Reappearance of Fine Structure as a Probe of Lifetime Broadening Mechanisms in the $4f^N \rightarrow 4f^{N-1}5d$ Excitation Spectra of Tb^{3+}, Er^{3+}, and Tm^{3+} in CaF_2 and $LiYF_4$

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High-energy transitions in the $4f^N \rightarrow 4f^{N-1}5d$ excitation spectra of lanthanide ions in host crystals are usually broadened due to the short excited-state lifetimes, whereas low-energy transitions, with longer excited-state lifetimes, may show fine structure. We report the surprising observation that for some materials fine structure is observed not only for the low-energy excitation bands but also for some high-energy transitions. The excited states that display fine structure are those for which the $5d$ electron is in the lowest crystal-field level but the $4f^{N-1}$ core is in a highly excited state, indicating that the broadening depends only on the energy of the $5d$ electron and not on the total energy of the $4f^{N-1}5d$ excited state.

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There is intense interest in the vacuum ultraviolet (VUV) spectroscopy of lanthanide ions in crystalline hosts, in particular the luminescence of lanthanide ions upon VUV excitation. New luminescent materials for the conversion of VUV radiation are required for flat-panel displays (plasma display panels) and mercury-free fluorescent tubes. In addition, scintillator materials, VUV detectors applied in the new generation of 157 nm wafer steppers, and designs for tunable VUV lasers rely on lanthanide luminescence upon high-energy excitation. Research on the VUV spectroscopy of lanthanide ions focuses on understanding the energy level structure and the relaxation mechanisms from high-energy excited states to the lower-energy states that emit visible light. The complex energy-level diagrams of lanthanide ions have a $4f^N$ ground configuration split primarily by the Coulomb and spin-orbit interactions into multiplets labeled by term symbols representing the spin, orbital, and total angular momentum quantum numbers ($^{2S+1}L_J$), with a small additional splitting by the crystal-field interaction with the lattice. The $4f^N \rightarrow 4f^N$ spectra are dominated by sharp zero-phonon lines and the observed energy levels may be modeled very accurately [1]. At higher energies one of the $4f$ electrons can be excited into a $5d$ orbital. The $5d$ orbitals are much more extended than the $4f$ orbitals so their interaction with the lattice is much stronger and the $4f^N \rightarrow 4f^{N-1}5d$ excitation spectra consist of both zero-phonon lines and vibronic bands. While a considerable body of data exists [2,3] detailed comparisons between experimental and theoretical energy levels and transition intensities have only recently become practical [4,5]. The observation of sharp spectral lines is crucial to such detailed comparisons. This "fine structure" is commonly seen for transitions to low-energy $4f^{N-1}5d$ states. It is well known, particularly for divalent lanthanides, that the fine structure disappears for transitions to higher-energy $4f^{N-1}5d$ states [6,7], which is attributed to line broadening associated with the reduction of excited-state lifetimes by rapid ionization of the $5d$ electron into the conduction band. Photoconductivity measurements [8–11] give strong evidence for this mechanism.

This Letter reports the remarkable observation of the reappearance of fine structure at very high energies, close to the band gap of the host lattice. This reappearance is most clearly observed for Tb^{3+} in CaF_2 and $LiYF_4$ but is also seen in the excitation spectra for Er^{3+} and Tm^{3+}. Our interpretation is that the high-energy states exhibiting fine structure are those for which the $5d$ electron is in the lowest crystal-field level, but the $4f^{N-1}$ "core" states are highly excited.

The absence of fast relaxation from these highly excited states has important implications for the understanding of the dynamics of the $4f^{N-1}5d$ configuration, suggesting that the $4f^{N-1}$ core and the $5d$ crystal-field levels are not strongly coupled. This may have a significant impact on the design of luminescent materials. The strongly allowed $4f^N \rightarrow 4f^{N-1}5d$ transitions are commonly used for efficient absorption of (V)UV radiation and fast ionization can strongly reduce the luminescence efficiency [10]. Our work suggests that the careful matching of excitation wavelengths to particular absorption bands may yield gains in efficiency for some materials.

Experimental techniques have been described previously [12]. CaF_2 and $LiYF_4$ crystals were doped with Tb^{3+}, Er^{3+}, and Tm^{3+} using methods described in Refs. [13,14]. Single crystals with a dopant concentration of 0.1% or higher were powdered to minimize saturation effects. NaF was added to the CaF_2 crystals to provide charge compensation by Na^+ ions and hence promote the formation of predominantly cubic sites [15]. UV and VUV excitation measurements were performed at the HIGITI experimental station [16] of the DESY synchrotron in Hamburg, Germany. In excitation the spectral resolution was about 0.3 nm using a modified Wadsworth Mounting 1 m monochromator with a 1200 l/mm grating blazed at

150 nm. Measurements were performed at 10 K using a cold-finger cryostat.

For Ce^{3+} there are no $4f$ electrons in the excited configuration, only a single $5d$ electron, so the spectra are very simple. In eightfold cubic coordination the $5d$ electronic states split into crystal-field levels of ^2E (lowest energy) and $^2T_2$ symmetry. There is a further small splitting of the $^2T_2$ crystal-field levels by the spin-orbit interaction. As discussed above, lanthanide ions doped into CaF_2 codoped with Na^+ form predominantly cubic sites, with a splitting between the ^2E and $^2T_2$ crystal-field levels of about 20 000 cm^{-1} for Ce^{3+} [13]. In $LiYF_4$ the site symmetry is lower (S_4) , and the $5d$ states of Ce^{3+} split into five crystal-field levels, but with an overall splitting similar to Ce^{3+} in CaF_2 [13]. For other lanthanide ions the presence of $4f$ electrons in the $4f^{N-1}5d$ excited configuration gives a more complicated energy-level structure. This structure may be modeled by extending the well-established techniques [1] for the $4f^N$ configuration [4,5]. In addition to the Coulomb, spin-orbit, and crystal-field interactions for the $4f^{N-1}$ core, and the crystal-field and spin-orbit interactions for the $5d$ electron, the Coulomb interaction between the $4f$ and $5d$ electrons must be included.

Of the trivalent lanthanide ions with both $4f$ and $5d$ electrons in the $4f^{N-1}5d$ configuration the $4f^75d$ states of Tb^{3+} spectra are particularly amenable to analysis because the energy difference between the lowest-energy states of the $4f^7$ core (of predominantly ^8S character) and the next-lowest energy states (^6P and ^6I) is approximately 30 000 cm^{-1}, larger than the crystal-field splitting of the $5d$ states. The Coulomb interaction between the $4f$ and $5d$ electrons couples the $4f^75d$ states, modifying the energies and giving rise to strong spin-allowed and weak spin-forbidden $4f^N \rightarrow 4f^{N-1}5d$ transitions [14]. Here we focus on the spin-allowed transitions, and take the picture of $4f^7$ (^8S, ^6P, and ^6I) states superimposed on the $5d$ crystal-field levels as a useful approximation.

The excitation spectrum for CaF_2:Tb^{3+} is shown in Fig. 1(a) and a schematic energy-level diagram in Fig. 1(c). Four strong excitation bands are observed, labeled A (216 nm), B (154 nm), C (133 nm), and D (127 nm). Detailed calculations [5,14] indicate that $4f^75d$ states of band A are predominantly $5d\,^2E$ crystal-field level coupled to $4f^7\ ^8S$ states, which we write as $^2E(^8S)$. Bands B, C, and D are assigned to $^2T_2(^8S)$, $^2E(^6P)$, and $^2E(^6I)$. The splitting between bands A and B, which arises from $5d$ crystal-field splitting, is about 19 000 cm^{-1}, similar to the crystal-field splitting observed for Ce^{3+}. The energy difference between bands A and C, about 28 000 cm^{-1}, is similar to the energy difference between the ^8S and ^6P states of Gd^{3+} ($4f^7$), which is about 32 000 cm^{-1} [1].

Sharp zero-phonon lines are observed for the transitions to the lowest-energy $5d$ crystal-field level (band A), while transitions to the higher-energy $5d$ crystal-field levels (band B) have no fine structure, giving only a broad structureless band. This is interpreted as an effect of the short lifetime of the higher-energy $5d$ crystal-field levels. Surprisingly, for bands C and D, where the $5d$ electron is in the lowest crystal-field level and the $4f^{N-1}$ core in an

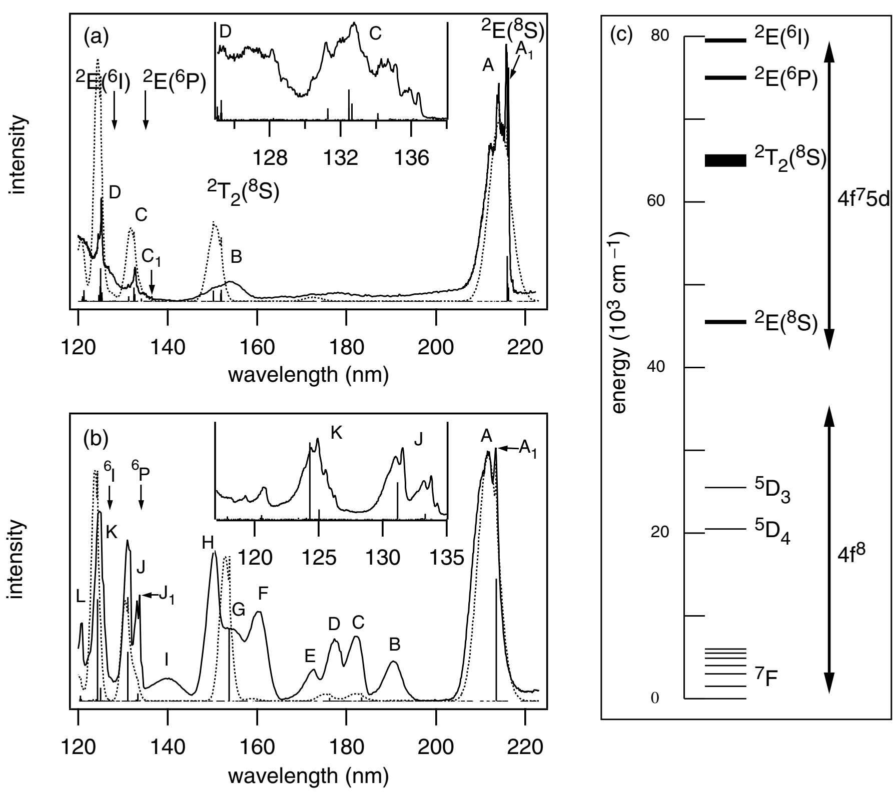

FIG. 1. Excitation spectra for (a) powdered CaF_2:0.1% Tb^{3+} monitoring the $^5D_3 \rightarrow {}^7F_6$ emission at 388 nm at 10 K and (b) powdered $LiYF_4$:1% Tb^{3+} recorded monitoring the $^5D_4 \rightarrow {}^7F_5$ emission at 544 nm at 10 K. The solid line shows the excitation spectrum measured at DESY and the dotted line is the calculated spectrum. Positions of the calculated electronic states are indicated by vertical lines. In the insets high-resolution excitation spectra are given for the wavelength regions 125–138 nm (a) and 117–135 nm (b) showing the reappearance of fine structure at high energies. (c) Schematic energy-level diagram of selected states of Tb^{3+} in CaF_2.

excited state, fine structure reappears. This implies that lifetime broadening occurs only when the $5d$ electron is in the higher crystal-field levels.

The excitation spectrum of $LiYF_4:Tb^{3+}$ is shown in Fig. 1(b). Since Tb^{3+} is at a lower-symmetry site (S_4) in $LiYF_4$ than in CaF_2 the $5d$ states split into five crystal-field levels and the spectrum is more complicated than for $CaF_2:Tb^{3+}$. Comparing the spectrum with the excitation spectrum of Ce^{3+} [13] we see that the bands with maxima at 212 nm (A), 182 nm (C), 160 nm (F), 154 nm (G), and 151 nm (H) have a similar spacing to the five $5d$ crystal-field levels observed in $LiYF_4:Ce^{3+}$. Additional bands arise due to the Coulomb interaction between the $4f$ and $5d$ electrons. A more detailed discussion of the assignments may be found in Ref. [14]. The $4f^N \rightarrow 4f^{N-1}5d$ transitions involving the lowest-energy $5d$ crystal-field level (band A) shows fine structure and the transitions to the higher-energy $5d$ crystal-field levels (bands C, F, G, H) result in broad structureless excitation bands indicating the presence of a fast relaxation process. In the higher-energy bands around 133 nm (J) and 126 nm (K), where the energy-level calculations indicate that the $5d$ electron is in the lowest crystal-field level, fine structure reappears.

For Er^{3+} the $4f^{N-1}5d$ states are situated at higher energies than for Tb^{3+}. The excitation spectrum of $CaF_2:Er^{3+}$ is shown in Fig. 2(a). Bands A (156 nm), B (146 nm), C (135 nm), and D (130 nm) are assigned to states where the $5d$ electron is in the ^2E crystal-field level and the $4f^{10}$ core is in the $^5I_8$, $^5I_7$, $^5I_5$, and $^5I_4$ states, respectively. The splittings between the different ^5I_J states is similar, though slightly smaller, than for the Ho^{3+} ($4f^{10}$) ion [1]. Fine structure is observed for all excitation bands, since the transitions are to excited $4f^{10}5d$ states involving the lowest $5d$ crystal-field level. Transitions to states involving the $5d$ $^2T_2$ crystal-field levels are calculated to start at around 120 nm. At this wavelength the CaF_2 host lattice starts to absorb and thus transitions to these states are not observed.

The excitation spectrum of $LiYF_4:Er^{3+}$ is shown in Fig. 2(b). Some features are similar to Fig. 2(a): excitation bands A, B, and D correspond to bands A, B, and C in Fig. 2(a) and are assigned to transitions to $4f^{10}5d$ states involving the lowest $5d$ crystal-field level. Fine structure is expected and observed. Bands C (140 nm) and E (130 nm) are broadbands that involve higher $5d$ crystal-field levels. Bands C and E are 7 000 cm^{-1} and 13 000 cm^{-1} above band A. These energy differences are close to the values found for the crystal-field splitting between the lowest $5d$ crystal-field level and the second and third $5d$ crystal-field levels from the excitation spectrum of Ce^{3+} in $LiYF_4:Ce^{3+}$ [13]. As in the case of Tb^{3+} the fine structure disappears for transitions to $4f^{10}5d$ states involving higher-energy $5d$ crystal-field levels and reappears at higher energies for transitions to $4f^{10}5d$ states involving the lowest-energy $5d$ crystal-field level and an excited $4f^{10}$ core state.

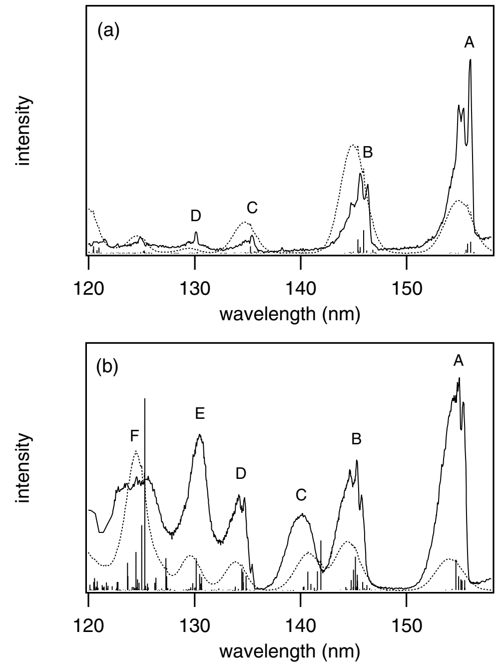

FIG. 2. Excitation spectra for (a) a CaF_2:0.001% Er^{3+} single crystal recorded monitoring the $4f^{N-1}5d \rightarrow 4f^N$ emission at 167 nm at 10 K and (b) powdered $LiYF_4$:1% Er^{3+} recorded monitoring the $^4S_{3/2} \rightarrow {^4I_{15/2}}$ emission at 550 nm at 10 K. The solid line shows the excitation spectrum measured at DESY and the dotted line is the calculated spectrum. Positions of the calculated electronic states are indicated by vertical lines.

Excitation spectra for $CaF_2:Tm^{3+}$ and $LiYF_4:Tm^{3+}$ are shown in Fig. 3. In $CaF_2:Tm^{3+}$ [Fig. 3(a)] three bands are observed. All three bands show fine structure and are assigned to transitions to $4f^{11}5d$ excited states in which the $5d$ electron is in the lowest-energy ^2E crystal-field level and the $4f^{11}$ core in the $^4I_{13/2}$ (A), $^4I_{11/2}$ (B), and $^4I_{9/2}$ (C) states. Transitions to states involving the higher-energy $5d$ $^2T_2$ crystal-field levels are not observed because, as for $CaF_2:Er^{3+}$, the transitions are obscured by host lattice absorption. In $LiYF_4:Tm^{3+}$ [Fig. 3(b)] three bands with fine structure (A, B, D) are observed at positions very similar to those for $CaF_2:Tm^{3+}$. In addition, broadbands are observed (C and E) for transitions to $4f^{11}5d$ states involving higher-energy $5d$ crystal-field levels, analogous to the situation for Tb^{3+} and Er^{3+}.

The reappearance of fine structure in the $4f^N \rightarrow 4f^{N-1}5d$ excitation spectra of lanthanide ions in CaF_2 and $LiYF_4$ suggests that line broadening due to photoionization (or other fast relaxation processes) occurs only for $4f^{N-1}5d$ states in which the $5d$ electron is not in the lowest crystal-field level. For $4f^{N-1}5d$ states involving the lowest $5d$ crystal-field level the lifetime broadening is limited and fine structure is observed, even if these states involve highly excited states within the $4f^{N-1}$ core. These surprising observations imply that the $4f^{N-1}$ core states and the $5d$ crystal-field levels of $4f^{N-1}5d$ are not strongly coupled, otherwise rapid relaxation to $4f^{N-1}5d$ with lower energy (but higher $5d$ crystal-field levels) would broaden the high-energy states. The observations

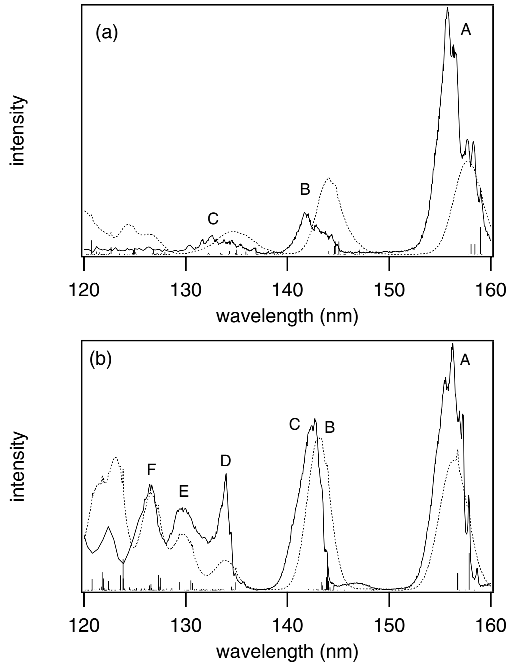

FIG. 3. Excitation spectra for (a) a CaF_2:0.001% Tm^{3+} single crystal recorded monitoring the $4f^{N-1}5d \rightarrow 4f^N$ emission at 166 nm at 10 K and (b) $LiYF_4$:1% Tm^{3+} recorded monitoring the $4f^{N-1}5d \rightarrow 4f^N$ emission at 170 nm at 10 K. The solid line shows the excitation spectrum measured at DESY and the dotted line is the calculated spectrum. Positions of the calculated electronic states are indicated by vertical lines.

have parallels with other cases of localized $4f$ orbitals interacting only weakly with more extended states. For example, $4f^7$ states with energies that overlap the $4f^6 5d$ configuration may be observed by two-photon absorption in Eu^{2+} [17] and $4f^N$ states that overlap the conduction band may be observed by excited-state absorption [18].

If ionization of the $5d$ electron into the conduction band is the dominant broadening mechanism then our observations suggest that, in the context of a band-structure picture, all of the $4f$ orbitals, but only the lowest $5d$ orbital, reside within the band gap. Electronic-structure calculations for Ce^{3+}-doped $LiYF_4$ [19] support this interpretation. It would be interesting to obtain further support by measuring VUV-induced free charge carriers. While VUV photoconductivity measurements on insulators are not expected to be feasible (due to a large VUV-induced background signal from contacts) it may be possible to measure a VUV-induced thermoluminescence band.

The interpretation presented in this work suggests that the presence or absence of fine structure may be used to aid the assignment $4f^N \rightarrow 4f^{N-1}5d$ excitation bands. In the crystals studied here bands showing fine structure may be assigned to $4f^{N-1}5d$ states involving the lowest $5d$ crystal-field level and broad structureless bands may be assigned to transitions involving higher $5d$ crystal-field levels. The excited states that show fine structure in the excitation spectra have well-defined energies and therefore relatively slow nonradiative relaxation, which could be important for luminescence applications. Furthermore, it might be possible to observe sharp (though weak) transitions between such states of the $4f^{N-1}5d$ configuration.

In conclusion, we have demonstrated that in the $4f^N \rightarrow 4f^{N-1}5d$ excitation spectra of lanthanide ions in CaF_2 and $LiYF_4$ fine structure is observed not only for the lower-energy $4f^N \rightarrow 4f^{N-1}5d$ excitation bands but also for transitions to other $4f^{N-1}5d$ states involving the lowest-energy $5d$ crystal-field level, irrespective of the energy of the $4f^{N-1}$ core. The fast relaxation that broadens some of the $4f^N \rightarrow 4f^{N-1}5d$ transitions appears to be a function only of the crystal-field level of the $5d$ electron.

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