PHYSICAL REVIEW B VOLUME 17, NUMBER 4 15 FEBRUARY 1978

Intrinsic luminescence excitation spectrum and extended x-ray absorption fine structure above the K edge in CaF_2†

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(Received 26 July 1977)

Excitation spectra of the 4.44-eV intrinsic luminescence in a single crystal of CaF_2 at liquid-nitrogen temperature was measured using synchrotron radiation in the x-ray region. The intrinsic luminescence at 4.44 eV is due to self-trapped exciton recombination. The intensity of the emitted uv light was measured as a function of the x-ray photon energy from below the calcium K edge to 200 eV above the edge. Dips were observed in the luminescence excitation spectrum corresponding to peaks in the absorption coefficient both in the core excitation region near the edge and in the region of excitation to the continuum far above the edge. The effect is correlated with mödulation of the radiative recombination probability of the core hole. The close relationship between the inverse of the luminescence yield and the extended x-ray absorption fine structure (EXAFS) after background subtraction shows that excitation spectra of uv luminescence can be used to measure EXAFS in thick single crystals and biological samples with suitable luminescence centers.

INTRODUCTION

In recent years, the use of synchrotron radiation has permitted the measurement of luminescence excitation spectra of ionic[1,2] and molecular[3,4] compounds over a large energy range in the ultraviolet. We report the first measurement of an intrinsic uv luminescence excitation spectrum using monochromatized x-ray photons over a continuous 300-eV range corresponding to absorption from the 1s core level of CaF_2. Under uv, x-ray, and electron bombardment, the CaF_2 crystal at LNT has a single luminescence emission peak at 4.44 eV.[5] The intrinsic luminescence in ionic compounds has been interpreted[6] in terms of recombination of self-trapped excitons (STE's). The STE luminescence in CaF_2 can be assigned to an excited triplet[6] state ($^3\Sigma_u^+$) since its lifetime (~40 ns) is relatively long.[5]

Dips in photoluminescence excitation spectra of the alkali halides and the solid rare gases have been observed previously. They have been attributed to the creation of excitons near the fundamental uv absorption edge.[1-4] Recently, their observation in the far ultraviolet was explained by the presence of core excitations.[2,6] Nevertheless, the physical origin of these dips is still under discussion, and both surface[7] and polariton[8] effects have been proposed to explain them.

Since the penetration depth of 4-KeV x rays is about 0.1 mm and the CaF_2 crystal is transparent to the 4.44-eV photons our measurements are not surface sensitive. By scanning the excitation energy region above the calcium K edge, we have found dips in photoluminescence not only due to the core excitations near the edge, but also due to transitions to the continuum more than 100 eV above the edge. The hypothesis that the effect is due to the increase of radiative recombination probability of the hole is discussed.

We have observed a close relationship between the inverse of the luminescence yield and the extended x-ray absorption fine structure (EXAFS). This result shows that it is possible to measure the EXAFS for structural information using the uv luminescence excitation spectrum. This opens up the possibility of investigating thick single crystals and biological samples with suitable luminescence centers.

EXPERIMENTAL

Measurements were taken on the focused x-ray beam line at the Stanford Synchrotron Radiation Project. The experimental setup, shown in Fig. 1, consisted of a platinum-coated mirror used to collect 10 mrad of x rays at 10 m from the storage ring and to focus them on the sample located 10 meters from the mirror. Two parallel Ge(111) crystals were used to monochromatize the incident radiation with a resolution of about 6 eV limited by the angular divergence of the incident beam. The incident intensity I_0 was monitored with an ionization chamber. The sample was a 2-mm thick CaF_2 single crystal cleaved along the (111) plane. P-polarized x rays were incident on the cleavage plane at an angle of 45°. The detector, a cooled RCA 31034A GaAs photomultiplier, was placed at

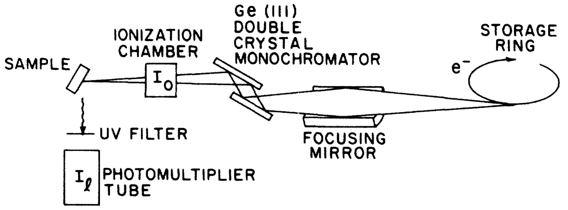

FIG. 1. Experimental setup. The synchrotron radiation is focused on a single crystal of CaF_2 cooled to LNT. The luminescence photons at 4.44 eV are detected at 90° from the incident radiation by a GaAs photomultiplier.

90° to the incident beam. To discriminate against radiation other than the 4.44 eV (279 nm) luminescence, a 275-nm uv interference filter with a 49-nm bandpass was placed in front of the photomultiplier. The sample was mounted in an evacuated LNT cryostat fitted with a kapton window for admission of x rays. The photoluminescence was viewed through a fused silica window.

We also measured the absorption coefficient and the fluorescence yield due to the radiative recombination of the K hole with an L shell electron. For this set of measurements, the CaF_2 crystal was too thick, so a thin sample of CaF_2 powder was prepared on kapton tape. A second ion chamber was placed behind the sample to monitor the transmitted intensity I_t. The fluorescence yield was measured with a nitrogen-cooled, lithium-drifted-silicon detector. All data was collected and stored by an on-line computer.

RESULTS AND DISCUSSION

In Fig. 2 (top), the CaF_2 luminescence excitation spectrum I_l/I_0 is shown plotted versus x-ray energy. The luminescence yield increases linearly with the x-ray energy below the K edge. This is the well-known behavior of the luminescence yield at high excitation energy due to the quantum conversion of high-energy photons into many low-energy photons. Above the Ca K edge, the luminescence intensity decreases 5% and a number of dips appear up to few hundred eV above the edge.

In the middle part of Fig. 2, the x-ray absorption spectrum of CaF_2 is shown. It is clear that the dips in the luminescence excitation spectrum correspond to the maxima in absorption. The uv absorption and reflection spectrum of CaF_2 has strong exciton peaks near the fundamental absorption edge[3] so that a large electron-hole interaction would be expected also at the K-absorption edge. The first strong peak in Fig. 2 (middle) should be assigned to transitions to p-like molecular states.[7] Our resolution was not good enough to resolve the transitions to the lower s- or d-like excited states[7] which are partially forbidden by the selection rules. The structures more than 50 eV above the edge can be associated with the transition matrix element modulated by the interference between the wave function of the outgoing photoelectron and the part which is backscattered by the neighboring atoms (EXAFS).[9,10] In both energy ranges the luminescence shows a dip as the oscillator strength of the electronic transition reaches a maximum.

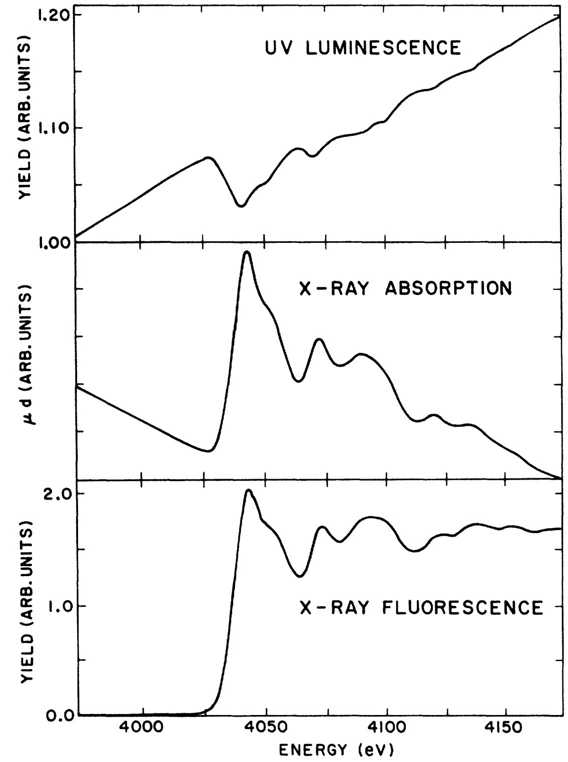

FIG. 2. Normalized uv luminescence yield I_l/I_0, as a function of incident x-ray energy is plotted at the top. For comparison, x-ray absorption and fluorescence excitation spectra of CaF_2 are shown in the middle and bottom, respectively.

Other authors have observed that there is no polarization relationship between the exciting photons and the luminescence photons, indicating that the process of the energy transfer can be considered a two-step process.[2] First, x-ray absorption produces high-energy photoelectrons. Second, electron-electron scattering leads to multiple e-h pair production followed by STE formation, recombination, and emission. This implies that far from the K edge, the luminescence yield will rise linearly with increasing the x-ray energy.

Since all the incoming x rays are absorbed in the bulk of our sample and it is transparent for the 4.44-eV photons produced in the bulk, the luminescence yield is not sensitive to the photoionization cross section of the material. At the K edge, the process competing with the STE emission is the radiative recombination of the core hole with emission of x rays at lower energy. This emission has a lower absorption cross section than the incident radiation and can escape the crystal. The dips in the luminescence spectrum shown in Fig. 2 (top) can be explained by a decrease in the integrated energy of all photoelectrons and Auger electrons due to the onset of a radiative recombination of the 1s hole above the K edge. In Fig. 2 (bottom) we show the x-ray fluorescence spectrum due to radiative decay of the 1s hole. Only the intensity of the $K\alpha$ line (~3700 KeV) was detected. This radiative decay channel is available only if there is a 1s hole so that x-ray emission is zero below the K edge, and above the edge its probability is proportional to the photoionization cross section of the 1s level, as shown in Fig. 2 (bottom).

We suggest that the dips in the STE luminescence yield of the alkali-halides observed by Beaumont *et al.*,[2,5] corresponding to core excitons in the soft x-ray region, can be clarified by our results. As in our x-ray spectra, they can be ascribed to an increase in the radiative recombination probability of core excitons. In uv excitation spectra, the penetration depth of the incident radiation is low and surface effects can play a significant role. Also, the rapid change of the reflectivity in the reflectivity in the uv complicates the interpretation of the luminescence excitation spectra.

One application of our technique is the measurement of EXAFS in thick, single crystals.[11] In Fig. 3, we plot the oscillatory part of the absorption (after background subtraction) in order to depict the EXAFS modulation. Treating the inverse of the luminescence yield in the same manner, we have found close correlation between the two spectra. The noise in the uv luminescence EXAFS is attributable mainly to counting statistics, since in this experiment, the photomultiplier, which had an active area of 20 mm^2, was located 12 cm from the sample. Thus, the detector was subtending a solid angle of about 10^{-4} sr. In the uv, one can use integrating optics to increase the signal I_l by a factor of $\sim 10^4$. Potentially, this could improve the STE-EXAFS signal-to-noise ratio by a factor of 100, providing an attractive alternative means of taking EXAFS measurements in thick single crystals. Additionally, it could be useful for the study of biological materials and dilute samples which have emission bands in the visible or the ultraviolet.

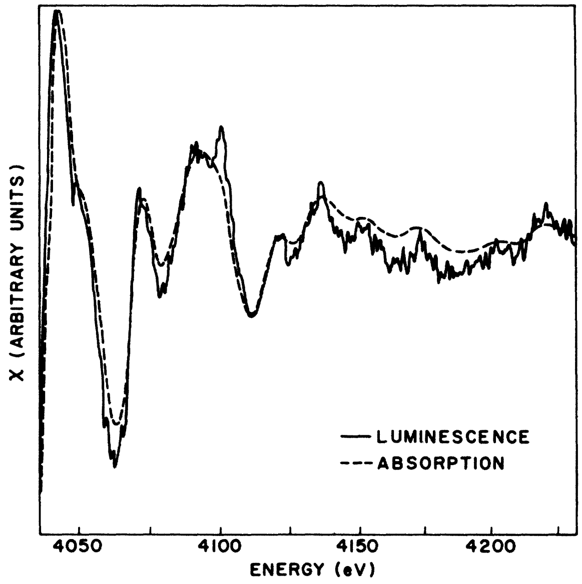

FIG. 3. Oscillatory part of the absorption coefficient (dashed line) is plotted with the oscillatory part of the inverse of the luminescence yield after background subtraction (solid line).

Further work will be necessary on a higher resolution x-ray monochromator to study the edge structure more closely. It is possible that one may be able to obtain information of the threshold position for transitions into the continuum by studying the differences in the absorption and luminescence spectra.

ACKNOWLEDGMENTS

Thanks are due to Professor S. Doniach for useful discussion of the data, to J. Kirby for helping us to take the x-ray fluorescence spectra, and to Professor H. Winick and all the staff of SSRP for continuous help in the experimental work.

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*On leave from Istituto di Fisica, Universita di Camerino, Camerino, Italy.

†Work supported by NSF Grant No. DMR73-07692 in cooperation with the Stanford Linear Accelerator Center and U.S. ERDA.

‡Supported in part by Bell Laboratories Cooperative Research Program.

§Supported in part by the NRC. Mailing Address: Bin

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