

Resonant Inelastic Soft X-Ray Scattering at Hollow Lithium States in Solid LiCl

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New types of states in LiCl, where both Li core electrons are excited, have been observed in resonant inelastic soft x-ray scattering. States with one, as well as both, of the excited electrons localized at the site of the bare Li nucleus are identified. The results add a dimension to the hypersatellite concept in x-ray emission, and demonstrate that resonant spectroscopy involving multiple core vacancies provides information about decay dynamics, electron correlation, and chemical environment.

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Atoms with more than one inner vacancy are referred to as hollow atoms [1]. In solids studies of hollow atoms have been mostly focused on their formation as highly charged ions impinge on a surface. The description of this process is a theoretical challenge [2], and increased understanding is important for technological applications of beams of highly charged ions [1].

The energy selectivity provided by tunable synchrotron radiation has facilitated resonant photoexcitation of hollow states in few-electron atoms, which has given a wealth of detailed information [1], especially regarding the prototype lithium atom. Resonant excitation of multiply excited states in solids has recently been demonstrated by monitoring the excitation-energy dependence of the x-ray satellite intensity [3]. For *hypersatellites*, associated with the radiative decay of multiple core vacancies, no corresponding resonances have so far been found. Photoexcitation of double $1s$ vacancies in solids has attracted attention in the hard x-ray regime [4], and the hypersatellite intensity shows a smooth monotonous increase as the energy is increased from threshold [5,6].

Here we report the observation of strong resonances in the inelastic soft x-ray scattering cross section close to the threshold for Li hypersatellites in *solid* LiCl. The resonant behavior is complex, and allows for identification of several different types of intermediate hollow states, which have so far not been discussed in the literature. Instead of decay from one doubly ionized state, we find resonances corresponding to, e.g., states where the two core electrons are excited to localized states, states with two core excitations and an additional valence excitation, and states where only one of the excited electrons stay localized during the intermediate state lifetime.

The measurements were made at beam line I511 [7] at MAX-lab. Radiative decay spectra were measured using a grazing incidence Rowland spectrometer [8] measuring in the direction of polarization of the incoming radiation. The energies of the monochromator and the spectrometer were matched using the diffuse reflection of the incoming

radiation, and calibrated to better than 0.1 eV. Diffuse reflection also established the spectrometer function [full width at half maximum (FWHM) \approx 0.3 eV at 89 eV]. The resolution of the monochromator was 0.05 eV at 148 eV. The photon flux was around 10^{12} photons/s delivered in a $20 \times 50 \mu\text{m}$ spot, and the data acquisition time was around 0.5 h/spectrum. Radiation damage in LiCl, associated with metallization is directly reflected in the appearance of the Li metal hypersatellite [9] in the emission spectra. In the present measurements a new spot on the sample was selected every 30 s. Under these circumstances no metal signal could be detected.

For interpretation of the results calculations were performed using the full-potential augmented plane wave plus local orbitals method (APW + lo) [10,11] as implemented in the WIEN2K package [12]. The Perdew-Wang generalized gradient approximation (PW-GGA) [13] was used to describe the exchange correlation within the density functional theory. In order to simulate the influence of the Li $1s$ core holes the excited atom was formally treated as an impurity in a $2 \times 2 \times 2$ LiCl supercell.

The most pronounced resonances appear in the 146–150 eV excitation energy range (Fig. 1) and the main emission features disperse with the excitation at 85–89 eV emission energy. The linear energy-dispersion indicates that the same final states are reached in the scattering process at all excitation energies in this energy range. Such a scattering process is difficult to understand, unless the excited electrons in the intermediate state also are localized. At these energies such states can only involve Li $1s$ double vacancies, and we can therefore conclude that the two core electrons are excited to localized states at the site of the lithium atom. We use a two-step picture and denote the scattering events in the energy scheme (Fig. 2) with Greek letters for the first step (α in this case), and a numerical subscript for the second step.

The energy loss corresponding to the most pronounced structure in the scattering process is 60.8 eV. This energy is almost identical to the excitation energy for the first

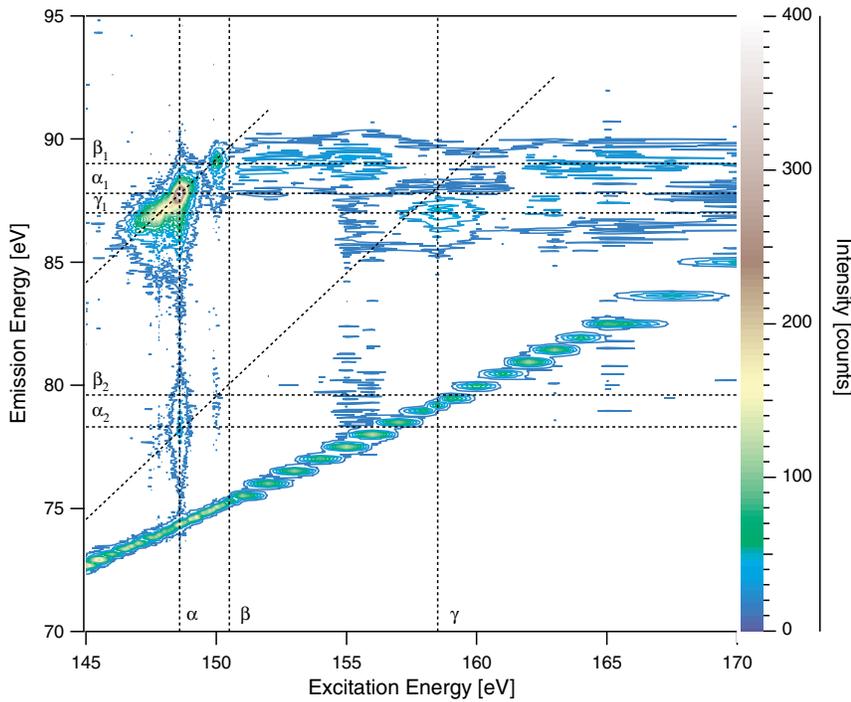


FIG. 1 (color). Contour map compiled from emission spectra excited at 49 different excitation energies. The acquisition time for each spectrum is 30 min. The sharp features appearing at an emission energy which is half of the excitation energy are due to elastic scattering measured in second order of diffraction, which we use for calibration purposes. The diagonal dashed lines have unity slope. To distinguish the scattering processes the features are denoted by a Greek letter for the excitation step, and a numerical subscript for the decay step. The labels are used in Fig. 2.

single-core hole excitation, which dominates the absorption spectrum [14–16]. We conclude that the direct absorption and the resonant scattering event reach the same final state, and that one of the localized electrons in the intermediate state returns to the Li 1s orbital in the radiative decay step (α_1). Before discussing the α_1 resonance in more detail we will assign the remaining features in the scattering spectra.

Excitation at the main resonance also shows substantial intensity at around 77–80 eV emission energy, corresponding to an additional energy loss of 9 eV, compared to the most intense feature. Since the band gap of LiCl is around 9.4 eV [17], we can directly assign this additional energy loss to valence band excitations (α_2) in the radiative decay step: final 2-hole–2-particle states are reached, with one vacancy in the Li 1s orbital, one in the valence band, and two excited electrons (Fig. 2). The linear dispersion of this structure with excitation energy again indicates that the scattering process populates the same final states throughout this excitation-energy region. The linear dispersion does not necessarily indicate final state localization. The large width of the spectral feature (FWHM \approx 3 eV) instead suggests that at least one of the electrons (and/or hole) is delocalized in the final state.

Above 150.5 eV excitation energy, the spectral features appear at constant emission energy (Fig. 1). Therefore this excitation energy can be unambiguously identified with the threshold for delocalization of one of the excited electrons, leaving the other in a localized state (β). Accordingly, the nondispersive feature at 89 eV emission energy is assigned to decay of intermediate states with only one of the excited electrons localized. When the

localized electron returns to the 1s orbital in the radiative decay step, final states with a single core hole and one electron in the conduction band are reached (β_1). Although the threshold for ionization in free Li^+ to $n = 2$ states of Li^{2+} is around 167 eV, much higher than the delocalization threshold in the solid, the observed emission energy is only 2.8 eV lower than the energy of the $n = 2 \rightarrow n = 1$ transition in free Li^{2+} .

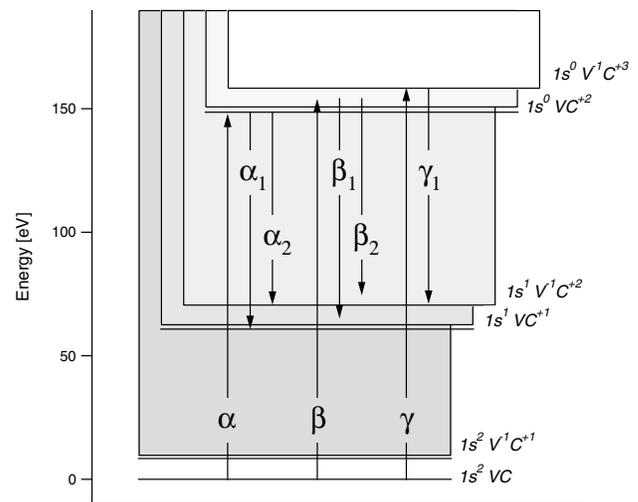


FIG. 2. Total energy scheme constructed from the experimental results. The states are denoted by $1s^k V^{-l} C^{+m}$ where 1s is the lithium core orbital with occupancy k . V and C are the valence and conduction bands, respectively, and l and m designate differences in occupancy compared to the ground state. Localization is indicated by discrete horizontal lines below the onset of the various continua.

Also β_1 scattering shows resonant behavior. An intensity maximum is found at 155 eV excitation energy, a minimum at 160 eV, and an intensity plateau towards higher energies. This excitation-energy dependence can be directly related to variations in the unoccupied density of states.

The faint emission structure around 80 eV found in this excitation-energy region can be assigned in analogy with the α_2 scattering event. The emission involves a valence-band to conduction-band excitation in addition to the transfer of an electron to the core level (β_2), and the final states are therefore 2-hole-2-particle states of the same type as reached in α_2 scattering. The lack of energy dispersion in this case indicates that states of increasing energy are reached as the excitation energy is raised.

At around 158 eV excitation energy a new resonant feature appears at 87 eV emission energy (Fig. 1). The excitation energy is sufficient for a valence-band to conduction-band excitation in addition to the double core excitation, and we assign this feature accordingly, to such triple excitations (γ). The excitation-energy width of the γ resonance is the same as the emission-energy width of the α_2 resonance. This is expected as the associated transitions both involve a valence-band to conduction-band excitation, the former associated with a doubly excited (γ) core, and the latter associated with a singly excited (α_2) core.

When one of the localized electrons in the triply excited states fills a core vacancy in the radiative decay, 2-hole-2-particle states are populated (γ_1). The final states are of the same type as those reached in the α_2 (and β_2) scattering. Identical final states would imply that the energy loss were identical in the two processes, as indicated by the diagonal dashed line in Fig. 1. The apparent low-energy shift of the γ_1 emission feature indicates excess energy loss in the γ_1 scattering compared to α_2 scattering. Furthermore, the lack of dispersion in the 158 eV resonance implies that the energy loss increases with excitation energy. Hence, γ_1 scattering preferentially populates more highly excited final states than α_2 scattering.

The partial fluorescence yield (PFY) spectrum (top of Fig. 3) monitors the integrated emission in the 84–90 eV energy region as a function of excitation energy. It shows a pronounced resonance with at least three features peaking at 147.8, 148.6, and 150.1 eV. The width of the sharpest structure is smaller (FWHM < 0.5 eV) than in the single-core absorption spectrum [15] (referred to the bottom energy axis in Fig. 3). It is, however, far from being determined by the lifetime broadening, which is below 0.1 eV for the free ion [18,19]. At excitation energies above the threshold for continuum excitations, these structures are followed by a comparatively flat intensity distribution.

The resonant scattering spectra, measured at the corresponding excitation energies, are shown on the final state energy scale, derived by subtracting the emission energy from the excitation energy. The principal feature

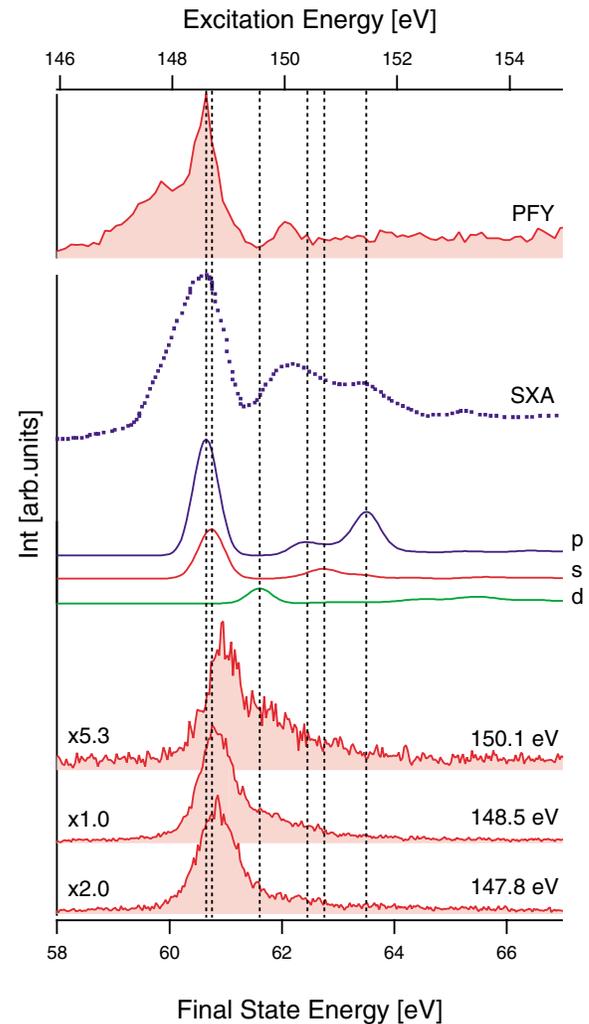


FIG. 3 (color online). Partial fluorescence yield (PFY), monitoring photons emitted in the 84–90 eV energy range, is shown on the excitation energy scale at the top of the figure. Inelastic scattering spectra, associated with the α_1 resonance, excited at 147.8, 148.6, and 150.1 eV, are normalized to the peak value (by multiplication by the displayed factors), shown in the final state energy scale at the bottom of the figure, and compared to the soft x-ray absorption (SXA) spectrum (dotted line) of Ref. [15]. Calculated local partial densities of states in the presence of one Li core hole, for the s , p , and d symmetry (solid lines), have been broadened by a Gaussian with FWHM = 0.5 eV, and are aligned so that the peaks of the p -LPDOS and the most intense SXA feature coincide.

in the α_1 scattering and in the direct absorption almost coincides. The width of the main peaks (FWHM = 0.8 eV) is very similar, and the scattering is slightly shifted towards higher final state energy, compared to the first direct absorption peak [14,15].

The unoccupied local partial density of states (LPDOS) of p symmetry, calculated in the presence of a core hole, gives a fairly good description of the absorption spectrum. States which become localized due to the influence of the core hole dominate the absorption spectrum [16]. As expected, this dominance is even more

pronounced in α_1 scattering, where hardly any intensity is found for the more delocalized final states at higher energies.

As the α_1 scattering process involves two photons, we expect the dipole selection rules to emphasize s and d LPDOS, as opposed to p LPDOS for the direct absorption. The calculations predict the localized s -state maximum to appear at slightly higher energies than the p -state maximum, in agreement with the observed high-energy shift of the scattering feature relative to the absorption peak. With higher excitation energies the α_1 scattering shows growing intensity at around 61.9 eV, without correspondence in the direct absorption. As this is the predicted energy for the first unoccupied localized state of d symmetry, the assignment is suggested accordingly. This interpretation is supported by the excitation-energy dependence, as we will see below.

The hollow states, monitored in the PFY spectrum, are determined both by correlation between the two electrons and interaction with the surrounding. The absorption spectrum of the free Li^+ ion has one prominent dipole-allowed transition ($1s^2\ ^1S \rightarrow 2s2p\ ^1P$ at 150.28 eV [18,19]) in this energy range. The proximity to the transition energies measured here demonstrates the quasiatomic nature of the localized electrons in the solid. To explain the PFY fine structure, we have considered that reduction of symmetry may lead to an effective relaxation of the strict atomic selection rules. Furthermore, it is well known that fluorescence yield spectra can differ substantially from absorption spectra, especially in few-electron systems [20]. The observed splitting is, however, far from any energy splitting between ionic states which can be considered [21].

Therefore we use solid state theory as a starting point. We make the ansatz that the electrons can be treated separately. Since LiCl is an insulator with a weak dielectric screening, one can assume that the central cell potential with a double core hole produces a long-range Coulombic tail that creates a localized hydrogenic exciton with one of the two electrons. The other electron will feel the long-range potential corresponding to a single core hole, together with the short-range electron-hole effects produced by the electron-hole potential. This situation can be approximated with a single core-hole potential, and we compare to the LPDOS in the presence of a single core hole in Fig. 3.

Although this model does not quantitatively describe the experimental results, it does predict three strongly localized states of s , p , and d symmetry with an energy spacing comparable to the spacing between the observed resonances. The identification of the 150.1 eV resonance as due to states of d symmetry (dipole allowed, if the excitonic electron has p character), is in agreement with the assignment of the high-energy loss shoulder in

the scattering spectrum as due to states of the same symmetry.

This interpretation disregards correlation between the two excited electrons, which is an obvious reason for the limited agreement with the experimental results. Here we must leave a quantitative description of these resonances as a challenge for theory.

In conclusion, several new states in LiCl , where both Li core electrons are excited, have been observed and assigned using resonant inelastic soft x-ray scattering. Resonant spectroscopy on hollow states in solids yields information about decay dynamics, electron correlation, and electronic environment, which may be used for chemical analysis, as well as being an asset in interpretation of experiments with highly charged ions. At new generations of synchrotron radiation sources and free electron lasers, the exploration of these types of "exotic" excitations will not be constrained by low count rate.

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