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Fluorescent emission spectra of lithium fluoride with use of synchrotron radiation

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The soft x-ray emission spectra of single-crystal LiF excited with synchrotron radiation are presented. The radiative decay of the lithium 1*s* core exciton is observed. Radiative transitions between the valence band and the core hole are also observed in undamaged samples. Spectra obtained with broadband synchrotron-light excitation are shown to be dominated by diffuse scattering from damaged sample surfaces. Excitation with photon energies between 100 and 150 eV generates true emission spectra. An important result is that electrons excited into the conduction band are frequently trapped in an exciton state before recombining with the core hole.

I. INTRODUCTION

The core-excited atom is the simplest cation defect that can be introduced into the technologically important ionic compound LiF.[1] The core-excited atom frequently binds an electron to form an exciton. This core exciton has been studied by many authors[2–19] so that its existence is well established and its properties generally known. However, the excitation and decay mechanisms for the exciton are still not completely understood.

In the soft x-ray region, Auger-electron yields are generally several orders of magnitude larger than the radiative yields. The dominance of the Auger process for filling core holes in the alkali halides was studied recently by Kamada *et al.*[16] The weak decay of the Li 1*s* core-excited atom in LiF was observed by Maiste[2] and studied by Arakawa and Williams[10] using electron-beam excitation of the core hole. Aita *et al.*[14] reported very different spectra using broadband synchrotron light excitation of the core hole. This study was undertaken to try to understand the difference in spectra obtained with photon and electron excitation.

From the work presented below, we conclude that the key factor producing the different spectra is that both energetic electrons and photons damage the LiF surface. For electron excitation, the LiF spectrum is rapidly replaced by a Li-metal spectrum indicating that fluorine is being driven off the sample, leaving the Li to accumulate in a layer on the surface. The emission spectrum must be measured over time and extrapolated to time zero to obtain accurate alkali-halide spectra using *e*-beam excitation.[10]

Desorption studies have shown that photons also degrade the surface and that the effect is greatly enhanced at energies greater than those required to excite a core exciton.[20] Our studies indicate that surface damage quickly accumulates on the photon excited surface and produces diffuse scattering of the incident radiation. If a broadband excitation source is used which includes the emission region, this scattered light dominates the much weaker true emission spectra. By restricting the excitation spectrum to photon energies well above the exciton energy of 62 eV, a true emission spectrum is observed which is similar to that observed with *e*-beam excitation.

A further result of our studies is that the exciton emission peak persists even when photon energies are used which do not permit direct transitions to the exciton state. This implies that electrons excited to the conduction band are frequently trapped in the exciton state before recombining with the core hole.

II. EXPERIMENTAL PROCEDURES

Measurements were carried out using radiation from the 284-MeV storage ring at the National Bureau of Standards Synchrotron Ultraviolet Radiation Facility (SURF II). The intensity distribution from SURF II has a maximum intensity at 80 eV and an average photon flux of the order of 10^{11} photons/s mrad nm mA.[21] Ten mrad of this radiation was focused to a (1×3)-mm spot. The average total flux incident on the sample in the energy interval 40–150 eV was about 10^{14} photons/s. Usually a thin-film filter was inserted between the sample and the radiation light source. The filter substantially cut down the intensity in the wavelength range of the emission from LiF and thus reduced the light scattered into the spectrometer. A silver filter 400 Å thick reduced the intensity at photon energies below 100 eV by an average factor of 160. It had a transmission of about 10% at photon energies greater than 100 eV.[22] White-light synchrotron radiation was used in the scattered light studies.

The study was made using a new, high-efficiency, soft x-ray emission spectrometer (SXES) designed for measuring low-yield fluorescence spectra. The performance of the spectrometer has been described in detail elsewhere.[23] The spectrometer uses a conventional Rowland circle design with a grating radius of 5 m and an angle of incidence of 86°. The input slit is located about 2 mm from the sample to improve the light collection. Four large toroidal gratings (4 × 10 cm), interchangeable under vacuum, are used to improve light collection and reduce aberrations. A high-efficiency, low-noise, two-dimensional, charge-coupled device (CCD), Si-diode-based detector coupled with a microchannel plate is employed for signal detection. These features provide the spectrometer with an efficiency about 3 orders of magnitude greater than other existing spectrometers of its type.

A 600-lines/mm grating was used for the experiments presented here. The width of the entrance slit was about 100 μm which corresponds to a spectral bandpass of 0.10 eV at a photon energy of 60 eV. The angle between the excitation beam and the entrance axis of the spectrometer was fixed at 30°, while the incident angle of the excitation beam on the sample was varied. The pressure inside the system was about 3×10^{-9} Torr during the measurements. The samples were prepared by cleaving in air melt-grown single crystals of LiF supplied by the Harshaw Chemical Company. These crystals were transferred to the sample chamber and baked under high vacuum at 100 °C for 24 h.

The detector was used in a spectrum mode rather than in a scanning mode. In this mode, with a 600-lines/mm grating, 15 Å can be covered at each positioning of the detector. Thus each spectrum, ranging from 155 to 310 Å (40 to 80 eV) was collected by moving the detector ten times along the Rowland circle. The final spectrum was then compiled by normalizing and matching the ten spectra. The grating efficiency as a function of wavelength has not yet been measured; therefore, the intensity ratios of the spectral features present at different photon energies could only be studied on a relative scale at this time. A PDP 11/23 computer interfaced with a CAMAC control unit was used for experimental control, data acquisition, and data analysis.

III. RESULTS AND DISCUSSION

In Fig. 1 we present the fluorescent emission spectrum of a single LiF crystal in the photon energy range 40–80 eV. Synchrotron radiation, filtered by the silver film, was used for exciting the sample at an incident angle of 55°. It took about 4 h to measure the complete spectrum. The spectrum consists of three peaks superimposed on a very broad band. The broad background follows approximately the expected efficiency curve of the 600-lines/mm grating. We believe that this background is radiation scattered by the sample and detected by the spectrometer. The peaks are located at 46.4, 54.4, and 61.9 eV, respectively, and have a time-dependent intensity. The solid line in Fig. 1 was obtained during a 20-min integration from a spot not previously exposed to synchrotron radiation and represents the spectrum of a LiF sample with minimum surface damage. The dashed curve is the spectrum after the surface has accumulated damage from the exciting beam. We describe the time evolution of each peak below.

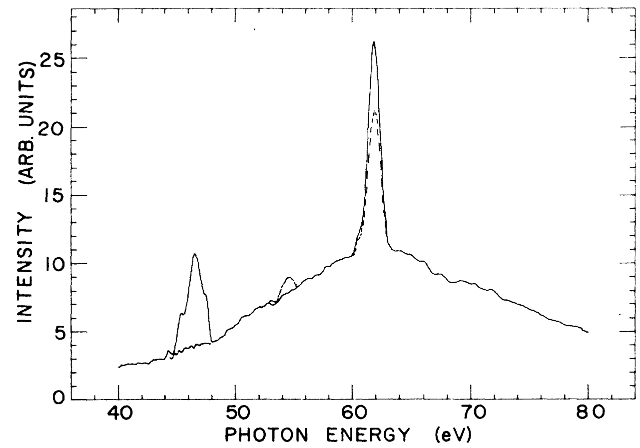

FIG. 1. Soft x-ray emission spectrum of single-crystal LiF produced by synchrotron light that is filtered to remove photon energies below 100 eV. Solid curve is initial spectrum. Dashed curve was made after $\gtrsim 1$ h exposure to filtered light.

The peak at 46.4 eV is emission from the valence band. This peak disappears after 1 h as shown by the dashed curve. The peak at 54.4 is emission from metallic lithium. It is initially absent. After 1 h a small peak is present as shown in the figure. This peak continues to increase with time, reaching a saturation value after about 6 h of exposure. The disappearance of the LiF valence-band peak and the appearance of the metallic Li peak provide strong evidence of surface damage.

The intensity of the exciton peak at 61.9 eV decreases with exposure time. After 2 h it is 65% of the original value as shown in the figure. It continues to decrease with time, reaching a stable value of 35% after 6–8 h. This final value is about 160 times smaller than the exciton peak magnitude obtained using "white" synchrotron radiation. This reduction factor of 160 is in agreement with the calculated attenuation of the Ag filter at 62 eV,[22] and we believe this residual peak represents scattered exciting light rather than true emission.

Some features of these results can be related to other studies. Similar time-dependent changes of the emission spectra were observed by Arakawa and Williams using electron beam excitation.[10] Under photon bombardment, the samples degrade more slowly than with electron bombardment. An estimate of the valence-band width of LiF may be obtained from the peak at 46.4 eV. It has a bandwidth of 3.6±0.1 eV which can be compared with a width of 4.6±0.3 eV reported by Pong and Inouye[11] and a width of 3.1 eV computed by Kunz.[15] The core exciton at 61.9 eV with a half maximum full width (HMFW) of 1.1±0.1 eV has a weak shoulder at 61.0 eV similar to that observed by Fields *et al.*[12] from momentum-transfer experiments and to the spectrum computed by Kunz *et al.*[18]

Several spectra obtained under white-light excitation conditions are shown in Fig. 2. The upper panel is a specular reflection spectrum obtained at an angle of incidence of 15°. The entire spectrum was obtained using a 10-s exposure. Although an apparently undamaged spot was used, the *K* emission band of metallic lithium is observable at 54 eV. The change in reflectivity is approximately proportional to the change in the absorption coefficient in this region of the spectrum where the real part of the index of refraction remains very near one. The observed spectrum between 40 and 80 eV follows the absorption coefficient. This spectrum is consistent with the features expected from the reflectivity. The observed spectral response is just the reflected radiation, except for the weak feature at 54 eV due to valence-core emission from metallic lithium.

Figure 2(b) was also recorded from a fresh surface spot. The angle of incidence on the sample was 55° so that the entrance axis of the spectrometer was 70° away from the specular beam. The spectrum was obtained in 10 min with an excitation current 1.7 times greater than that used to obtain the curve shown in Fig. 2(a), resulting in a normalized exposure time 100 times greater than that for the specular reflection spectrum. The two spectra are identical in almost every detail. The similarity suggests that no emission (other than from metallic Li) is detected, but only radiation diffusely scattered from the surface. The small Li peak visible at 54 eV also indicates the presence of damage. The spectrum in the lower panel [Fig. 2(c)] was obtained after the sample was exposed to filtered synchrotron radiation for 4 h. For this spectrum, the angle of incidence of the exciting beam was 55°; the total time to obtain the entire spectrum was 10 min, and the normalized exposure was 80 times that of Fig. 2(a). The Li peak at 54 eV is larger than in the other spectra, and there is increased background between 40 and 50 eV. The latter feature is most probably an indication of increased scattering. The major spectral features of each spectrum shown in Fig. 2 are essentially the same. In a series of measurements made over a period of 8 h, it was observed that the metallic lithium peak increases in intensity as does the background between 40 and 50 eV. Both changes are clearly evidence for increasing damage.

The spectra displayed in Fig. 2 are very similar to those reported by Aita *et al.* The similarity suggests that the spectra observed by Aita *et al.*[14] were primarily

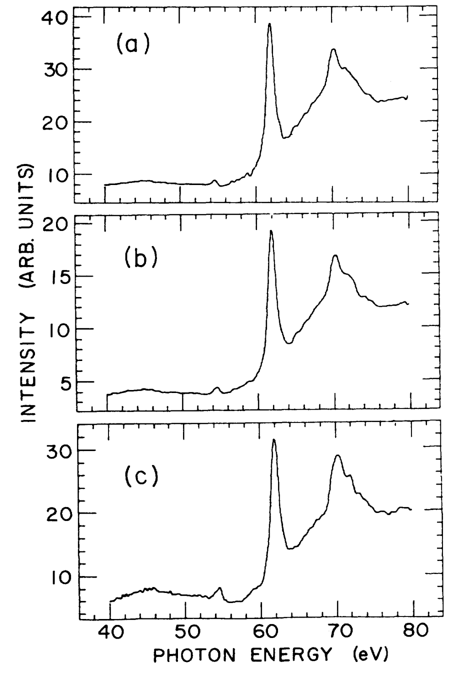

FIG. 2. Spectra observed with photon excitation which includes photon energies in the emission region. (a) Specular reflection spectrum. (b) and (c) Spectra taken with reflected beam 70° away from entrance axis of spectrometer. Normalized exposure times are 100 and 80 times greater than in (a). Similarity of spectra indicates that (b) and (c) represent diffuse scattering from a damaged surface.

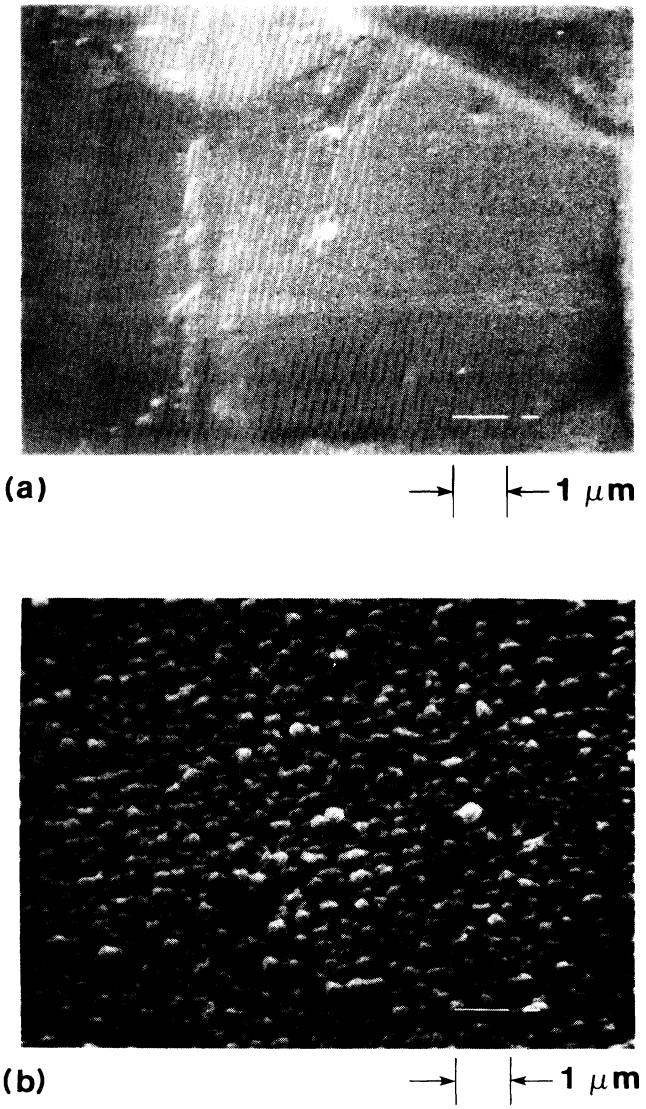

FIG. 3. Scanning electron micrograph of LiF sample before and after exposure to synchrotron light.

reflectance spectra produced by the diffuse scattering of soft x-ray induced surface roughness, which we believe to be the explanation of our results.

Figure 3 provides additional evidence of the fragility of the lithium fluoride surface. Figure 3(a) is a scanning electron micrograph of the surface before photon bombardment, and Fig. 3(b) is a scanning electron micrograph of the surface after photon bombardment. The observed photon-induced roughness makes it easy to believe that the surface will scatter strongly even at angles much greater than the angle corresponding to specular reflection.

Our work confirms the earlier studies which used electron-beam excitation. When light in the emission region was excluded from the exciting beam, exciton and valence band peaks were observed which decayed with time and were replaced by a metallic Li peak at 54.5 eV. They indicate, however, that photon excitation also rapidly damages the LiF surface so that surface damage quickly accumulates and produces diffuse scattering of the incident light. If broadband light is used, the scattered light entirely dominates the very weak emission spectra. An additional conclusion is that electrons excited to conduction band states are frequently trapped in the exciton state before recombining with core holes.

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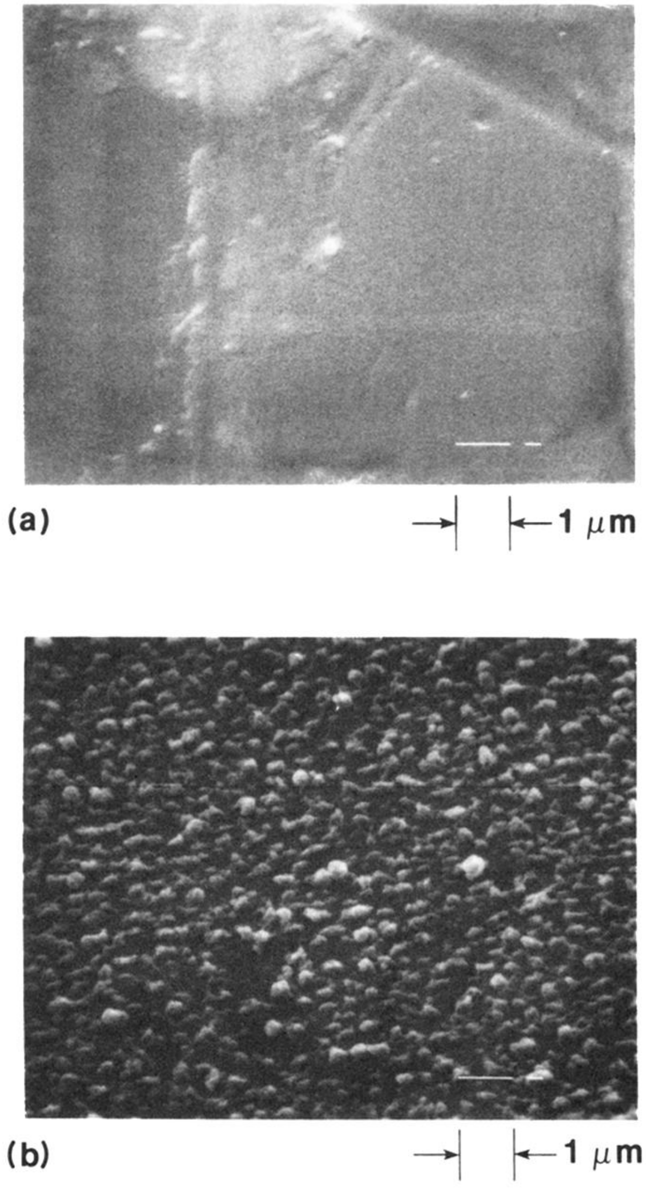

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