kOe at 1.65 K. The additional impurity $d$-spin conduction-electron spin-correlation effects on the host NMR linewidth initially noted by Golibersuch and Heeger have been shown to be the result of single Fe impurities in the Kondo state; these effects are destroyed at lower applied fields with increasing Fe concentration as a result of Fe–Fe interactions.

There has been a considerable amount of work on the Kondo problem in order to determine the basic properties of an isolated "magnetic impurity" at temperatures below the Kondo temperature, $T_K$. The most thoroughly studied Kondo system has been that of very dilute solutions of Fe in Cu, on which a wide variety of microscopic and macroscopic measurements have been made. The prime difficulty in interpreting the results of many of these experiments has been the separation of the single-Fe-impurity contribution from the contributions of pairs and clusters of Fe atoms. Of particular importance is the possible existence of a "quasiparticle" spin-polarization cloud surrounding an Fe impurity in the Kondo state. The existence of a relatively localized (<9 Å) spin-polarization cloud was inferred by Golibersuch and Heeger (hereafter referred to as GH) on the basis of observed non-linearities in the Fe-impurity contribution to the $^6$Cu-host NMR linewidths. Correlating this data with existing Mössbauer and susceptibility measurements, they concluded that additional correlations exist between the impurity $d$-spin and host conduction-electron spins, which are destroyed at magnetic fields much less than $kT_K/\mu_B$ and temperatures much less than $T_K$. However, the very detailed magnetization measure-