PHYSICAL REVIEW B VOLUME 23, NUMBER 11 1 JUNE 1981

Fluorescent emission and scattering spectra of lithium fluoride by using synchrotron radiation

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(Received 9 June 1980)

The fluorescent emission and scattering spectra of metallic lithium and lithium fluoride were obtained by using continuous radiation from the Institute for Nuclear Study synchrotron in the energy region of 40–80 eV. The spectrum of metallic lithium is in close resemblance with the one obtained by an ordinary electron excitation method. The spectrum of lithium fluoride, on the contrary, exhibits strong evidence of scattering by the exciton state and the continuum in addition to the ordinary fluorescence due to the valence-band-to-Li^+ $1s$-level electron transition. Other possibilities for the cause of the observed features were qualitatively discussed.

I. INTRODUCTION

The Li *K* emission spectra of lithium compounds have been investigated by many authors by means of the electron excitation method.[1–5] However, the spectra obtained by different groups are not in complete agreement mainly because the intensity distribution of soft x-ray spectra of halides depends appreciably on the energy and intensity of bombarding electrons and changes rapidly with time. Therefore, the fluorescence excitation method is more appropriate for observing the emission spectra of substances which decompose easily by electron bombardments. It is difficult, however, to use this method in the soft x-ray wavelength region beyond 20 Å, because the fluorescence yield is usually small in this wavelength region[6,7] and an x-ray tube with high power is required for this purpose.

In the present study we have used the continuous radiation from the synchrotron at the Institute for Nuclear Study (INS), University of Tokyo, as an x-ray source and have measured for the first time the soft x-ray emission spectra of metallic lithium and lithium fluoride (LiF) in the energy region of 40–80 eV. The Li *K* emission spectrum as well as the absorption threshold is observed in this energy range. The measurement by Kosuch *et al.*[8] with Deutsches Elektronen-Synchrotron (DESY) radiation was originally aimed at the Li *K* emission spectrum of LiF, but what they observed was the reflection spectrum in the Li *K* spectral region because both the angles of incident and outgoing beams against the sample surface were kept the same in their experiment.

Secondly, we have tried to investigate the presence of the radiative decay of a core exciton in the soft x-ray emission spectrum of LiF produced by the fluorescence excitation method. From results of various observations of soft x-ray absorption spectra of alkali halides it has been known that sharp absorption peaks are present near the absorption threshold in these materials.[9,10] The comparison with photoelectron spectra and optical data reveals that some of these peaks, in particular the first one at the threshold, are observed slightly below the core-to-conduction-band threshold energy.[11] Therefore, these sharp absorption lines were interpreted as being due to production of core excitons, and it is expected that the emission spectra due to the radiative decay of these excitons can be observed in the soft x-ray region. Élango and Maiste,[2] and Arakawa and Williams[5] have measured the emission spectrum of lithium halides in this energy region and ascribed one of the observed peaks to the radiative decay of a core exciton. However, their measurements were carried out with electron bombardments, and it is worthwhile to investigate the spectrum with the fluorescence excitation method.

The present measurement reveals the peak which corresponds to the valence-band-to-Li^+ $1s$-level emission spectrum. However, the peak near the absorption threshold, which should correspond to the radiative decay of a core exciton in the ordinary emission spectrum, turns out to be much larger in its intensity than the previous results. Also, several structures are observed in the energy region corresponding to the conduction-band-to-Li^+ $1s$-level transition. From these facts we have analyzed the observed spectrum as consisting of the ordinary emission, the radiative decay of a core exciton, and the scattering spectrum of incident radiation which reflects the exciton level and the empty density of states of the conduction band. In fact, we have found a close resemblance between the present spectrum and the absorption spectrum in the same energy region.

II. EXPERIMENTAL

Measurements were carried out with the 1.3-GeV electron synchrotron at INS, which has the intensity distribution suitable for the fluorescence excitation in the soft x-ray wavelength region. Since the fluorescence yield is small in this region, we have used a spectrometer specially designed for the present purpose. The characteristic feature of this spectrometer is that the distance between sample and entrance slit was reduced to about 3 cm and a platinized replica grating with a radius of 2 m and grooves of 1200/mm was used at the angle of incidence of 86.4°.

The widths of entrance and exit slits were about 100 μm in the present experiment, and the spectral width was 0.13 eV at the photon energy of 60 eV. The angle between the beams incident on and scattered from the sample was fixed at 77.5°, while the incident angle of the beam against the sample was varied. The pressure in the sample chamber was about 1×10^{-7} Torr during measurements. Spectra were recorded by a step-scanning method. The synchrotron was operated at 750 MeV for the case of metallic lithium and at 950 MeV for LiF. Other experimental procedures were the same as those in the previous experiment.[12]

Specimens of metallic lithium were prepared by evaporating onto a copper plate *in situ*. Immediately after evaporation the measurements were carried out in the photon energy ranging from 50 to 57 eV repeatedly to assure the reproducibility of the measurements. When the spectral shape was found to change in repeated runs, metallic lithium was newly evaporated *in situ* and then scanning was again started. In the case of LiF, specimens of single crystal freshly cleaved in air, film evaporated *in situ*, and pressed powder were used.

III. RESULTS AND DISCUSSION

In Fig. 1 we present for the first time the *K* emission spectrum of metallic lithium obtained by the fluorescence excitation method. The spectrum was obtained at the take-off angle of about 30° and by accumulating eight runs. It is found that the observed spectrum is in agreement with the one obtained by electron bombardment[13] except for the high background in the present measurement.

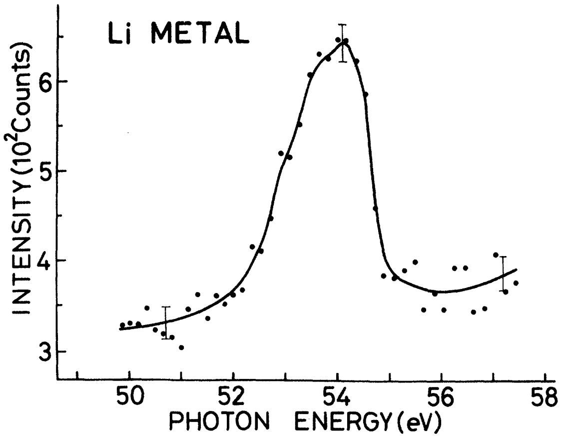

FIG. 1. *K* emission spectrum of metallic lithium obtained with the fluorescence excitation method.

One of the purposes of measuring this spectrum is to study possible changes in the spectrum due to the difference in excitation methods. Namely, a fluorescence excitation method produces the *K* hole by photoexcitation, whereas in the ordinary electron excitation method the *K* hole is produced by Coulomb interaction between impinging electron and *K* electron, and these two methods may leave different states in the sample. The fact that the present observation exhibits a close resemblance with the spectrum obtained by electron excitation indicates that the states produced by either of these two methods are essentially the same. However, because of a low production rate of the *K* hole in the present method the observed spectrum cannot present fine structures at the edge. It is also interesting to notice that there is a large amount of background counts, though the data points scatter appreciably. This is probably due to the scattering of incident x rays as is discussed later.

The fluorescence spectrum of LiF single crystal is shown in Fig. 2(a), for which the take-off angle was set at about 30°. It was found that similar spectra were also obtained with different take-off angles and also with specimens of pressed powder and evaporated film. As is observed in the figure the spectrum is characterized by (i) a broad peak at 45 eV, (ii) a distinctly sharp peak at 61.7 eV, and (iii) structure in the energy region above the sharp peak. The spectrum obtained by accumulating eight runs is also shown in Fig. 2(b) in the energy region of 41–65 eV. The broad band around 45 eV exhibits a multicomponent structure in this case. For the sake of comparison the absorption spectrum of LiF obtained by Haensel *et al.*[10] is shown by broken lines in Fig. 2. It is important to note that there is a close resemblance in the peak and structure above 60 eV between the fluorescence and the absorption spectra.

The x-ray photoemission spectroscopy (XPS) data of LiF obtained by Kowalczyk *et al.*[14] indicate that

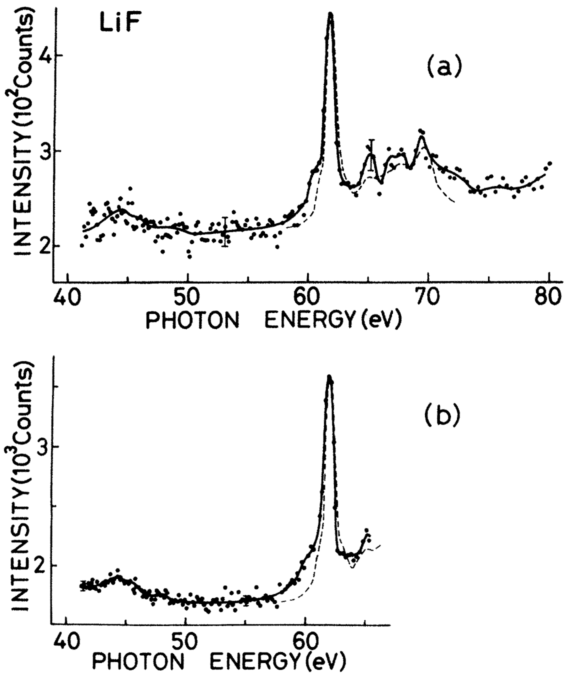

FIG. 2. (a) Fluorescence spectrum of LiF single crystal is shown by dots. The Li K absorption spectrum of LiF obtained by Haensel *et al.* is also shown by a broken line (Ref. 10). (b) The fluorescence spectrum of LiF single crystal (dots) is shown in the energy range of 41–65 eV with the Li K absorption spectrum (broken line).

the energy difference between the Li^+ $1s$ photoelectron and the peak position of the XPS from the valence band is 47.2 eV with a bandwidth of about 6.5 eV. Also, the valence-band width estimated by Poole *et al.*[15] from their ultraviolet photoemission spectroscopy data is 6.1 eV. Therefore, the broad band observed around 45 eV with the bandwidth of about 6.5 eV in the present fluorescence spectrum can be ascribed to the radiative transition of the valence electrons into the Li^+ K hole. A slight difference in the peak position among these measurements is probably due to the difference in the selection rule for the respective transitions.

The emission spectrum of LiF produced by electron bombardment was obtained by Arakawa and Williams[5] with an attempt to minimize effects of radiation damages. They also observed a similar broad peak around 46.5 eV and interpreted it as the valence-band emission spectrum. Furthermore, they observed a peak at 61 eV with an intensity about a half of the one at 46.5 eV, but no structure in the energy region corresponding to the continuum state, and attributed this peak to the radiative decay of a core exciton strongly localized around the Li^{2+} ion. When compared with their data, the present spectrum differs markedly in the energy region beyond 60 eV.

We first discuss the intensities of these peaks at 46.5 and 61.7 eV. Apart from the radiative decay probabilities of the valence electron (V-K) and the core exciton both of which are independent of the excitation method (electron bombardment or fluorescence excitation) the intensities of the V-K radiative transition and the radiative decay of a core exciton are, respectively, proportional to the probability of producing the K hole and that of forming the core exciton that can decay radiatively ($q=0$) to the ground state. In the case of electron bombardments the latter probability is expected to be much smaller than the former which contains excitations of both $q=0$ and $\neq 0$ states, whereas in the case of fluorescence excitation ($q=0$) an appreciable portion of the probability of exciting the K electron is subject to the formation of the excitons that can undergo a radiative decay intrinsically. It is, therefore, reasonable to expect that the intensity of the exciton peak relative to the valence-band emission spectrum is higher in the fluorescence method in comparison to the electron excitation case. If this were the case, the peak at 61.7 eV should be due to "absorption followed by luminescence" via the core exciton state associated with the Li^+ K hole and the structure in the conduction band would be caused by radiative decay of the electron excited to the conduction band back into the hole before it moves away from the Li^{2+} site. However, it is known that an electron excited into the conduction band decays thermally into the bottom of the conduction band or into the exciton level.[5] Therefore, even if the peak at 61.7 eV were due to the exciton, we should seek for the cause for observing the structured fluorescence spectrum in the energy region of the continuum state.

We then put focus on the close similarity between the fluorescence and the absorption spectra above 60 eV. Since the absorption spectrum of this case reflects the p-type partial density of states of conduction band and possibly of the exciton level, the structure observed above 60 eV should be expected to be caused by electronic transition processes that involve these excited states as the final or intermediate state. We also note that the structure of our interest was not observed in the electron excited spectrum by Arakawa and Williams.[5] Therefore, the peak and structure above 60 eV can be interpreted as being characteristic to the fluorescence excitation with continuous radiation.

As one of the possible optical processes associated with continuous radiation we consider the reflection of incident continuous radiation by LiF crystal. If we apply the ordinary dispersion theory for a uniform medium and use the macroscopic theory for reflection, then the reflectivity can be expressed as

$$R=\left|\frac{\cos\theta_0-(\epsilon-\sin^2\theta_0)^{1/2}}{\cos\theta_0+(\epsilon-\sin^2\theta_0)^{1/2}}\right|^2 ,$$

where θ_0 is the angle of incidence and ϵ is the complex dielectric constant defined by $\epsilon_1 + i\epsilon_2$. If the anomalous dispersion is neglected and weak absorption such as $\epsilon_2 << 2\cos\theta_0$ is assumed, then the reflectivity is approximately given by

$$R \simeq \frac{\epsilon_2^2}{16\cos^4\theta_0 + \epsilon_2^2} ,$$

where ϵ_1 is taken to be unity. Therefore, the reflection spectrum should exhibit the structure similar to the one observed in the absorption spectrum which is linearly proportional to ϵ_2. This is the case in the long-wavelength region such as uv and visible radiation. In the present case, however, we would rule out this possibility because the wavelengths of incident radiation are not long enough for the macroscopic theory to be applied, and the spectrum covers the energy region of anomalous dispersion at the threshold. Furthermore, in the present experiment the geometrical arrangement was such that the incident and take-off angles against the sample surface are not the same, and also the form of the samples (single crystal, polycrystal, or pressed powder) gives no appreciable change in the observed spectra. These facts suggest that the observed spectrum is better not to be considered as a reflection spectrum.

We have then tried to interpret the spectrum as a scattering spectrum of incident continuous radiation by LiF sample from a microscopic stand point.[16] Since the total absorption coefficient of LiF is about 3×10^5 cm^{-1} at the Li K absorption threshold,[17] scattering takes place at most within a few hundreds Å thick surface layer. Also, the wavelengths of incident radiation are much larger than atomic dimension so that the scattering due to the A^2 term, which contributes to the atomic form factor and the structure factor in the ordinary diffraction theory, gives rise to only a uniform intense background. In fact, we observed a high background in both metallic lithium and LiF spectra. It is interesting to note that the intensity of the Li K emission amounts to as much as the background intensity in the case of metallic lithium sample, while in the case of LiF the intensity of the valence-to-K-hole transition is much smaller because the valence-band wave function is localized mainly in the vicinity of halogen ions. A quantitative analysis of these intensities against the background intensity seems quite interesting because we can then compare the absolute values of scattering rate, radiative emission rate, and production rate of the Li K-hole which is connected to the absorption cross section integrated over the spectral range of the incident continuous radiation.

The second-order process of the pA term, which gives rise to the dispersion in the case of coherent x-ray scattering or Raman process in the inelastic x-ray scattering, could contribute appreciably to the scattering intensity if energies of incident radiation are resonant with the excitation energy of the system. When this resonant scattering of incident continuous radiation takes place in the system, the observed fluorescence spectrum should be interpreted as "absorption followed by luminescence," where absorption and emission occur successively as a single quantum process without suffering much the relaxation effect of excited electrons. Assuming that apart from an instrumental width the linewidth is dominantly associated with the K hole, we have extended a conventional formalism of resonance fluorescence for a two-level system to the present case.[16] Then, it can be shown that the intensity of fluorescence radiation is proportional to[18]

$$I(\omega) \propto \int \frac{|\langle m|pA|0\rangle|^2 \rho(\omega_m)}{[\omega - (\omega_m - \omega_0)]^2 + \Gamma^2/4} d\omega_m ,$$

if the incident radiation has a constant spectral distribution. Here, the indices 0 and m refer to the Li$^+$ $1s$ level and the intermediate state which is one of excited states with a p-type symmetry, Γ the lifetime broadening of the Li$^+$ $1s$ hole, $\rho(\omega_m)$ the partial density of states. It is clear from this expression that the spectrum exhibits the structure very similar to the absorption spectrum. At the energy corresponding to the exciton excitation energy we would expect to observe a sharp fluorescence radiation with a Lorentzian shape. By means of a crude fit of a Lorentzian shape to the observed sharp peak it has been estimated that Γ is approximately equal to 0.94 eV. Since the instrumental width is about 0.13 eV, the intrinsic linewidth turns out to be about 0.8 eV, which seems too large to be merely due to the K-hole lifetime. The difference may be due to phonon broadening of a core level.[19] It is also expected from this analysis that the observed spectrum should reflect the partial density of states of the continuum state. Further theoretical analysis is under way.

In the case of metallic lithium the Coulomb interaction induced by the K hole is much reduced by screening of conduction electrons and the excitonic effect appears as the edge anomaly or the localization of the density of states for the conduction electrons. Also, the K hole interacts more strongly with the conduction electrons in this case than with the valence electrons in the case of LiF, since the wave function of the conduction electron has a fair amount of amplitude at the Li$^+$ ion site in contrast to that of the valence band of LiF which is mainly localized in the vicinity of F$^-$ ion sites. In other words the Li K hole interacts mainly with the excited K electron itself in LiF, whereas it interacts mainly with the conduction electron in metallic lithium. Therefore, we would expect that the resonance fluorescence via localized exciton level and structured density of states of the empty conduction band should not appear in the case of metallic lithium, and even if it should exist, the spectrum is buried within the noise or in the background.

Finally, it is hoped as a next step that a monochromatized x-ray beam is used to observe the fluorescence spectrum by scanning wavelengths. Then if the spectrum observed in LiF is only due to radiative decay of the excited electron, we should not observe the structure in the energy region above the absorption edge, because the excited electron relaxes predominantly to the bottom of conduction band, then to the core exciton level.

In conclusion we have measured the fluorescence spectra of metallic lithium and lithium fluoride associated with the Li *K* hole. As the one of possibilities the structure above 60 eV observed with LiF was interpreted as the resonance fluorescence of incident continuous radiation by the exciton and continuum states. The valence-band-to-*K*-hole emission was found to be much weaker than the resonance fluorescence.

ACKNOWLEDGMENT

This work was supported in part by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

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