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SOFT X-RAY EMISSION SPECTRA OF LITHIUM FLUORIDE EXCITED BY SYNCHROTRON RADIATION

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A core excited Li atom is perhaps the simplest cation defect that can be introduced into LiF. It frequently binds an electron in an excitonic state, whose properties dominate both the soft x-ray absorption and soft x-ray emission properties of LiF. Though many authors have studied this excitonic state, its properties are still not completely understood.

In the soft x-ray region, Auger yields are several orders of magnitude larger than radiative yields so that emission spectra are very weak. The weak radiative decay of the core excited Li atom in LiF was studied by Arakawa and Williams using electron beam excitation of the core hole.[1] Peaks in the emission spectra were observed that result from decay of the exciton (at 62 eV), and from filling of the core hole by valence electrons (46 eV). In these studies the e-beam rapidly degraded the surface, with the LiF spectrum being replaced by a metallic Li spectrum. To obtain the pure LiF spectrum, emission spectra were measured as a function of time and peak intensities extrapolated to time zero.

Alta et. al. reported very different spectra using broadband synchrotron light excitation of the core hole.[2] Spectral peaks were observed at the position of the exciton peak and at higher energies at the energy position of the normally empty conduction band states. The spectra were interpreted as resonance fluorescence from the exciton and conduction band states.

This study was undertaken to try to understand the very different spectra obtained with photon and electron excitation, and especially to re-examine the very unusual photon excited spectra apparently associated with empty conduction band states. The studies were carried out with a new, very high efficiency, emission spectrometer that was initially installed at the National Bureau of Standards synchrotron light source and later moved to the National Synchrotron Light Source at Brookhaven National Laboratory.[3]

Our work confirmed the earlier studies which used e-beam excitation. Exciton and valence band peaks were observed which decay with time and are replaced by a metallic Li peak at 54 eV.

Our studies indicate, however, that photon excitation also rapidly damages the surface, a result in agreement with desorption studies which show a greatly enhanced desorption of atoms above the threshold for core excitation.[4] We conclude that the surface damage quickly accumulates and produces diffuse scattering of the incident light. If broadband excitation is used, the scattered light entirely dominates the very weak emission spectra. If the exciting light is restricted to photon energies above the exciton energy of 62 eV, a true emission spectrum is observed that is similar to the e-beam spectrum. A further conclusion of the study is that the exciton emission peak persists even when electrons are not directly excited into the exciton states. This implies that electrons excited to conduction band states are frequently trapped in the exciton state before recombining with the core hole.

These conclusions are based on several experimental studies. Using an electron microscope, we found that even lightly irradiated LiF shows granular surface damage, which might be expected to scatter strongly. A second study used broadband excitation and measured the soft x-ray as a function of incident angle. The results are shown in Fig. 1. The spectra measured with the reflected

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beam 70° away from the entrance axis of the spectrometer (Fig. 1b) were essentially the same, except for a 60 fold reduction in intensity, as the true reflection spectra with the exciting light reflected directly into the spectrometer (Fig. 1a). The changing height of the Li metal peak indicates an accumulation of surface damage as the measurements were in progress. At intermediate angles, the intensity increased as the specular angle was approached. This behavior is fully consistent with diffuse scattering by small surface structure.

The reflection spectra in Fig. 1. are very similar to the absorption spectra of LiF in this region.[5] This is to be expected since the absorption coefficient is the major factor modulating the reflectance in this region.

In other measurements, synchrotron light was filtered by a 400Å silver film to remove photon energies below 100 eV [4,6]. This filter reduced the intensity in the emission region below 100 eV by a factor of about 160. Above 100 eV, the film transmitted about 10% of the incident light. The resulting spectrum is shown in Fig. 2. The spectrum was recorded in segments, in each of which the signal was integrated for twenty minutes. The broad triangular background is an artifact related to the scattered light in the spectrometer which is greatest in the center of the scanning range. The peaks at 46, 54 and 62 eV are respectively the valence band peak, the Li metal peak and the exciton peak.

The entire set of data was recorded over a four hour period. The solid scan was recorded first. A small valence band peak and a larger exciton peak are visible. In a later scan (dotted line), the valence band peak has disappeared and a small Li metal peak is visible at 54 eV. A small exciton peak still persists after several hours. This is probably from scattered light that has passed through the filter.

Fig. 1. Soft x-ray spectra made with broadband excitation. a) Specular reflection spectrum. b) Spectra with reflected beam 70° away from entrance axis of spectrometer. Exposure time 60 times greater than in a). Similarity of spectra indicates diffuse scattering.

Fig. 2. SKE spectrum of LiF produced by synchrotron light filtered to remove photon energies below 100 eV. Solid line is initial spectrum. Dotted spectrum made after = 1 hour.

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