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Localized Ba 4*d* and 5*p* excitations above the ionization limit observed in BaF$_2$

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Radiative decay spectra of BaF$_2$ excited in the energy region around the Ba $4d^{-1}4f$ resonances have been measured. In the decay of selectively excited triplet states final states of the $5p^{-1}4f$ configuration are identified. Resonant behavior in spectra excited above the $4d$ ionization limit indicates that the excited electron is localized during the core hole lifetime. Localized $5p$ excitations above the ionization limit are also found, and their relevance for the interpretation of the stimulated uv emission from BaF$_2$ is discussed.

The $4d \rightarrow 4f$ resonances in the lanthanides have been intensively studied over the years.[1] In most cases the absorption spectra are independent of the chemical surrounding, and interest has been focused on the atomiclike coupling in the excited $4d^9 4f^{n+1}$ states. It has been found that the effective potential for the f electron sensitively depends on the exchange and spin-orbit interactions in a complicated way. $5p \rightarrow 4f$ excitations, on the other hand, have so far yielded little interest, mainly because they are, due to dipole selection, unimportant in the direct absorption spectra. $5p^5 4f^{n+1}$ states can, however, readily be reached in a two-step absorption-followed-by-emission process[2] of the type $4d^{10}5p^6 4f^n \rightarrow 4d^9 5p^6 4f^{n+1} \rightarrow 4d^{10} 5p^5 4f^{n+1}$. Efforts to study such transitions by means of low-energy electron excitation,[3,4] and also using synchrotron radiation[5] have been made earlier without, however, achieving a selectivity sufficient to separate emission from specific intermediate states. Here we present radiative decay spectra of BaF$_2$, excited with monochromatized synchrotron radiation in the energy region of the Ba $4d \rightarrow 4f$ resonances.

In the emission spectra we identify transitions to localized Ba $5p^5 4f$ states above as well as below the $5p$ ionization limit. Furthermore we use the decay spectra to characterize the initial $4d$ excitation. The case of Ba^{2+} ions is of special interest, since in contrast to most lanthanide ions the absorption spectrum of the free ion differs markedly from that of the ion in a crystal.[6,7] Peaks found in the spectrum of the free ion have been attributed to excitations of mainly $5f$, $6f$, and $6p$ character,[6,8] states that are found to be sensitive to the chemical surrounding.[7] Radiative decay spectra of BaF$_2$ excited in the corresponding energy region show a steep resonant behavior, indicating localized but weakly coupled electrons above the $4d$ ionization limit. Resonances are found where only faint shoulders are seen in the absorption spectrum and where no sharp resonances are found in the electronic decay channel. Hence, the study of the radiative decay is essential for the characterization of the excitations.

Special interest has been devoted to BaF$_2$ due to uv luminiscence from long-lived states. This observation suggests a possible application as a laser material and recently stimulated emission from BaF$_2$ was observed.[9] We will discuss the relevance of the localized $5p$ excitations with respect to the long-lived luminescent states in BaF$_2$.

The experiment was carried out at the recently commissioned modified SX-700 beamline BW3 (Ref. 10) at HASYLAB, Hamburg, and the radiation emitted horizontally at right angle from the incoming beam was analyzed in a grazing incidence Rowland spectrometer that will be described elsewhere.[11] The resolution of the exciting radiation was set to 72 meV, and the combined monochromator-spectrometer function was a Gaussian with a full width at half maximum (FWHM) of 180 meV as determined from direct reflection of the primary beam into the spectrometer. This procedure also calibrated the energy scales of the monochromator and the spectrometer relative to each other. At below threshold excitation no intensity from fluorescence excited by higher orders from the monochromator could be detected. Diffuse reflection spectra were measured using a channeltron collecting photons in a large solid angle in the direction 45° vertically displaced from the incoming beam. The sample was a BaF$_2$ crystal of 99.9% purity, mounted at a 30° glancing angle realtive to the incoming beam. All measurements were made at room temperature.

The diffuse reflection spectrum of BaF$_2$ (Fig. 1) shows the same features as previously measured absorption spectra.[7] The Ba $4d^{-1}4f$ configuration is essential for the interpretation of the spectrum. In LS coupling only the ^1P term can be reached from the ^1S ground state, but due to spin-orbit interaction also the ^3P and ^3D states are populated. The narrow peaks at 90.46 eV and 94.29 eV are assigned to the latter two states, respectively, and the broad, intense maximum above the ionization limit is associated with the ^1P term. The importance of other configurations has been discussed. In the absorption spectrum of free Ba^{2+} several sharp peaks[6]

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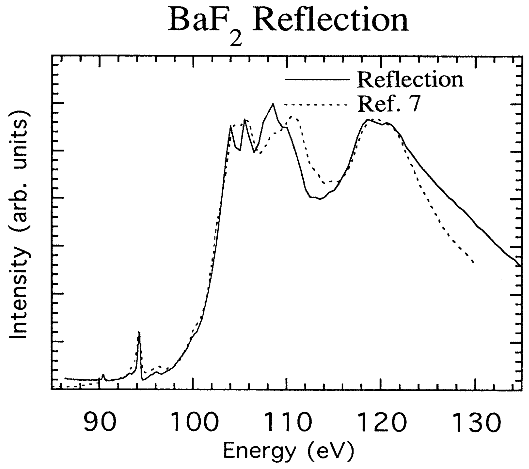

FIG. 1. Diffuse reflection spectrum of BaF_2. The dashed line is the absorption spectrum from Miyahara *et al.* (Ref. 7).

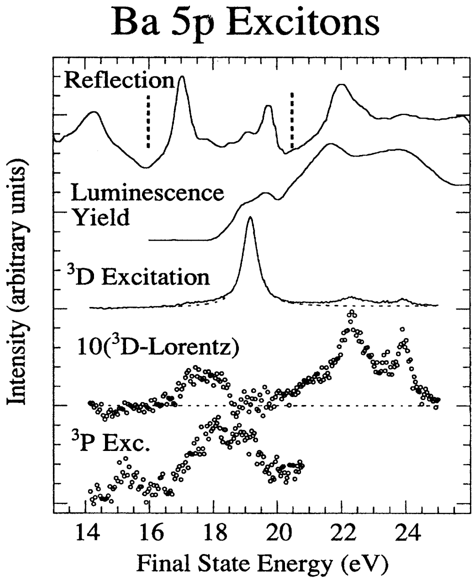

FIG. 2. Radiative decay spectra excited on the Ba $4d^{-1}4f$ ^3P (90.46 eV) and ^3D (94.29 eV) states. The latter spectrum is also shown after the subtraction of a Lorentzian (FWHM=540 meV) and a linear background, shown as a dashed curve under the original spectrum. The binding energy scale is achieved by subtracting the emission energy from the excitation energy. The uppermost curve is the reflection spectrum at room temperature according to Rubloff (Ref. 12), and the vertical dashed lines mark the onset of $5p$ excitons (16 eV) and the $5p$ ionization threshold (20.5 eV). The uv luminescence yield spectrum(Ref. 14) is also included.

are observed, which have been assigned to states of mainly $4d^{-1}5f$, $4d^{-1}6f$, and $4d^{-1}6p$ configurations.[6,8] This led Miyahara *et al.*[7] to the following tentative assignment of the structures in BaF_2. The structure around 96 eV and the shoulder at 100 eV are mostly due to $4d^{-1}6p$ states and the structures between 100 eV and 110 eV are dominated by $4d^{-1}5f$ and $4d^{-1}6f$ configurations. The $4d$ binding energies relative to the bottom of the conduction band are 95.5 eV and 98.2 eV as determined by combining band gap [11 eV (Ref. 12)] and photoemission data for the energy difference between the top of the valence band and the $4d$ levels [84.5 eV for $4d_{5/2}$ and 87.2 eV for $4d_{3/2}$ (Ref. 13)]. Thus, most of the discussed structures are clearly located above the ionization limit.

In Fig. 2 we show the radiative decay spectra where the energy of the exciting radiation is tuned to the triplet states below the ionization limit. The spectra are shown on a final state energy to compare with the uv reflection spectrum measured by Rubloff[12] and the luminescence yield spectrum[14] associated with the long-lived states. The vertical dashed lines mark the onset of $5p$ conduction band excitons, and the $5p$ ionization limit.[12] The decay spectrum excited at the ^3D state shows one dominating peak centered at 19.17 eV, with weaker structures, including peaks at 22.3 eV and 23.9 eV. We find that the intense peak is well simulated with a Lorentzian with FWHM=540 meV. This simulation reveals some additional intensity around 17 eV, and the spectrum where the Lorentzian is subtracted with the constraint of no negative residual intensity is also shown in Fig. 2. The spectrum excited on the ^3P resonance shows no sharp peaks but a broad and very weak structure around 17–19 eV final state energy.

We expect the final states of these transitions to be dominated by the $5p^{-1}4f$ configuration. Term values with $J=0$, 1, and 2 are allowed after two dipole transitions, thus we have ^3F, ^3D, and ^1D. In pure LS coupling $^3D \rightarrow {}^3F$ would be allowed and we therefore assign the 19.17 eV peak to the ^3F state. Likewise one would expect a population of the ^3D state following the ^3P excitation. The intensity is, however, smeared out over the energy region where the directly excited excitons are found in the reflection spectrum. Contrary to the ^3F symmetry the ^3D symmetry can be reached from the ground state under the $\Delta J=1$ selection rule. We propose that the smearing of the intensity can be explained in terms of an interaction between configurations of this symmetry.

Due to the spin-orbit interaction we expect intensity also from transitions that are forbidden in pure LS coupling. Thus the decay of the $4d^{-1}4f$ ^3D state populates also $5p^{-1}4f$ ^3D and ^1D states. Intensity attributed to the former is, again, smeared out around 17 eV, and we expect intensity attributed to the latter at higher final state energies. The sharp peak at 23.9 eV and the broader structure at 22.3 eV may both be due to the ^1D final state. In this energy region also shake-off of the $4f$ electron through the centrifugal barrier may contribute to the spectrum. A conclusive assignment must await theoretical verification, but we note that at least one energetically sharp, localized $5p^{-1}4f$ state is situated above the ionization limit.

Radiative decay spectra excited above the Ba $4d$ ionization limit are shown in Fig. 3. Three peaks are noted at 75.2, 75.9, and 77.8 eV. In the ionized system we expect the $4d^{-1}_{5/2} \rightarrow 5p^{-1}_{3/2}$, $4d^{-1}_{3/2} \rightarrow 5p^{-1}_{1/2}$, and $4d^{-1}_{3/2} \rightarrow 5p^{-1}_{3/2}$ transitions from photoemission data[13] at 75.0, 76.0, and 77.7 eV. The close agreement makes it tempting to assign the peaks to transitions where the excited electron is decoupled. Several observations, however, contradict such an interpretation.

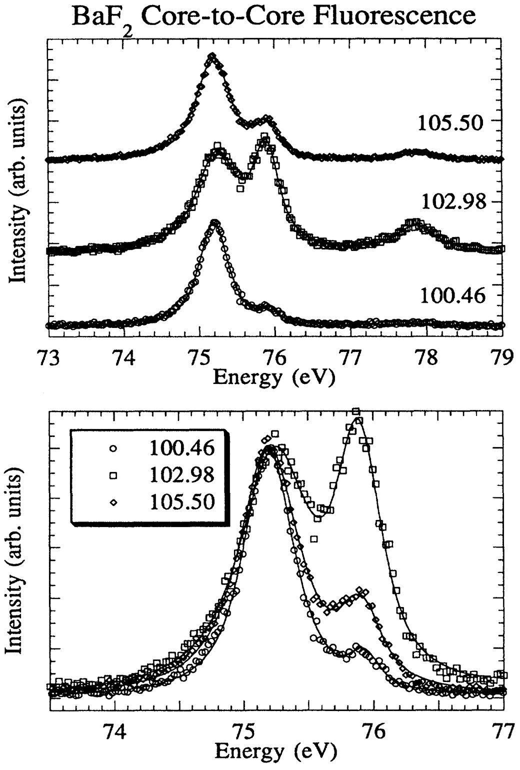

FIG. 3. Decay spectra excited at energies above the Ba 4d ionization limit.

First, the peak at 75.9 eV is in all spectra narrower than the 75.2 eV peak. The former peak should, according to the above interpretation, be associated with higher excited states than the latter, which makes an explanation of the difference in peak width in terms of lifetime broadening questionable. Second, the relative intensity ratios show a steep excitation energy dependence, the "$4d_{5/2}^{-1}\rightarrow 5p_{3/2}^{-1}$-to-$4d_{3/2}^{-1}\rightarrow 5p_{1/2}^{-1}$" intensity ratio varies in one case up to one order of magnitude within a 1 eV variation of the excitation energy. Third, the widths of the peaks are varying with excitation energy, especially we note that the width of the lowest energy peak is smaller when its relative intensity is high. The full lines in Fig. 3 are the results of Voigt fits where we have locked the Gaussian width to 180 meV, given by the combined monochromator-spectrometer function. Results of such fits are summarized in Fig. 4. We note the sharp resonance at 100.5 eV, with the width of around 0.5 eV. At these energies only a faint shoulder is seen in the absorption[7] and in constant initial state spectra monitoring specific electronic decay channels.[13] The small width of the resonance and the accompanying narrowing of the intense peak in the emission spectrum are indicative of localization, i.e., the excited state has only a weak interaction with the continuum. We are here well above the ionization limit, and the transition energies are, as mentioned above, compatible with transitions from two ionized spin-orbit split 4d states.

The observations can be understood by assuming that the excited states are linear combinations of spin-orbit coupled 4d configurations with a weakly coupled excited electron. The steep intensity variation found in our spectra is due to the mixing of the different configurations in different intermediate states at energies selected by the monochromator function.[2] A consistent explanation of the peak width variation can be based on a contribution from $|4d_{5/2}\epsilon l\rangle$ and $|4d_{3/2}\epsilon' l'\rangle$ continuum states. The spectral features are thus assigned to superpositions of transitions in the ionized system and transitions with a bound, but weakly coupled, spectator electron. At the 100.5 eV and 105 eV resonances the contribution from bound states dominates, resulting in a line narrowing. Off resonance several configurations contribute and overlap, which leads to an apparent broadening of the peaks.

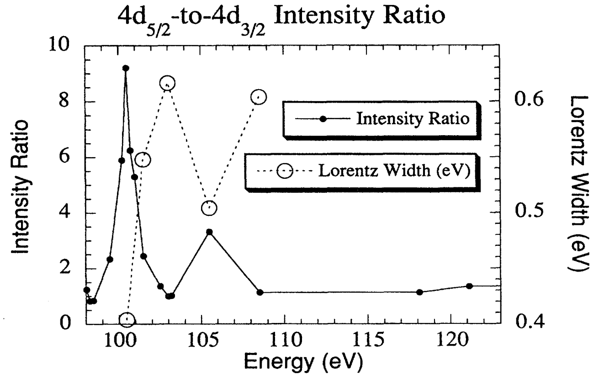

FIG. 4. Ratios of the intensities of the two most intense peaks whose energy positions correspond to the $4d_{5/2}\rightarrow 5p_{3/2}$ and the $4d_{3/2}\rightarrow 5p_{1/2}$ transitions. The intensities are measured in a Voigt fit with a locked Gaussian contribution (FWHM=180 meV). No absolute intensities have been determined, i.e., the variation in the intensity ratio may reflect cross section variations for either the $4d_{5/2}$ or for the $4d_{3/2}$ parental states or both. Significant differences in the widths were found, and the Lorentz contribution to the "$4d_{5/2}\rightarrow 5p_{3/2}$" peak is shown. The width of the $4d_{3/2}\rightarrow 5p_{1/2}$ peak was in all cases smaller.

The fact that the peaks are found at emission energies corresponding to transitions in the ionized system directly indicates that the spin-orbit and exchange interactions between the excited electron, unlike in the case of the $4d^{-1}4f$ and $5p^{-1}4f$ configurations, are small. Since the radiative decay spectra only probe the difference between the Coulomb interaction energies in the 4d and 5d hole states, we cannot rule out that this interaction still may be important. The Coulomb interaction is normally reflected in the exciton binding energies. Since we are above the ionization limit this rule cannot be applied in this case. The excited electron does not, however, delocalize since this would lead to a smearing out of the spectral features. The localized final $5p^{-1}nl$ states must be spread out over an energy region around 25–30 eV, far above the 5p ionization limit. We recall that sharp features at high final state energies were found already in the spectrum excited at the ^3D state.

BaF$_2$ is known to exhibit luminescence from long-lived ($\tau \geq 1$ ns) states at 5.6 and 6.4 eV.[14,15] Due to the long lifetime these states can be pumped, and stimulated emission has been observed.[9] The luminescence is assigned to transitions of valence electrons into the 5p core holes, and the long lifetime is explained by the fact that the Auger decay of the initial states is energetically forbidden. From direct photoemission, however, one expects the valence band (VB) $\rightarrow 5p_{3/2}$ transition at 7.3 eV, and the VB $\rightarrow 5p_{1/2}$ at 9 eV.[13] Furthermore, the 5.6 eV luminescence yield (LY) spectrum[14,15] shows distinct structures, unrelated to the reflection spectrum (Fig. 2). These structures are found in the same energy region as the localized states found in our experiment, notably the energy position of the first peak in the LY spectrum coincides with the $5p^{-1}4f\ {}^3F$ state. These observations suggest that $5p^{-1}nl$ states reached via the $4d$ excitations, such as $J=2$ states, are involved in the luminescence process. The probability to populate such states in direct absorption is very small due to the dipole selection rule, which would explain the lack of correspondence between the LY spectrum and the reflection spectrum. Dipole selection likewise forbids recombination of $J=2$ $5p^{-1}nl$ states, and Auger decay cannot occur without involving the valence electrons, making the states long-lived. The importance of the $5p^{-1}nl$-like states for the the luminescence in BaF_2 will be investigated by calculations and further experiments.

In conclusion we have presented radiative decay spectra of selectively excited Ba $4d$ states in BaF_2. Ba $5p^{-1}4f$ states were identified, and further localized states were found above both the $5p$ and $4d$ ionization limits. Selectively excited core-to-core fluorescence is shown to reveal new aspects of the electronic dynamics, and in the future we will extend the method to lanthanide compounds.

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[1] See, e.g., *Giant Resonances in Atoms, Molecules and Solids*, Vol. 151 of *NATO Advanced Study Institute, Series B: Physical Sciences*, edited by J. P. Connerade, J. M. Esteva, and R. C. Karnatak (Plenum, New York, 1986), and references therein.

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