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Selectively excited core-to-core fluorescence of potassium halides

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Core-to-core fluorescence transitions from resonantly excited K $2p^{-1}3d$ states in KF and KI have been measured and specific interaction energies of the final $3s^{-1}3d$ configuration were determined. Delocalization of the excited electron in the $2p^{-1}3d$ states was observed to compete with the core hole decay. Furthermore, evidence for an influence of the chemical surrounding on potassium properties such as the $3s$ core hole lifetime, the $3s3d$ exchange splitting, and the configuration interaction of the $3s$ core hole state was found.

I. INTRODUCTION

In conventional soft x-ray emission (SXE) spectroscopy transitions between shallow core levels and the valence band are investigated. These data have been used to study local electronic structure. Tunable synchrotron radiation makes it feasible to study the excitation energy dependence of SXE spectra. With high resolution in both channels, numerous prospects are at hand, e.g., one can study excitation-emission dynamics, resonant inelastic scattering, and previously unreachable electronic states.

Recently, it was shown that triplet and singlet coupled Ca $3s^{-1}3d$ states in CaF_2 could be populated in core-to-core fluorescence from selectively excited $2p^{-1}3d$ states.[1,2] Thus, the $3s3d$ exchange interaction could be measured and a dependence of the ligand field was found. In general, threshold excited core-to-core fluorescence spectroscopy makes it feasible to study the exchange interaction as a function of $3d$ population, and in this paper, we apply the method to KF and KI.

The potassium salts are typical ionic compounds with a closed shell structure in the ground state. At the potassium site the configuration is K $2p^6 3s^2 3p^6$, and the valence band is basically formed by the outermost valence orbitals of the halide, which locally constitute a filled shell. In KF these are the F $2p$ orbitals, in KI the I $5p$ orbitals. The ionicity in KI, however, is much smaller than in KF, and by comparing the two compounds we can study the influence of the ligand orbitals on the potassium site.

Potassium L absorption spectra have been measured and discussed previously.[3,4] The main absorption structures are identified as excitonic states and discussed without reference to the unoccupied density of states. The nature of the excited states has also been studied in electronic deexcitation spectra,[5–7] partly confirming the excitonic nature of the excitations.

By studying electron excited K L emission spectra of KCl Cooper and LaVilla[8] showed that the K $2p^{-1} \rightarrow 3s^{-1}$ transition in KCl was accompanied by a pronounced low-energy satellite structure, due to configuration interaction in the final state. The structure was studied by Valjakka[9] in all potassium halides and he showed that the final state is dominated by the $3p^{-2}nl$ configurations. These electron excited spectra are all affected by double hole satellites, which are suppressed in excitations close to threshold. Here, we show that the configuration interaction mixing is dependent on the chemical surrounding. Additionally, our data show a chemical influence on the K $3s$ core hole lifetime and the K $3s3d$ exchange splitting.

II. EXPERIMENT

The experiment was performed at the high resolution spherical grating monochromator of the X1B undulator beamline at the National Synchrotron Light Source in Brookhaven.[10] By choice of the widths of the input and output slit, the resolution was set to 0.6 eV and the monochromatized beam from the movable output slit was refocused onto the sample with a bendable float-glass mirror.

The fluorescence was studied with a recently constructed grazing incidence Rowland spectrometer.[11] For the spectral range of the K $L_{2,3}$ core-to-core fluorescence around 260 eV, we used a 5 m grating with 1200 lines/mm and we chose a 30 μm wide input slit to get a resolution of 0.3 eV in the first order. The spectrometer is equipped with a position sensitive multichannel plates detector. To calibrate the energy scale we used binding energies from photoemission spectra (PES) of KCl,[6] for determining the K $2p_{1/2}^{-1} \rightarrow 3s^{-1}$ and $2p_{3/2}^{-1} \rightarrow 3s^{-1}$ fluorescence energies. Our high energy excited spectra of KF and KI show no shift compared to each other. From this we conclude that the chemical shift of the core-to-core transition energies is negligible, permitting us to use the photoemission data of KCl for the determination of the energy difference between the various core hole states. It is well known that phonon relaxation may introduce shifts between SXE and energies deduced from PES,[12] but since we are mainly interested in core-to-core transitions, we expect these shifts to be small. Be that as it may, a sion that concerns energy differences.

For the overview spectra, we removed the input slit and tilted the detector by 30° off the Rowland circle to

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detect the whole energy range at once. This adjustment which is done *in situ* gives us a very high through put with resolution sufficient to separate the main features, whose relative intensities could readily be determined.

All measurements were carried out at room temperature. The KF and KI samples were high purity crystalline powders pressed into an indium foil.

III. RESULTS AND DISCUSSION

In Fig. 1, we present the L photoabsorption spectra of KF and KI measured by total electron yield spectroscopy. These spectra are essentially identical to the spectra reported earlier[3] and we did not observe any changes due to radiation damage during the series of experiments. Nevertheless, we limited the exposure to the intense radiation of X1B to 1 h for each sample spot.

The L absorption spectra of the potassium halides have been successfully interpreted by de Groot *et al.*[4] on the basis of atomic multiplet parameter calculations. The calculations were performed in intermediate coupling: The core electrons are basically treated in a jj coupling scheme to take their large spin-orbit interaction into account, while the outer electrons are considered in LS coupling because of their weaker spin-orbit interaction. Thus, in the final state of the absorption process, the angular momentum cannot be unambiguously assigned to orbital momentum $\underline{L}$, and spin momentum $\underline{S}$. In the discussion of the emission spectra, we will come back to this point.

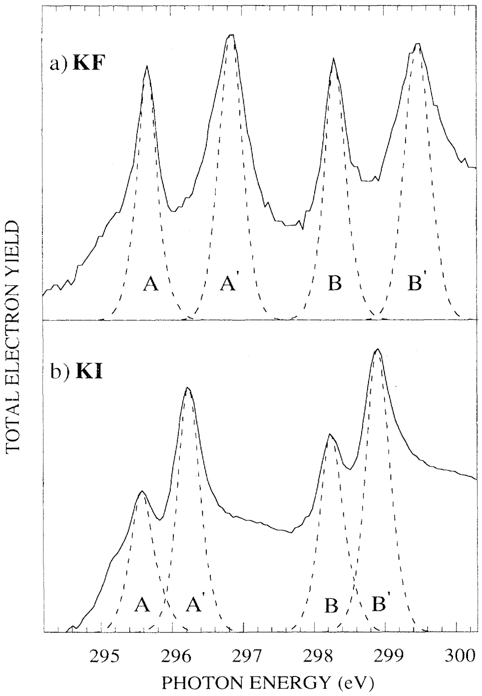

FIG. 1. Potassium $L_{2,3}$ electron yield absorption spectra taken at room temperature on (a) KF and (b) KI (solid lines). The dotted lines are the excitation functions for the emission spectra in Fig. 2. They are given by the absorption spectrum multiplied with the monochromator functions which are normalized Gaussians of 0.6 eV FWHM.

The four dominant peaks of the absorption spectra were identified as resonant transitions from the K^+ $2p^6 3s^2 3p^6 3d^0$ ground state to the core-excitonic $2p^5 3s^2 3p^6 3d^1$ states in the sixfold (octahedral) cubic crystal field of the ionic halides (in the following we will discard the filled shells in our notation). In the core-excitonic final states the K $3d$ orbitals are contracted towards the positively charged K $2p$ core hole and they have stronger atomic character than in the ground state. Compared with the K $2p^{-1}3d$ absorption resonances the cross section of the direct ionization ($2p^6 \rightarrow 2p^5 \epsilon s$) is very small.

In a simplifying picture, the four dominant absorption lines can be interpreted as follows: The cubic crystal field splits the atomiclike $3d$ states in orbitals of e_g and t_{2g} symmetry (in the following referred to as e_g and t_{2g} states) directed towards the halide atoms and in between them, respectively. Together with the spin-orbit splitting of the potassium $2p$ level this results in four absorption resonances, associated with the final states $2p^{-1}_{3/2}t_{2g}$, $2p^{-1}_{3/2}e_g$, $2p^{-1}_{1/2}t_{2g}$, and $2p^{-1}_{1/2}e_g$ with increasing transition energy in this order (denoted as A, A', B, and B' in Fig. 1). The reduction of the crystal field splitting going from KF to KI is explained in the 10Dq model[3] by the increased lattice constant.

We included in Fig. 1 the excitation functions used for our emission spectra, which are given by the products of the absorption spectrum with the photon energy distributions of the exciting beam, i.e., normalized Gaussians with a full width at half maximum (FWHM) of 0.6 eV.

In Fig. 2 we plot the soft x-ray emission spectra of KF and KI excited at the absorption resonances and well above the $2p$ ionization threshold (at 400 eV in the case of KF and at 340 eV for KI). We observe peaks whose energy position, shape, and relative intensity are varying with excitation energy. The proper theoretical starting point for the interpretation of such spectra is the soft x-ray inelastic scattering picture.[13] In our case, however, they can be interpreted within the simpler two-step absorption-followed-by-emission picture. This is because the energy separation of the possible intermediate states is large compared with their inherent lifetime width[4] and the energy bandwidth of the exciting photon beam. Therefore, in the exciting absorption process only one state is populated (as shown by the excitation functions in Fig. 1) and the two pictures are equivalent. Hence, we follow the conceptually simpler two-step model and we discuss the final states populated via the decay of the various excited intermediate $2p^{-1}$ or $2p^{-1}3d$ states.

The emission spectra excited high above threshold consist of two well-separated peaks, which have nearly proper Lorentzian lineshapes. We assign them to the core-to-core transitions from the ionized spin-orbit split K $2p^{-1}$ states to the same final K $3s^{-1}$ state. As we discuss later, in the final $3s^{-1}$ state, observable configuration interaction occurs and the validity of the one electron picture is limited. Nevertheless, the interpretation

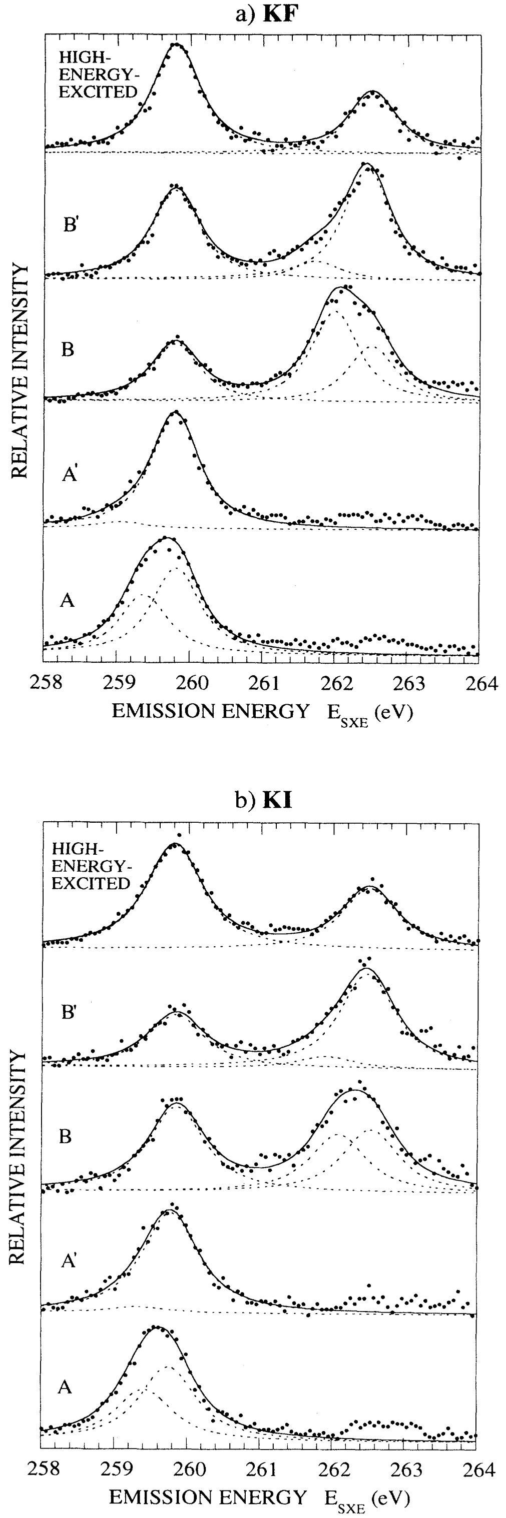

FIG. 2. Soft x-ray emission spectra of (a) KF and (b) KI excited well above the $2p$ ionization threshold (top) and on the resonances corresponding to peaks A, A', B, and B' in Fig. 1. The solid lines are the result of the line shape analysis as described in the text, the dotted lines are Voigt functions, which show the contribution of the different transitions to the spectra.

within this approximation leads to a good understanding of the energy dependence of the soft x-ray emission spectra.

In order to take the resolution of the spectrometer into account, we used Voigt functions with a fixed Gaussian contribution of 0.3 eV FWHM to fit the high energy excited spectra. The FWHM of the Lorentzian contribution to the Voigt functions is 0.68 eV (0.84 eV) in the case of KF (KI). We assign the width of the Lorentzians essentially to the lifetime broadening of the final K $3s^{-1}$ core hole states on the following grounds: The peaks in the absorption spectra have a smaller width than the emission peaks. As the absorption peak widths are dominated by phonon broadening,[4] the K $2p$ core hole lifetime does not contribute significantly to the emission peak width. The phonon broadening should affect the absorption process more than the core-to-core transition, therefore, phonon broadening is also of less importance for the emission peak width. This is supported by the fact that the phonon broadening influences the absorption spectrum of KF more than that of KI, but in emission the KF peaks are narrower than those of KI. No core hole lifetime information can be extracted from the K $3s$ direct photoemission line because it is phonon broadened to nearly a pure Gaussian of around 1.3 eV FWHM.[6]

The K $3s$ core hole can decay via the Coster-Kronig (CK) process: While the $3s^{-1}3p^6 \rightarrow 3s^2 3p^4$ CK decay is energetically forbidden, there is the possibility of CK decays involving valence electrons which have mainly F $2p$ (I $5p$) character in KF (KI). The importance of this channel is demonstrated by the different FWHM in our emission spectra. Due to the lower ionic character of KI, the density of valence electrons is increased in the vicinity of the K atom resulting in an increased CK transition rate and a shorter lifetime. Thus, the 20% larger FWHM of KI demonstrates that the chemical surrounding influences the core hole lifetime.

The small deviations from the fitted Voigt functions in the high energy excited spectra of Fig. 2 are assigned to transitions between multiply excited states, which are populated in the absorption process because of the energy surplus.[14] The additionally excited vacancies stay as spectators during the subsequent decay shifting the emission energy. The intensity ratio of the peaks in the high energy excited emission spectra differs with 1.8:1 (1.7:1) for KF (KI) from the statistical 2:1.

In the emission spectra A and A', in Fig. 2, we find small structures around 262 eV, which are due to transitions from K $2p_{1/2}$ core holes, excited by higher diffraction orders of the primary beam. The low intensity indicates that higher order excited transitions do not contribute significantly to our emission structures.

The emission spectra B and B' (excited on the $2p_{1/2}^{-1}3d$ absorption resonances) consist of an emission structure around 262 eV and a peak at 259.8 eV, which agrees in position and line shape with the low energy emission peak of the high energy excited spectra. Therefore, we assign this peak to decays of $2p_{3/2}$ core holes populated by direct ionization or CK decay of the resonantly excited $2p_{1/2}^{-1}3d$ state with participation of the $3d$ electron.

We now turn our attention to the emission spectra which were excited at energies promoting a K $2p$ electron into an orbital of t_{2g} symmetry (spectrum A and the high energy peak of spectrum B in Fig. 2). It is obvious that the emission structures are broadened and shifted to lower emission energies compared with the peaks of the high energy excited spectra. In addition, they do not possess the shape of a single peak. A lineshape analysis of each peak with Voigt functions as Ansatz (the Gaussian contribution fixed at 0.3 eV) results in two peaks of comparable width and intensity. The energy separation of the two Voigt functions has for the decay of a $2p_{1/2}$ and a $2p_{3/2}$ core hole a mean value of 0.47 ± 0.05 eV for KF (0.39 ± 0.05 eV for KI). The Lorentzian contributions of all fitted Voigt functions agree within ± 0.02 eV for KF (± 0.05 eV for KI) with each other, and with the value of the high energy excited spectra.

Next we concentrate on the emission spectra A' and B' in Fig. 2. In the excitation absorption process, a K $2p$ electron is lifted into an orbital of e_g symmetry (directed towards the halide atoms). At first sight the emission spectra seem to agree in peak positions and line shape with the high energy excited spectra. But fitting single Voigt functions to the spectra resolves systematic deviations at the low energy side of the peaks. Therefore, we refitted the emission structures with two Voigt functions, whose Gaussian and Lorentzian contribution was locked to 0.3 eV and 0.68 eV (0.84 eV) FWHM for KF (KI), respectively. These fits demonstrated that the emission structures consist of two peaks as in the previous case of emission spectra A and B, but with very small intensity for the low energy peak. Hence, the intensity and the position of the low energy peaks should be taken only as crude estimates.

The results of these spectral deconvolutions are summarized in Fig. 3, where we plot the energies of the fitted Voigt functions against the exciting photon energies. For these data, we used for all spectra Voigt functions with fixed Gaussian and Lorentzian contribution as described above. The use of fixed FWHM is justified by the assumption that each peak corresponds to a final state with a $3s$ core hole, whose lifetime broadening dominates the peak width. To show the contribution of the various Voigt functions to the emission spectra, they are inserted as dotted lines in Fig. 2.

The dotted horizontal lines in Fig. 3 give the excitation energy independent emission energies of the high energy excited spectra. For the excitation energies corresponding to the absorption resonances B and B', one finds on the low energy line the peaks corresponding to decays of the ionized K $2p^{-1}_{3/2}$ core hole states, which we discussed above. The dashed lines with slope 1 represent the equations $E_{\mathrm{FS}} = E_{\mathrm{Exc}} - E_{\mathrm{SXE}}$, where E_{Exc} and E_{SXE} are the primary excitation and the secondary emission energies. Transitions from various intermediate to the same final state of energy E_{FS} would follow such a line.

Following the considerations of Rubensson *et al.*[2] concerning their similar study of $\mathrm{CaF_2}$, we assign each double peak to transitions from the resonantly excited K $2p^{-1}3d$ intermediate to K $3s^{-1}3d$ final states. These are split into doublets by the exchange interaction of the remaining $3s$ with the excitonic $3d$ electron, resulting in two final states for each symmetry. The observation that the unlocked Lorentzian contribution of the Voigt functions fitted to the different spectra does not depend on the excitation energy indicates that an excitonic $3d$ electron does not influence the $3s$ core hole lifetime within our experimental accuracy. This was also observed for Ca $3s$ core holes in $\mathrm{CaF_2}$.[2]

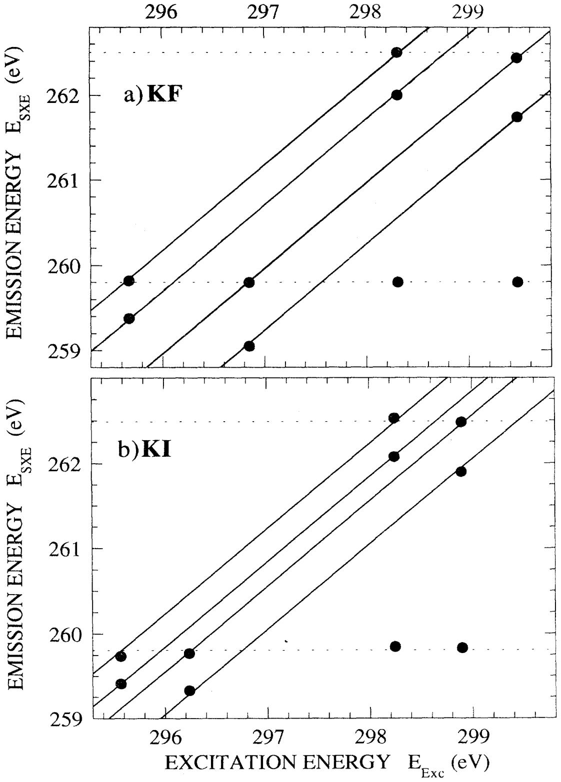

FIG. 3. Peak positions of the Voigt functions for the spectra of Fig. 2 fitted with a Lorentzian contribution of 0.68 eV (0.84 eV) FWHM for KF (KI). The solid lines have slope 1 and correspond to transitions into the same final state. The dotted lines mark the energies of the transitions in the high energy excited spectra.

Our fit procedure gives for KF the final state energies $E_{\mathrm{FS}} = 37.76$ eV, 37.04 eV, 36.30 eV, and 35.83 eV above the ground state (for KI 36.95 eV, 36.44 eV, 36.16 eV, and 35.77 eV) for $3s^{-1}3d$ states with ${}^1e_g$, ${}^3e_g$, ${}^1t_{2g}$, and ${}^3t_{2g}$ symmetry, respectively.

The assignment is supported by the following argumentation: The emission spectra excited at the absorption resonances differ all in the same way from the high energy excited spectra by exhibiting a double peak structure. This demonstrates that the $3d$ electron of the excitonic $2p^{-1}3d$ intermediate states influences the decay. We can exclude that the $3d$ electron is generally unbound in the final state because this would result in a single emission line at lower energy compared to the high energy excited transitions. Hopping of the $3d$ electron from e_g to t_{2g} states would give completely different emission spectra; however, this process is very unlikely because of the different spatial orientation of the e_g and t_{2g} orbitals.

Consequently, the excitonic $3d$ electron stays as a spectator during the decay of the $2p$ core hole. The final states are characterized as a K $3s^{-1}3d$ configuration split by the exchange interaction into a singlet and a triplet state. Remembering that the spin is not well defined in the intermediate state, both final states can be excited even when starting with a singlet ground state.

We observe that transitions to triplet states have the same energy as transitions in the ionized system and accordingly we cannot separate them. The very low relative intensity of transitions to singlet states with e_g symmetry suggests that decays of ionized K $2p^{-1}$ states contribute substantially to these spectra. The ionized states cannot be directly excited, due to the excitonic character of the e_g absorption resonances. We propose that in the K $2p^{-1}3d$ intermediate states the $3d$ electron has a delocalization rate larger than the core hole decay rate, due to hybridization of the K $3d$ orbitals of e_g symmetry with the surrounding. As the e_g orbitals are directed towards the halogen atoms, they hybridize more with the halogen states than the orbitals of t_{2g} symmetry, leading to an increased delocalization rate. And since the transition in the ionized system overlaps accidentally with the transitions into final triplet states, this results in the observed lower singlet to triplet ratio for transitions involving states of e_g symmetry.

We find support for our interpretation of the SXE spectra in terms of a spectator decay with symmetry depending delocalization rates, in a deexcitation study of the $L_{2,3}$ edge in KF (Ref. 5) and KCl (Ref. 6). In contrast to the rather pure spectator decay spectra from the t_{2g} excitations, the e_g decay spectra were found to be dominated by decays of delocalized states. Thus, we conclude that for t_{2g} symmetry the high energy peak has only a negligible contribution of transitions from ionized states, and the ratio of the triplet to singlet intensity reflects the importance of the spin-orbit interaction in the intermediate $2p^{-1}3d$ states in the following way: Neglecting the crystal field one has two possible intermediate states, either A and B, or A' and B'. These states can be described as linear combinations of states with well-defined spin and angular momentum. From the $J = 0$ ground state only intermediate states, $|\Psi_i\rangle$, with $J = 1$ can be reached within the dipole approximation, and we have

$$\Psi_i = a\,|^3P\rangle + b\,|^3D\rangle + c\,|^1P\rangle.$$

In the subsequent emission decay to a final $3s^{-1}3d$ configuration, the rate R_3 of transitions to the $|^3D\rangle$ final state is determined by $(\Delta S = 0)$

$$R_3 \propto |\langle ^3D|T|\Psi_i\rangle|^2 = a^2\,|\langle ^3D|T|^3P\rangle|^2,$$

where T is the dipole operator. Analogously, the rate R_1 of transitions to $|^1D\rangle$ states is

$$R_1 \propto |\langle ^1D|T|\Psi_i\rangle|^2 = c^2\,|\langle ^1D|T|^1P\rangle|^2,$$

and we find that the variation in R_3/R_1, the triplet to singlet intensity ratio, is directly related to variations in $(a/c)^2$, i.e., to the ^3P to ^1P character ratio in the intermediate states.

Our measurements indicate that this ratio is smaller for the higher energy excitation (B) than for the lower energy excitation (A). According to this analysis, the ^1P component is more dominating in the state associated with the absorption peak B than in A. This is in line with the notion that peak B is associated with ^1P in the LS coupling limit. We find for KF the intensity ratios $R_3/R_1 = 1.4$ in spectrum A and $R_3/R_1 = 0.6$ in spectrum B ($R_3/R_1 = 1.4$ and $R_3/R_1 = 1.1$ for KI, respectively).

A thorough analysis of the intensities has to involve the crystal field interaction. It was shown in the case of CaF_2 (Ref. 2) that this interaction has a large impact on the triplet to singlet intensity ratio.

In Fig. 4, we plot the energy scheme of the final $3s^{-1}3d$ configurations for KF and KI. Because of the low intensity peaks in the spectra of e_g symmetry, the exchange splitting value for this symmetry should be taken as a rough estimate only. Nevertheless, the crystal field splittings that we can deduce from the energy schemes are with mean values of 1.34 eV for KF and 0.73 eV for KI in good agreement with the splittings in the absorption spectra. A calculation for free K^+ ions[16] based on the density functional theory in the local spin density approximation, including exchange and correlation from the homogeneous electron gas, predicts the exchange splitting to be 0.56 eV close to our measured value of 0.47 eV (0.39 eV) for KF (KI) in t_{2g} symmetry. Our data suggest that the exchange splitting is slightly larger in KF than in KI. This difference is on the order of our measurement accuracy but can be observed directly in the t_{2g} emission structures, which are broader in KF than in KI although the single Lorentzians are narrower.

By comparing the energy of the spectator decay with the transition energy in the ionized system, we can determine the difference, ΔC, between the Coulomb interaction of a $2p^{-1}3d$ and a $3s^{-1}3d$ exciton. Assuming that

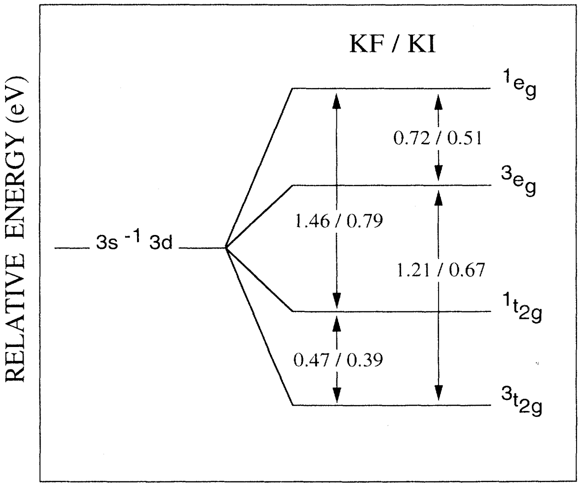

FIG. 4. Energy scheme for the final K $3s^{-1}3d$ configuration with the experimentally determined exchange and crystal field splitting in eV. First values are for KF, the second one for KI.

the exchange energy splits the final state symmetrically according to the simple rule of adding and subtracting the exchange integral for singlet and triplet state, we find from our fit results a value of ΔC=0.23 eV for both, KF and KI. The meaning of this value is that the $2p^{-1}3d$ Coulomb interaction is larger than the $3s^{-1}3d$ reflecting the stronger localization of the $2p$ core holes. It has been observed for other ionic compounds[12] that the ionized intermediate states may be subject to phonon relaxation more than the excitonic states before the decay takes place. This would affect our ΔC value and, therefore, one has to regard it as an upper limit.

Sugiura and Yamasaki *et al.*[15] recently determined the K $2p^{-1}3d$ exciton binding energies in the potassium halides to be some eV. This is in agreement with values obtained from the combination of direct photoemission[6] and band gap data. This apparently contradicts our observation of substantial intensity from ionized $2p^{-1}$ states when exciting the $2p^{-1}3d$ resonances of e_g symmetry. A similar contradiction between the predicted ionization limit and the energy at which emission from ionized states appears was found in CaF_2 by Rubensson *et al.*[2] The contradiction would be resolved by assuming the existence of an excitonic state, where the excited electron does not influence the decay spectra. We speculate that such a state could involve an electron capture in the potential wells of the neighboring potassium atoms.

Taking the $2p^{-1}3d$ exciton binding energies from Sugiura and Yamasaki,[15] we can calculate the values for the $3s^{-1}3d$ excitons with t_{2g} symmetry. We find the binding energies to 2.3 and 1.8 eV for KF (1.2 and 0.8 eV for KI) in $^3t_{2g}$ and $^1t_{2g}$ symmetry, respectively. An uncertainty of ±0.4 eV results mainly from the $2p^{-1}3d$ binding energies.

In the following, we discuss the configuration interaction in the final state of the emission process. For that purpose, we show in Fig. 5 overview spectra for KF (a) and KI (b), which are observed with the detector tilted 30° off the Rowland circle and a wide entrance slit in the spectrometer. Both spectra consist of a main peak at 260 eV, the previously discussed K $2p^{-1} \rightarrow 3s^{-1}$ core-to-core transitions, and a smaller peak at lower energy. The overview spectrum from KI has an additional peak at higher energy, due to transitions from the mainly I $5p$ valence band to the K core hole. These interatomic transitions represent (18 ± 1)% of the whole spectral intensity. We do not detect corresponding intensity for KF, since the density of valence band electrons is reduced substantially in the vicinity of the K^+ anions, according to the stronger ionic character of KF. This observation demonstrates that the interatomic contributions to the soft x-ray emission intensity are small. In K emission, interatomic transitions from the valence band are assigned to the so-called $K\beta_5$ structure. The relative intensity of the $K\beta_5$ line is, however, less in KI than in KF,[15] obviously not in line with our results and ionicity arguments. Furthermore, the $K\beta_5$ line in the KI spectrum lacks the fine structure of the I $5p$ band seen in photoemission. These observations suggest that other mechanism may contribute to the K emission spectra.

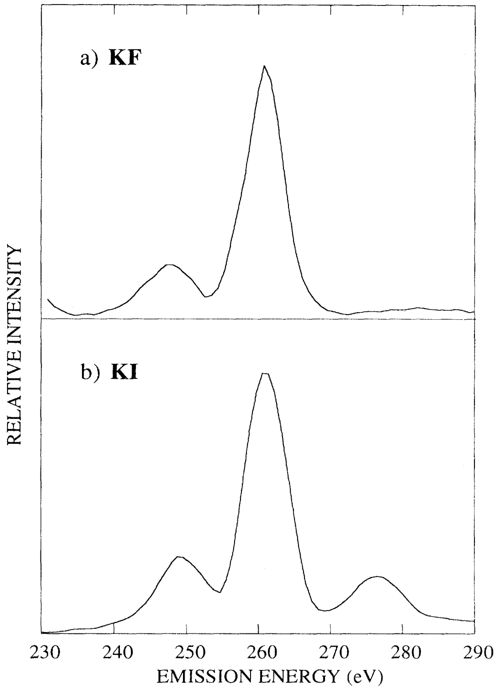

FIG. 5. Overview spectra of (a) KF and (b) KI measured with off-Rowland tilted detector.

The low energy peak is associated to transitions into final states of mainly the $3p^{-2}$ configuration with an extra excited electron. Such satellites were first seen by Cooper and LaVilla[8] and later studied for the potassium salts by Valjakka.[9] Dipole transitions to these states occur since the $3p^{-2}nl$ and $3s^{-1}$ configurations are mixed,[9] and the importance of the configuration interaction can be directly measured via the satellite to main peak intensity ratio. We find that (21±1)% of the spectral weight of the two peaks is in the satellite for KF and (26 ± 1)% for KI. These values are, within our measurement accuracy, independent of the excitation energy, i.e., an excitonically bound $3d$ electron in the intermediate state does not influence the intensity distribution.

IV. CONCLUSION AND OUTLOOK

We used core-to-core transitions to study the K $3s^{-1}3d$ configuration in KF and KI and found that the $3d$ electron is excitonically bound to the $3s$ core hole. We determined the binding energies of the various excitonic states, the exchange splittings, and the crystal field splittings. The importance of the spin-orbit interaction in the $2p^{-1}3d$ states manifests itself in the intensity ratio of transitions into final singlet states vs transitions into final triplet states, that cannot be reached in purely LS-coupled systems. Furthermore, we observed an influence of the chemical surrounding on the lifetime of the K $3s$ core holes and the configuration interaction.

In the future, we will extend the studies of threshold excited core-to-core fluorescence to other ionic compounds like paramagnetic salts and rare earth compounds. Apart from the determination of interaction energies in the final states, one can compare the delocalization rate of the excited electrons with the core hole decay rate. The present data and earlier measurements on CaF_2 suggest that the electron is locally decoupled below the ionization limit predicted from PES and optical absorption. This may be a general feature for ionic compounds.

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