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Double core excitations in lithium halides

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Resonant inelastic x-ray scattering spectra of LiF, LiCl, LiBr, and LiI excited in the vicinity of the Li double core hole resonances are presented. All lithium halides show similar phenomenology, including scattering via states where both excited electrons are localized during the scattering process, as well as states where one electron delocalizes. Also transitions that involve additional band excitations are observed. A strong influence of the chemical surrounding is found, and it is discussed in terms of the ionic character of the chemical bond.

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I. INTRODUCTION

Recently we reported the observation of resonant inelastic x-ray scattering (RIXS) at states in solid LiCl, where both Li core electrons are excited.[1,2] The spectra revealed a rich phenomenology, with a plethora of spectral features representing various electronic states and resonances. States in which both electrons are localized at the double core hole site were found, as well as states in which one of the electrons delocalizes during the scattering duration time. It was shown that a coupling to the surrounding chlorine atoms led to induced band transitions, accompanying the local double core excitation, and it was concluded that the excitations to a large extent are dependent on the chemical surrounding of the lithium ions. This suggests the possibility of using RIXS associated with double core excitations for chemical analysis, motivating the extension of the investigations to other compounds. In this work, we present a study of a series of lithium halides: LiF, LiCl, LiBr, and LiI. In general, we find the same type of excitations in all the compounds, and we discuss differences and similarities.

II. EXPERIMENTAL

The measurements were made at the I511-3 beamline[3] at MAX-lab, Sweden. This is an undulator beam line with a photon flux at the end station of approximately 10^{13} photons per second. The incoming light was monchromatized using a modified SX-700 monochromator with a resolution of 100 meV in the energy region of 140–170 eV. The beam was focused to a 20 μm (vertical) by 50 μm (horizontal) spot using Kirkpatrick-Baez mounted elliptical refocusing mirrors. Soft x-ray emission (SXE) spectra were measured with a Gammadata Scienta XES-300 (Ref. 4) grazing incidence grating spectrometer in the plane of polarization (horizontal). The XES-300 was operated in slitless mode using the beam spot as source in the spectrometer optics. Using the elastically scattered exciting radiation the spectrometer resolution was determined to be ~0.3 eV. Partial fluorescence yield (PFY) measurements were made with the XES-300, with the detector gated to only accept events in a certain energy interval covering the emission features of interest. The count rate from the integrated detector signal was recorded as a function of excitation energy.

Polycrystalline samples of LiF, LiCl, LiBr, and LiI were made from polycrystalline grain salts that were compressed into solid tablets of approximately 10 mm diameter and 2 mm thickness. The LiI crystals had to be reduced in size prior to compression into a tablet using a pestle. To avoid sample damage during the measurements, the samples were moved at regular intervals so that the synchrotron radiation successively hit a different spot on the sample after a given time. For LiF the time between movements was 5 s in PFY and 10 s in SXE, for LiCl the time was 5 s in the PFY and 10–30 s in SXE, LiBr had 10–20 s in PFY and 20–25 s in SXE, and LiI had 5 s in PFY and 10 s in SXE. There are still traces of sample damage in some of the measurements, primarily in LiBr. Sample damage is obvious by the appearance of the Li metal hypersatellite[5] at 83 eV emission energy. We do not observe any other exposure-time dependent spectral changes. The samples were probed for homogeneity by ensuring that the signal was independent of spot position over the whole scanning region. The total acquisition time for an SXE spectrum is on the order of 30 min for LiF, LiCl, and LiBr, and 70 min for LiI. For PFY spectra, several energy scans have been added so that each energy point represents about 60 s of radiation exposure.

III. RESULTS AND DISCUSSION

A. Assignment of the main features

Figure 1 shows an overview of the measured SXE spectra of LiF, LiCl, LiBr, and LiI, excited in the 140–170 eV excitation energy range. The maps are "equi-intensity" contour diagrams showing scattering intensity as a function of emission energy (E_2) on the horizontal axis and excitation energy (E_1) on the vertical axis. To the right of each map are PFY spectra monitoring the integrated signal in the main emission energy interval.

In the scattering maps there are some artifacts that are not directly related to the double hole resonances. The dots in the diagonal line of intensity crossing the scattering map from the lower left corner, $E_1 \approx 150$ eV, $E_2 \approx 75$ eV, up to $E_1 \approx 170$ eV, $E_2 \approx 85$ eV, are due to elastically scattered radiation in second order of diffraction. These lines are used for energy calibration and determination of the spectrometer resolution but are otherwise ignored. The dots also illustrate

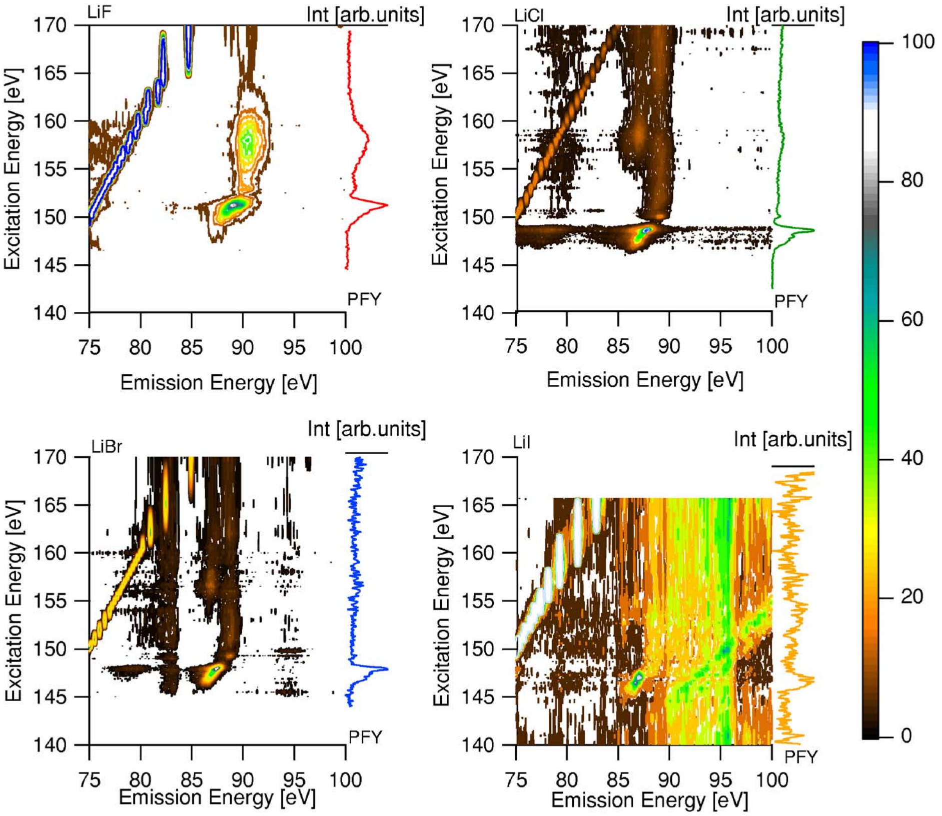

FIG. 1. (Color online) Scattering maps for the four investigated lithium halides. Each map consists of several emission spectra taken at different excitation energies. To the right of each spectrum, the measured PFY spectra are shown, with increasing intensity towards the right.

the number of measured SXE spectra per excitation energy interval, which limits the vertical energy resolution in the scattering map. In regions of sharp resonances, the density of spectra is large, while at higher excitation energies we have chosen larger excitation-energy spacing, indicated by larger vertical extension of the elastic peaks.

In LiBr and, to some extent, in the other lithium halides there is intensity at constant $E_2=83$ eV. This is emission from the Li metal hypersatellite,[5] indicative of some remaining radiation damage. There is also background intensity in the region of $E_2=90-97$ eV, seen primarily in the LiI map but also in LiBr and LiF and spectra. This signal is found at constant emission energy and resembles the soft X-ray emission spectrum associated with transitions to Si 2*p* vacancies (Si L emission) in SiO_2.[6] Although we cannot account for the mechanism for SiO_2 contamination in the sample preparation procedure, we must assign it accordingly. Note that the signals of interest are relatively weak and a minute SiO_2 contamination would lead to an appreciable signal at these excitation energies. Since this signal has a constant shape and is unrelated to the lithium signal, it is ignored. When this signal is subtracted, this is clearly stated.

There are also some horizontal lines seen in the background. These are artifacts from normalization between spectra with slightly different backgrounds rather than real intensity variations. Normalization of emission intensities has been done by matching the energy region and the integrated intensity in the SXE spectra with the measured PFY.

In the scattering signal, several common features are observed. All lithium halides show a resonant feature around $E_1=145-150$ eV and $E_2=84-89$ eV. The emission is dispersing with excitation energy indicating a scattering event where the same final state is reached over the whole range of excitation energies, as we found for LiCl.[1,2] First we summarize the assignments of features and notation in Ref. 2.

With GS and e_L denoting the ground state and an electron localized at the lithium site, respectively, the main dispersing features at around $E_1=145-150$ eV is assigned to α_1 scattering, which in a simplified one-electron picture can be written

$$GS \rightarrow 1s^{-2}e_L^2 \rightarrow 1s^{-1}e_L^1.$$

At excitation energies higher than ~150 eV, emission appears at a constant emission energy of approximately ~87–90 eV. Here, one of the excited electrons in the intermediate state delocalizes in the conduction band, and with e_{CB} denoting a conduction band electron, the process (β_1) can be written

$$GS \rightarrow 1s^{-2}e_L^1 e_{CB}^1 \rightarrow 1s^{-1}e_{CB}^1.$$

We also find scattering features at $E_1=146-148$ eV and $E_2=77-79$ eV, involving the excitation of a valence band electron to the conduction band during the emission step. With e_{VB} representing a valence band electron, the process (α_2) can be written

$$GS \rightarrow 1s^{-2}e_L^2 \rightarrow 1s^{-1}e_L^1 e_{VB}^{-1} e_{CB}^1.$$

At higher excitation energies, where one of the excited electrons in the intermediate states is delocalized, there is also intensity at $E_2=75-80$ eV, also corresponding to additional band excitations during the emission step. This process (β_2) can be written

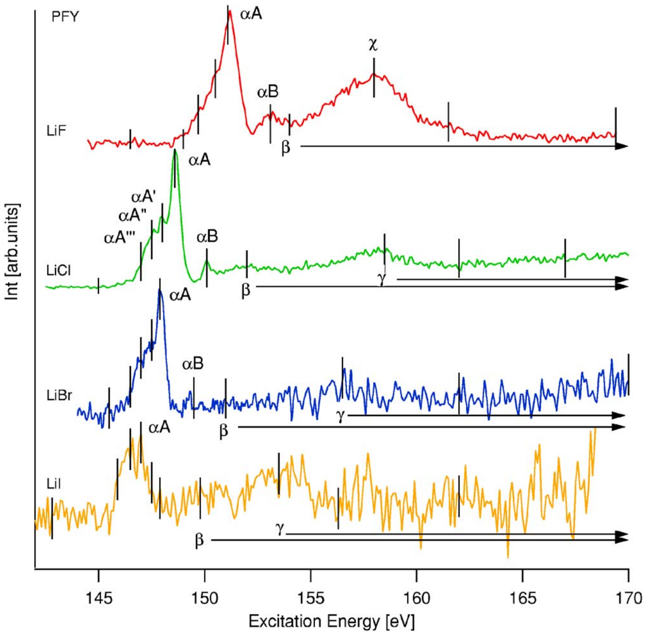

FIG. 2. (Color online) The PFY spectra monitor the integrated emission in a limited energy region, 85–96 eV in LiF, 84–92 eV in LiCl, 83–95 eV in LiBr, and 83–92 eV in LiI. The features are labeled according to the assignments discussed in the text. The vertical bars in the PFY spectra mark the excitation energies used for measuring the SXE spectra presented in Figs. 5–8.

$$GS \to 1s^{-2}e_L^1e_{CB}^1 \to 1s^{-1}e_{VB}^{-1}e_{CB}^2.$$

For $E_1 = 153-158$ eV, and higher a further feature appears at constant emission energy $E_2 = 85-87$ eV. This signal is assigned to a process where a band transition occurs in conjunction with the initial double excitation. This process (γ_1) is written

$$GS \to 1s^{-2}e_L^2e_{VB}^{-1}e_{CB}^1 \to 1s^{-1}e_L^1e_{VB}^{-1}e_{CB}^1.$$

Most of the described scattering processes get substantial intensity in all lithium halides, albeit with differences in relative intensity and energy positions. Below we discuss similarities and differences in some detail.

B. Partial fluorescence yield

Figure 2 shows the PFY spectra of the four lithium halides, monitoring the integrated intensity in a small emission energy window as a function of excitation energy. The energy windows are 85–96 eV for LiF, 84–92 eV for LiCl, 83–95 eV for LiBr, and 83–92 eV for LiI. The α resonance can be separated into two main regions (as done for LiCl in Ref. 2), where α-A is the first most intense resonance after which there is small dip in the intensity, followed by the α-B resonance, which is located close to the β excitation thresholds. The intensity and shape of the α-B resonance is varying with halide, being quite weak in LiBr, and below the detection limit in LiI. Subfeatures in the α-A resonance of LiCl (Ref. 2) are denoted α-A, α-A', α-A'', and α-A''' in Fig. 2. Counterparts are found in the other halide PFY spectra, although with different relative intensities. In Ref. 2, PFY spectra were measured in both vertical and horizontal directions. These measurements showed a strong angular anisotropy, indicating that the main α-A peak can be associated with scattering primarily to final states with large s character, whereas the primed features are associated either with final states of more d character or a general symmetry breaking, which leads to loss of angular anisotropy. Since no angular-resolved measurements have been performed for the other halides, no conclusive symmetry assignments can be made. The similarity of the spectra, however, makes it plausible that the structures seen in the α-A resonance corresponds to similar states as in LiCl.

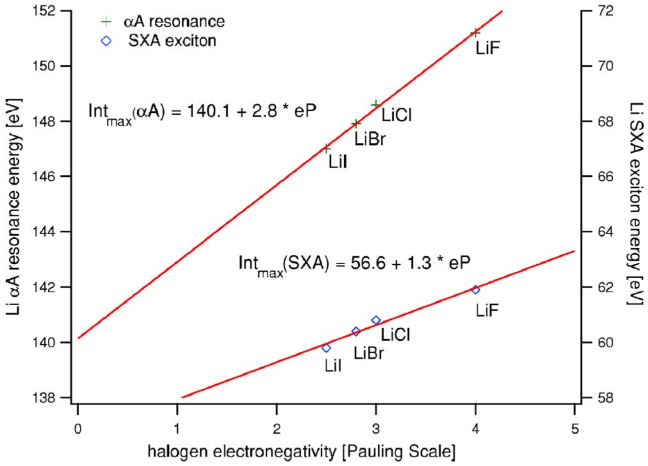

FIG. 3. (Color online) The peak position of the double excitation (α-A), and the SXA exciton position (Ref. 10) in LiF, LiCl, LiBr, and LiI as a function of electronegativity (Pauling scale) of the halogen atom.

The relative intensities of the primed and the unprimed main α-A feature vary with halide. Tentatively, we attribute the trend to increased breaking of the atomic angular-momentum symmetry, as the localization decreases when the halogen atom electronegativity decreases going from LiCl to LiI. In LiF the α-A peak is broader than in the other halides and the identification of primed and unprimed regions is not unambiguous.

The energy position of the main α-A resonance is different in the lithium halides. There is a monotonic shift towards lower excitation energies as the atomic number of the halogen atom increases. In Fig. 3 we demonstrate that the α-A peak position to a good approximation is linearly dependent on the Pauling scale electronegativity of the halogen atom. A fitted line to the α-A peak position gives a slope of 2.8 eV/Pauling unit. Also for the main peak in SXA a straight line can be fitted, and here the slope becomes around 1.3 eV/Pauling unit. Thus, the double excitations are more sensitive to the chemical surrounding than the single core excitations. This is in line with the predictions of Cederbaum and co-workers[7,8] that binding energies associated with double core vacancies are more sensitive to the chemical surrounding than single core hole binding energies. In general, this is attributed both to differences in Coulomb repulsion and excited state relaxation.

At energies above the α resonance (A and B in Fig. 2), is a region where the β excitations are found at almost constant intensity. Small variations with excitation energy may represent variations in density of states (DOS) in the conduction band. In the region of 153–158 eV excitation energy, there is an intensity increase in all PFY spectra. This energy corresponds to the main α-A resonance energy plus the band gap energy in LiCl (9.4 eV), LiBr (7.6 eV), and LiI (6.1 eV) as taken from Ref. 9. Therefore, we attribute the increase in the PFY intensity to additional band (γ) excitations.

In LiF the energy position of the intensity maximum (χ) at 158 eV is too low for assignment to additional band excitations [band gap=13.6 eV (Ref. 9)]. Furthermore, the emission energy does not agree with an interpretation as γ_1 scattering (see Fig. 1 and RIXS discussion). A possible interpretation as a resonance in the β_1 channel due to structures in the unoccupied DOS can be ruled out, because of significant changes in the emission profile at resonance. We speculate that a localization may occur at these energies corresponding to excitations with one excited electron in $n=2$ and the other in $n=3$. Such states would be highly influenced by the ligand atoms and a broad structure with little dispersion is expected. With this interpretation, the observations imply that LiF is the only halide for which this phenomenon can be experimentally confirmed, suggesting that only here the wave functions are sufficiently local for quasiatomic $n=2$, 3 excitations.

C. Resonant inelastic scattering

1. General

In Fig. 4, the RIXS spectra excited at the α resonance are plotted on the final state energy scale and compared to the SXA spectra measured by Haensel *et al.*[10] The excitonic nature of the excitations is obvious when comparing the energy positions to the estimated energy for the bottom of the conduction band, indicated by arrows in Fig. 4. Most of the intensity in the resonantly excited emission spectra coincides with the intensity of the SXA exciton peaks. This suggests that the final states for the scattering at the double excitations in the lithium halides are similar to the exciton states reached in K-edge absorption. The LiCl and LiBr spectra also show a high-energy tail extending beyond the ionization limit. These tails have been interpreted[2] as representing a shake-off process where the remaining excited electron is promoted to the conduction band during the radiative decay,

$$GS \rightarrow 1s^{-2}e_L^2 \rightarrow 1s^{-1}e_{CB}^1.$$

Note that the emission is dispersing on the final state energy scale within the energies of the SXA excitons, indicating that final states of higher energy are reached as the excitation energy increases within the α resonance. This dispersion on the final state scale is due to excitation of unresolved states at different energies. The angular dependence found in LiCl suggests that these excitations are of electronic as well as vibronic nature.[2]

Changing the excitation energy from the α-A to the α-B resonances leads to a shift in final state energy, which is decreasing through the halide series. In LiF this shift is ~0.9 eV, in LiCl is ~0.2 eV, and in LiBr it is ~0. In LiI, a distinct α-B resonance cannot be identified, and no shift is observed in spectra excited directly above the α-A resonance. This shows that the formation of states corresponding to α-B resonance is highly dependent on the ionicity of the bond. In Figs. 5–8 the SXE spectra, covering the whole excitation energy region, are shown on the emission energy scale. The excitation energies are marked in Fig. 2, and the spectra represent a selection of the SXE spectra constituting the data shown in Fig. 1.

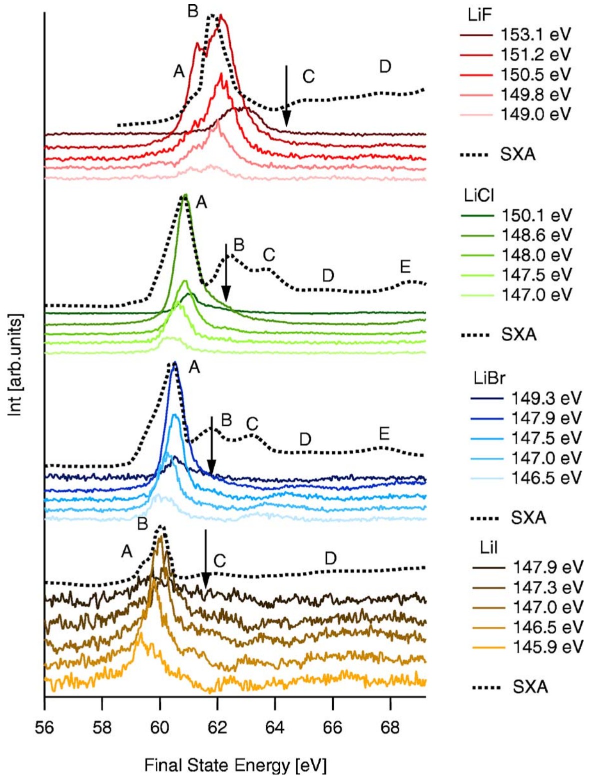

FIG. 4. (Color online) RIXS spectra excited at the α-A and α-B resonances, shown on the final state energy scale together with SXA spectra measured by Haensel *et al.* (Ref. 10). Arrows mark the bottom of the conduction band, 64.4 eV, 62.3 eV, 61.8 eV, and 61.6 eV for LiF, LiCl, LiBr, and LiI, respectively.

2. LiF

The α_1 scattering spectra of LiF (Figs. 4 and 5) show two peaks separated by 0.8 eV. The splitting agrees with the splitting in the SXA spectrum (Fig. 4) between the low-energy shoulder (A) and the main exciton peak (B). Also, the absolute energy positions of the features in SXA and the scattering spectra coincide. The relative intensities of these two structures vary with excitation energy. At low-excitation energies, they have about the same intensity, and as the excitation energy increases the relative α_1-B intensity increases and reaches a maximum at 150.5 eV, while the whole feature has its intensity maximum at 151.2 eV excitation energy (Fig. 5). We conclude that the α_1 scattering populates similar states as the direct absorption process. The excitation energy dependence is in line with the assignment of two exciton states of different symmetry to the main feature in the SXA spectrum. In addition, it shows that several electronically

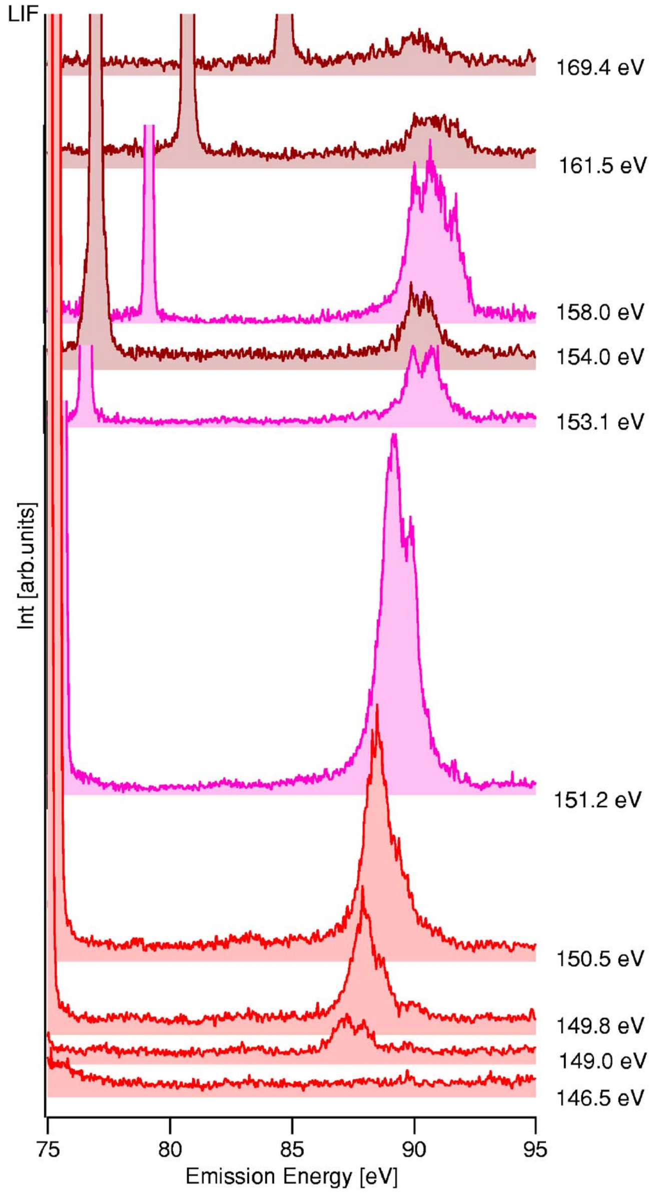

FIG. 5. (Color online) Emission spectra of LiF excited at the indicated energies, which are also marked in the PFY spectra in Fig. 2. Spectra excited at 151.2 eV, 153.1 eV, and 158.0 eV are measured with a slightly higher energy resolution (~0.25 eV) than the other spectra (0.3 eV).

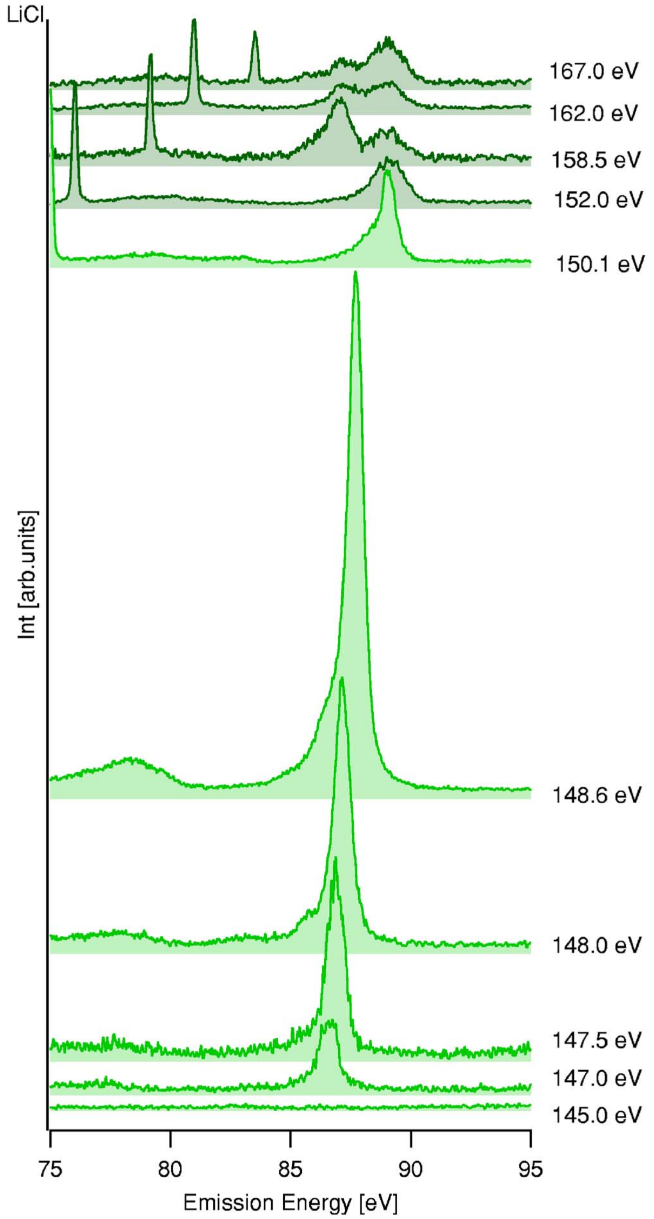

FIG. 6. (Color online) Emission spectra of LiCl excited at the indicated energies, which are also marked in the PFY spectra in Fig. 2.

different intermediate states contribute to the RIXS resonance (153.1. eV).

The β_1 scattering in LiF is best represented by the spectrum excited at 154.0 eV (Fig. 5). A double structure with components at E_2=89.9 eV and E_2=90.5 eV is found. The features are shifted to somewhat lower emission energies compared to the spectrum excited at the α-B resonance. This is in concordance with what is found for LiCl, for which a slight dispersion of the emission peaks occurs as several inequivalent delocalization thresholds are reached.[2]

As discussed earlier, the increased intensity at excitation energies around 158 eV cannot be explained by resonant β scattering. This is obvious due to the pronounced shape changes in the emission profile. With the interpretation of this resonance as due to local n=2, 3 states, the changes in the spectra at these energies can be attributed to the influence of a local n=3 electron.

Evidence for α_2 and β_2 scattering is found at the edge of the spectrometer window at E_2=75−77 eV. The overlap with the elastically scattered excitation radiation diffracted in second order makes it difficult draw any conclusion regarding their intensity and spectral shape, although the intensity relative to the main peak seems smaller than in the other halides.

Intensity due to γ_1 scattering, prominent in the spectra of the other halides, is below the detection limit in the LiF spectrum. This indicates that the coupling between double core excitations and the valence electrons is much weaker in LiF than in the other halides. This is reasonable, considering the higher ionicity of the bond.

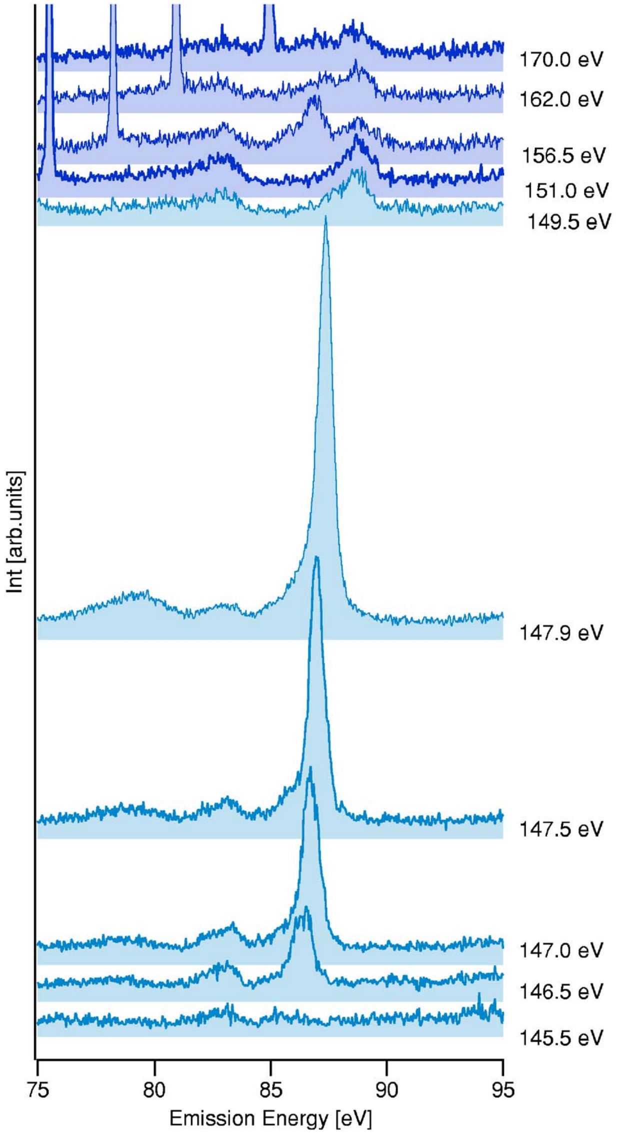

FIG. 7. (Color online) Emission spectra of LiBr excited at the indicated energies, which are also marked in the PFY spectrum in Fig. 2.

3. LiCl

The LiCl spectra (Fig. 6) have been discussed at some length in Ref. 2, and here the main conclusions are briefly summarized.

From the angular resolved measurements, it was concluded that there are several sharp final states of *s* character contributing to the main emission peak. As excitation energies are increased intensity shifts to higher final state energies, states with *d* character (or with mixed symmetry due to vibronic coupling) are spread out over a broader energy range. States of *s*, *p*, and *d* character are represented over the whole range of the SXA-*A* peak.

The α_2 emission is most clearly visible at $E_2=77.8$ eV for $E_1=148.6$ eV. It appears about 9 eV below the main α_1 peak.

At 152.0 eV excitation energy and above (Fig. 6), the excited states in LiCl are delocalized and the spectrum represents β_1 emission. This feature does not disperse with excitation energy and does not change shape to any large degree as the excitation energy is varied. There are some intensity variations most likely reflecting the variations in the unoccupied DOS.

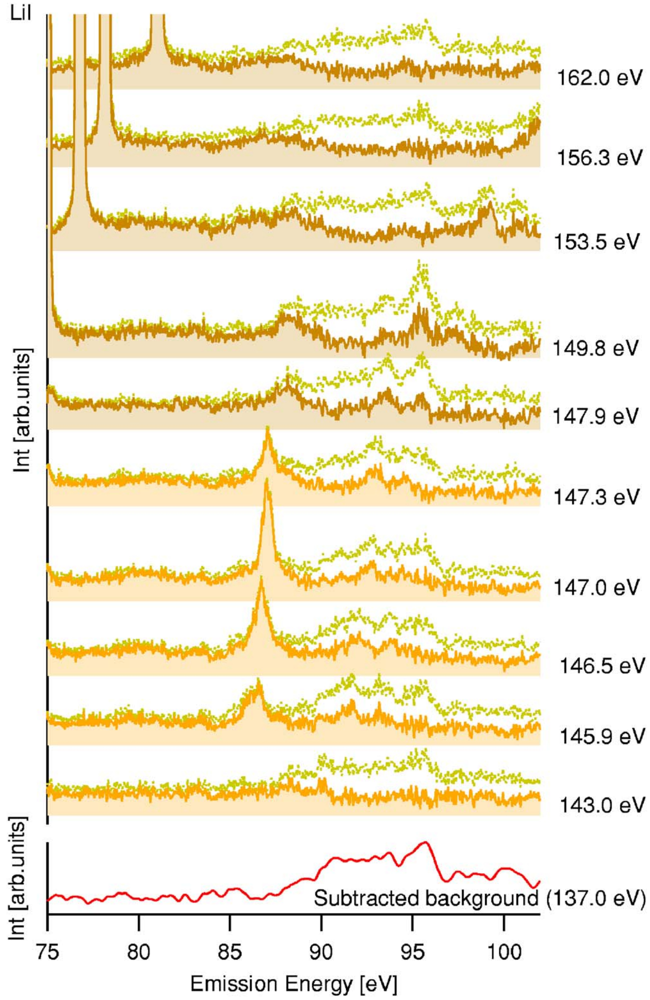

FIG. 8. (Color online) Emission spectra of LiI excited at the indicated energies, which are also marked in the PFY spectrum in Fig. 2. Spectra are presented both as raw data (green) and with the background determined by the spectrum excited far below thresholds (137 eV) subtracted (yellow).

The β_2 emission feature is found 9 eV below β_1, in line with the interpretation as an additional band excitation.

At 158.5 eV excitation energy, the γ_1 scattering reaches its maximum intensity at $E_2=87.1$ eV. In Ref. 2 we found that the general structure of this peak resembles the α_1 scattering profile, reflecting the fact that the doubly excited core at the lithium site is not influenced to any great extent by the conduction band electron and the valence hole. The minimum in β_1 scattering coinciding with the γ_1 maximum was discussed in terms of interference effects in Ref. 2.

4. LiBr

The double core hole scattering phenomena in the LiBr spectra (Fig. 7) are very similar to those of LiCl, where all principal features find their counterparts. The similarities include the slight dispersion on the final state energy scale, and the high-energy tails, indicating a population of delocalized final states (Fig. 4). The intensity ratio between the main peak and the tail at the resonance is somewhat smaller in LiBr than in LiCl (Fig. 4), suggesting a higher presence of *d*-character states (or increased symmetry breaking) at energies beyond the main SXA-*A* peak.

Also at higher excitation energies, the emission spectra of LiBr (Fig. 7) are similar to LiCl, and the features can be assigned accordingly. With increasing excitation energy, the LiBr emission dispersion is lost and β_1 scattering appears as broad structure at E_2=88.7 eV.

At 156.6 eV the energy for the γ_1 resonance is found, similar to the LiCl resonance, but at a lower excitation energy, corresponding to the smaller band gap in LiBr.

LiBr is, however, more sensitive to radiation damage than LiCl, and therefore the Li metal hypersatellite at 83 eV emission energy is more pronounced. This feature is partly overlapping the β_2 emission, making it difficult to be specific about the spectral profile.

5. LiI

For the spectra presented in Fig. 8, a structured background has been subtracted. The spectrum measured below the Li double excitation resonances at E_1=137.0 eV has a form with similarities to the Si L emission spectrum of SiO$_2$. Assuming that the spectral shape of this signal is independent of excitation energy, a maximum of this signal was subtracted with the constraint that the residual intensity must be positive.

Regarding α_1 scattering we find similar behavior in LiI and LiF. In Fig. 4 it can be seen that the scattering at all α excitations is confined to the SXA-*A* and -*B* peaks. Contrary to what is found in the LiF scattering spectrum, there is no clear split in the main emission feature. There is, however, a shoulder coinciding with the SXA-*A* peak for excitation energies of 145.9 and 146.5 eV. The split between the *A* and *B* peaks in the SXA is 0.4 eV,[10] very close to the experimental resolution (0.3 eV). Most of the intensity is concentrated to the exciton peak, and there is no significant signal corresponding to population states in the region marked *C* in the SXA spectrum. At excitation energies larger than the resonance energy, E_1=147.9 eV, the emission spectrum consists of one broad peak without any apparent internal structure.

There is no distinct transition from α_1 to β_1 scattering as the energy increases, indicating that the α resonance is located close to the delocalization thresholds. Intensity just below 90 eV in the emission spectrum excited at 147.9 eV is assumed to represent β_1 scattering. Around E_2=80 eV, the α_2/β_2 emission can be seen as a broad structure just above the background. At 153.5 eV excitation energy, γ_1 scattering is observed at E_2=86.6 eV. The intensity does not, however, exceed the β_1 emission intensity as it does in the corresponding LiBr and LiCl spectra.

In addition to what is found for the other halides, two dispersive features are observed at around E_2=88 eV for E_1=143.0 eV and around E_2=98.5 eV for E_1=153.5 eV excitation energy (Fig. 8). These two peaks disperse with excitation energy, indicating a scattering event to the same final states for all excitation energies. These features are assigned to final states with *I*4*d* holes. The intermediate states for populating such states in RIXS are the highly correlated states, which involve $I3p^{-1}$ and $4d^{-2}4f$ configurations, thus constituting another example of double core hole RIXS. The population mechanism for these final states will be further discussed elsewhere.[11]

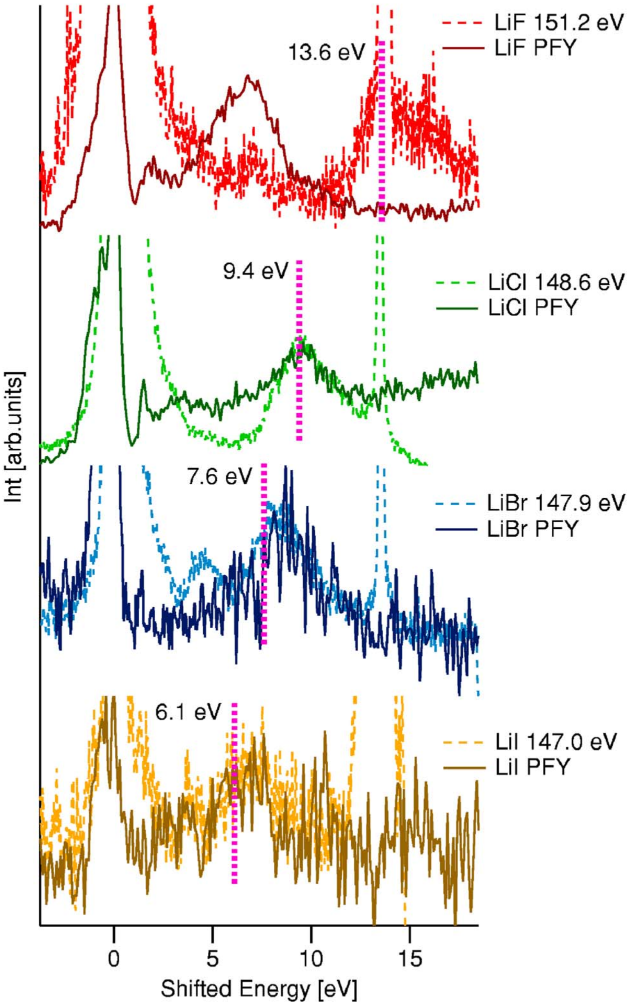

FIG. 9. (Color online) The α_2 emission from the double excitation resonance, excited at 151.2, 148.6, 147.9, and 147.0 eV for LiF, LiCl, LiBr, and LiI, respectively. The spectra are shown on the final state energy scale, from which the SXA exciton energy (Ref. 10) has been subtracted, 61.9 eV for LiF, 60.8 eV for LiCl, 60.4 eV for LiBr, and 59.8 eV for LiI. The PFY spectra are shifted by the αA resonance energy as given above. The vertical dotted bars show the band gap energies (Ref. 9).

6. Band excitations in the first and second steps

In Fig. 9 SXE spectra excited at the α-*A* resonances are shown on the final state energy scale, where the exciton energy[10] has been subtracted: 61.9 eV for LiF, 60.8 eV for LiCl, 60.4 eV for LiBr, and 59.8 eV for LiI. Here, the energy positions correspond to excess energies relative to the exciton final state. The PFY spectra are shifted by the α-*A* peak energy, i.e., the same energy as the excitation energy of the

SXE spectra: 151.2 eV for LiF, 148.6 eV for LiCl, 147.9 eV for LiBr, and 147.1 eV for LiI. Here, the energy positions correspond to excess energies relative to the localized doubly excited state. The vertical dotted bars indicate the band gap energy[9] for the four lithium halides, 13.6 eV, 9.4 eV, 7.6 eV, and 6.1 eV, in order of increasing halogen atom number. The normalization of the spectra has been chosen to emphasize the α_2 feature in the SXE spectra and the γ peak in the PFY. Figure 9 demonstrates that the energy position of the α_2 emission feature for all the halides is closely related to the respective band gap energy. The γ peak in the PFY spectrum is also closely related to the band gap energies, except in the LiF spectrum, where no γ peak is observed. Note the remarkable resemblance between the α_2 emission peak and the γ PFY spectrum. Both the energy position on this energy scale and the general shape are similar. These observations suggest that the mechanism for the additional band excitation is similar in the two cases, both when the parental transition is a localized double excitation of the type $GS \rightarrow 1s^{-2}e_L^2$ and when it is a radiative decay to singly excited states of the type $1s^{-2}e_L^2 \rightarrow 1s^{-1}e_L^1$.

In accordance with what has been discussed above, we note that LiF lacks any intensity in the PFY corresponding to γ excitation, even though there is a clear signal representing the α_2 emission. This corroborates the conclusion that the band excitation in connection with the double excitation is weaker in LiF, and that the PFY feature at around 6 eV above the main peak must be interpreted differently.

IV. CONCLUSIONS

All lithium halides show similar phenomenology in resonant inelastic scattering spectra excited in the vicinity of Li double core resonances. This includes scattering via states where both excited electrons are localized during the scattering process, where one electron delocalizes, and also transitions that involve additional band excitations.

The spectra are very sensitive to the chemical surrounding, reflected in the relative intensities, as well as energy positions and spectral shapes.

The assignments are based on the excitation-energy dependence of the scattering spectra, and the earlier published analysis of the LiCl spectra.[1,2] A proper theoretical description of inelastic photon scattering at double-core resonances in solids is presently not at hand. As it must involve both the electron correlation at the excitation site and the interaction with the valence electrons of the surrounding atoms, this is a theoretical challenge. We anticipate that these types of excitations will manifest themselves also in other core-level spectroscopies. Especially, as other and brighter photon sources are taken into use, processes with low cross section, such as those discussed here, will become increasingly important. This again emphasizes the need for theoretical development in this field.

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