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# Vacuum-ultraviolet excitation studies of $5d^1 4f^{n-1}$ to $4f^n$ and $4f^n$ to $4f^n$ transitions of $Nd^{3+}$-, $Er^{3+}$-, and $Tm^{3+}$-doped trifluorides

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We have measured the vacuum-uv excitation spectra of interconfiguration ($5d^1 4f^{n-1}$ to $4f^n$) and intraconfiguration ($4f^n$ to $4f^n$) transitions of Nd-, Er-, and Tm-doped $LaF_3$, $YF_3$, $LuF_3$, and $LiYF_4$. In Nd-doped samples the observed vacuum-uv excitation spectra of interconfiguration transitions differ completely from those of intraconfiguration transitions. The difference is also striking in the Er- and Tm-doped samples. The excitation spectra of interconfiguration transitions of Nd-doped samples can be explained by the crystal-field splitting of a $5d$ state, the corresponding excitation spectra for Er- and Tm-doped samples being more complicated. The vacuum-uv excitation spectra of interconfiguration transitions of rare-earth doped trifluorides show a strong excitation peak around 1200 Å which overlaps the host-lattice absorption, and exhibit concentration-quenching characteristics different from those of interconfiguration transitions. The location of this excitation peak suggests that it is associated with a process involving energy transfer from the host lattice to the rare-earth ion dopants. The large Stokes shift (~ 6 eV) observed for the emission resulting from this excitation suggests also that the transfer process is accompanied by a strong lattice relaxation similar to that observed for self-trapped holes in alkaline-earth fluorides. Attempts to observe the recombination radiation of self-trapped excitons in pure $YF_3$ and $LiYF_4$ hosts were unsuccessful. Similar attempts on pure $LaF_3$ and $LuF_3$ hosts are complicated by the presence of rare-earth impurities.

## I. INTRODUCTION

The optical properties of trivalent rare-earth ions doped into a variety of host lattices have been studied and the spectra, in general, are now well understood. The transitions that have been fully studied occur between Stark manifolds belonging to the same $4f^n$ electronic configuration and correspond to energies in the infrared and visible. The ultraviolet (uv) and vacuum-uv fluorescence resulting from the $5d4f^{n-1}$ to $4f^n$ transition of trivalent rare-earth ion doped trifluorides has not been well characterized. Elias *et al.*[1] have reported the excitation and fluorescence studies of Ce- and Pr-doped $LaF_3$. Yang *et al.*[2] have reported the excitation and fluorescence spectra of Ce-doped $LaF_3$ and $LuF_3$. Piper *et al.*[3] have reported the fluorescence of $Pr^{3+}$ ions in several trifluorides excited by 185-nm radiation. In some hosts, such as $LiYF_4$, the fluorescence of $Pr^{3+}$ ions originates from $4f5d$-to-$4f^2$ transition. Heaps *et al.*[4] have reported the observation of vacuum-uv or uv excitation and absorption bands of Ce-, Pr-, Nd-, Sm-, Gd-, Tb-, Dy-, Ho-, Er-, and Tm-doped $LaF_3$. However, their measurements failed to differentiate between the excitation spectra associated with interconfiguration transitions ($5d4f^{n-1}$ to $4f^n$) and excitation spectra associated with intraconfiguration transitions ($4f^n$ to $4f^n$) in the rare-earth ion dopants. In a previous paper[5] we reported the observation of vacuum-uv fluorescence of Nd-, Er-, and Tm-doped trifluorides. We have determined that the vacuum-uv fluorescence arises from interconfiguration transitions. In this paper we will report detailed vacuum-uv excitation studies of interconfiguration and intraconfiguration transitions of Nd-, Er-, and Tm-doped $LaF_3$, $YF_3$, $LuF_3$, and $LiYF_4$.

We also report the vacuum-uv excitation spectra of intraconfiguration transitions in Gd-doped $YF_3$ and Pr-doped $LiYF_4$. We report the search for the recombination radiation of self-trapped excitons in pure $YF_3$, $LiYF_4$, $LaF_3$, and $LuF_3$.

## II. EXPERIMENTAL METHODS

Vacuum-uv excitation studies of interconfiguration and intraconfiguration transitions of rare-earth-doped trifluorides require the assignment of the observed emission peaks to the corresponding interconfiguration or intraconfiguration transitions. It is known that crystal-field perturbations of the $4f^n$ configuration of trivalent rare-earth ions in solid hosts are much smaller than the highly localized spin-orbit interactions of $4f$ electrons.

In different solid hosts the emission frequency resulting from transitions between the states of the $4f^n$ configuration varies by a small amount, usually only of the order of 100 cm$^{-1}$. The $4f$ electrons do not interact strongly with the crystal lattice and, consequently, the spectral lines resulting from transitions within the $4f^n$ configuration are sharp. If a $4f^n$ electron is excited into a $5d$ level, the crystal-field perturbation becomes much stronger than the spin-orbit interaction because of the large radius of a $5d$ electron. The

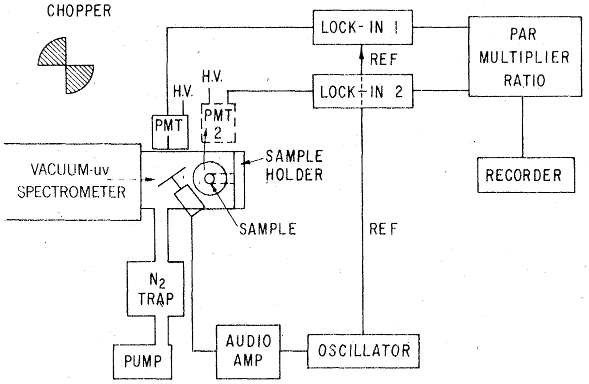

FIG. 1. Schematic diagram of the double-beam vacuum-uv spectrometer used to measure the vacuum-uv excitation spectra of interconfiguration and intraconfiguration transitions of rare-earth doped trifluorides.

strong crystal-field interaction results in broad bandwidth emission for interconfiguration transitions. For the same trivalent rare-earth ion in different solid hosts, the emission frequency shifts substantially, usually of the order of several thousand inverse centimeters. Therefore, by exciting the samples with an E beam and comparing the emission spectra for the same rare-earth ion in different hosts, we were able to distinguish between the intraconfiguration emissions and the interconfiguration emissions. Using E beam excitation we observed that Nd-, Er-, and Tm-doped trifluorides emit in the vacuum-uv region as well as at longer wavelengths. The center of the broad band vacuum-uv emission of a given dopant shifts considerably between different hosts so that a straightforward identification of this emission as resulting from interconfiguration transitions can be made. The final verification[5] was made by recording the corresponding excitation spectra. We also identified the intraconfiguration emissions in the visible region by their relative independence of the host material and by comparison with known emission lines of $4f$ transitions in rare-earth ions.[6]

Figure 1 shows schematically the experimental scheme used for the measurement of vacuum-uv excitation spectra for both inter- and intraconfiguration transitions of trivalent rare-earth-doped trifluorides. A hydrogen-arc monochromator[7] with a LiF output window was used as the excitation source. The slit width of the monochromator which was fixed at 0.25 mm corresponds to a spectral bandwidth of approximately 4.5 Å. A double-beam-attachment was placed at the output of the monochromator. A metal chopper, spray-coated with a layer of sodium salicylate, was tilted at 45° with respect to the output radiation. The chopped vacuum-uv radiation was converted into visible radiation by the sodium salicylate on the chopper blades. An EMI 9844A photomultiplier (PMT1) used to detect the visible radiation served as a reference signal. The sample was excited by the vacuum-uv radiation passing through the empty slot of the chopper. The vacuum-uv fluorescence, after passing through appropriate filters such as Suprasil or KCl crystal, was detected by a "solar blind" tube having a CsI cathode on a $MgF_2$ window (PMT2). To detect the visible fluorescence, an EMI 9635A photomultiplier was used in combination with appropriate narrow-band interference filters. The sample was also tilted 45° with respect to both the incident vacuum-uv radiation and the signal-detection system (PMT2). The latter was placed with the center of axis perpendicular to the plane of the drawing of Fig. 1 facing the sample. A lock-in amplifier synchronized to the chopper frequency at 51 Hz was used for each of the signal and reference channels. After the signal was divided by the reference via a PAR multiplier, it was displayed on a recorder. The $Q$ factor of both lock-in amplifiers was set at a value of 15 and the time constant was fixed at either 300 msec (6dB/octave) or 1 sec (6dB/octave). The time constant of the multiplier was set at the same value as the lock-in amplifiers. The sweeping speed of the vacuum-uv monochromator was about 120 Å min. The sample chamber was evacuated to a pressure of approximately $3\times10^{-3}$ Torr by a mechanical pump through a liquid-nitrogen cold trap which is necessary to prevent contamination of the sample by the pump oil.

The powder samples of rare-earth-doped $YF_3$, $LaF_3$, and $LuF_3$ were prepared by firing the corresponding mixed oxides in an Ar-HF atmosphere at 1100°C, the mixed oxides having been obtained by firing the appropriate coprecipitated oxalates in $O_2$. The ternary fluorides were prepared by mixing together the appropriate binary fluorides and firing the mixture in an Ar-HF atmosphere.

## III. EXPERIMENTAL RESULTS AND INTERPRETATION

The vacuum-uv excitation spectra of vacuum-uv fluorescence resulting from interconfiguration transitions of Nd-doped trifluorides are shown in Fig. 2. The site symmetry of neodymium in $LiYF_4$ is $S_4$,[8] in $LaF_3$ is $C_2$,[9] while in both $YF_3$ and $LuF_3$ it is $C_{1h}$.[10] For all these crystal symmetries a $5d$ state should split into five levels. For the $YF_3$, $LaF_3$, and $LuF_3$ samples four peaks were observed. The number of peaks and their locations are consistent with the reflectivity spectrum measured on a single crystal of $NdF_3$ by Olson *et al.*[11] For the ideal case of a $5d$ state due to a single $5d$ electron

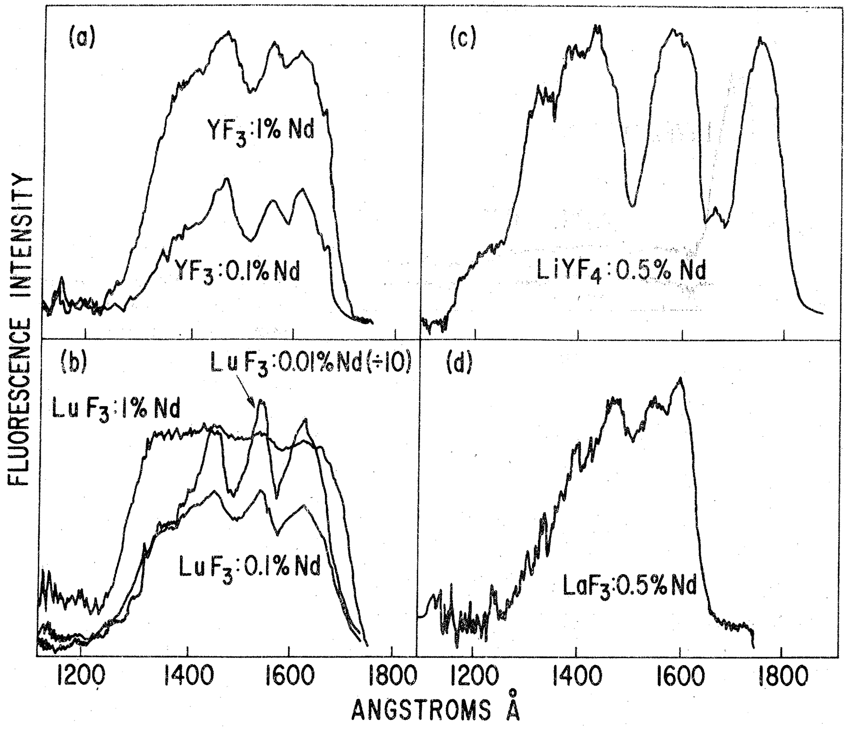

FIG. 2. Vacuum-uv excitation spectra of vacuum-uv fluorescence due to transitions from $5d^14f^2$ to $4f^3$ of Nd-doped trifluorides.

as is found for Ce $^{3+}$ in LaF$_3$ or LuF$_3$,[2] five excitation peaks are observed, as expected from crystal-field splittings. However, the peak at the high-energy side is smaller than the other four peaks. In NdF$_3$, the fifth peak at the high-energy side might have a lower absorption constant so that it does not appear in the reflectivity spectrum. A likely explanation for the absence of this high-energy peak in Nd-doped LaF$_3$, YF$_3$, and LuF$_3$ is that it overlaps with the host-lattice absorptions. The spectrum of the LiYF$_4$ sample exhibited either five or six peaks, the identification of the higher-energy peak being ambiguous. From Fig. 2 we can see that the crystal field depression of the energy levels of $5d^14f^2$ configuration of Nd$^{3+}$ ions is strongest in LiYF$_4$ so that the high-energy peak is no longer completely obscured by the host-lattice absorption and is partially resolved. In YF$_3$ and LuF$_3$ excitation spectra of different Nd$^{3+}$ concentrations were taken by changing the sample only while keeping all instrumental settings unchanged. This method was used to determine the concentration dependence described later in this paper. The results show that at Nd$^{3+}$ concentrations up to 1 mol % there is no evidence of concentration quenching of the vacuum-uv fluorescence. In the LuF$_3$ sample the four excitation peaks are well separated at Nd$^{3+}$ concentrations of 0.01 and 0.1 mol %, whereas in the 1 mol % Nd$^{3+}$ sample they are broadened and overlap to the extent that they are almost indistinguishable. However, in YF$_3$: 1 mol% Nd the four excitation peaks can still be identified.

Figure 3 shows the excitation spectra of visible fluorescence due to intraconfiguration ($4f^3$) transitions. For these measurements, an interference filter (center wavelength 3900 Å, bandwidth of 83 Å at 50% of peak transmission) was used to isolate the emission line at ~3880 Å. In order to see the variations of the double-beam traces, undoped hosts were also measured and the results are shown for comparison. The experimental results, shown in Fig. 3, indicate that there exists a strong excitation peak around 1200 Å. As shown in Fig. 3, for all four hosts the excitation spectra of intraconfiguration transitions exhibit a single peak, in strong contrast to the excitation spectra of interconfiguration transitions. The single peak is situated at a higher energy than the corresponding excitation spectrum of interconfiguration transitions and overlaps with host-lattice absorption.

It is apparent that the excitation spectra shown in Fig. 2 arise from transitions involving the energy levels of $5d^14f^2$ configuration of the Nd$^{3+}$ ions in the corresponding trifluoride host. When the Nd$^{3+}$ ion is excited from the ground state to these energy levels, experimental evidence[12] shows that they relax via phonon emission to the lowest level of the $5d^14f^2$ configuration. Phonon

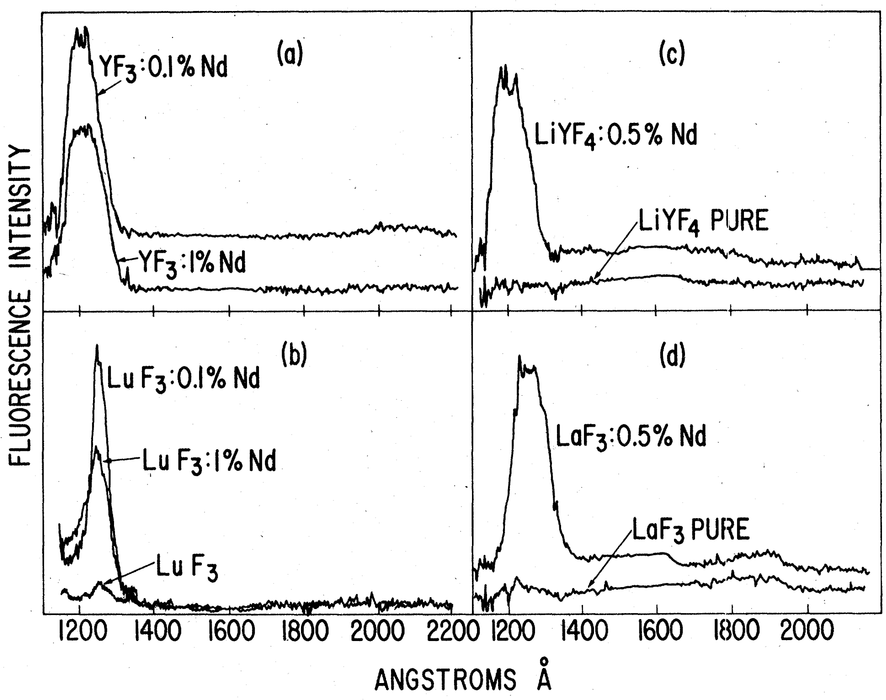

FIG. 3. Vacuum-uv excitation spectra of an emission line centered around 3880 Å resulting from the transitions within the $4f^3$ configuration of *Nd*-doped trifluorides.

relaxation is highly probable because the energy levels of $5d^14f^2$ configuration interact so strongly with the crystal lattice. From the lowest $5d^14f^2$ level, the probability of phonon (or multiphonon) relaxation to a nearby energy level of $4f^3$ configuration is low because the difference in energy involved for phonon relaxation is prohibitively large. However, the transition from energy levels of $5d^1 4f^2$ configuration to energy levels of $4f^3$ configuration is an electric-dipole allowed transition. The electric-dipole transition rate is proportional to $w^3 |\gamma_{12}|^2$, where $w$ is the frequency of the radiation and $|\gamma_{12}|$ is the electric-dipole matrix element. The $w^3$ dependence favors the transition to the ground state. The magnitude of $|\gamma_{12}|$ depends on the wave functions involved in the transition and on the selection rules.

We have determined the fluorescence quantum yield[2,5] of the transition from the lowest level of $5d^14f^2$ configuration to the $4f^3$ ground state. The measured vacuum-uv fluorescence quantum yields[5] for $YF_3$:0.1-mol % Nd and $LuF_3$:0.1-mol % Nd were 0.75 ± 0.1 and 0.80 ± 0.1 when the excitation wavelengths were at 1610 and 1625 Å, respectively. The reabsorption of vacuum-uv fluorescence by the host is small because the emission is characterized by a large Stokes shift. This large fluorescence quantum yield implies that most of the excited $Nd^{3+}$ ions return from the $5d^14f^2$ level to the ground state by emitting vacuum-uv photons and only rarely do they return by cascading through energy levels of the $4f^3$ configuration. This is the reason that the excitation spectra of intraconfiguration transitions shown in Fig. 3 reveal no peaks at wavelengths corresponding to the energy levels of $5d^14f^2$ configuration of $Nd^{3+}$.

The overlap of the excitation peaks of the intraconfiguration suggests that this process involves energy transfer from the host lattice to the impurity ion. The large Stokes shift (~6 eV) of the emission resulting from this excitation suggests that the transfer process is accompanied by a strong lattice relaxation, other than direct lattice relaxation via phonon emission. If relaxation occurred via phonon emission, the host would transfer the absorbed energy to the impurity ions, thereby exciting them from the ground state to energy levels of $5d^14f^2$ configuration since those energy levels are close to host-lattice absorption and are accessible through resonant energy transfer or nonresonant energy transfer by phonon emission. If this were the case, there would have been no excitation peak associated with intraconfiguration transitions and the excitation spectrum of interconfiguration transitions would have extended itself further into the short-wavelength region.

The amplitude of the single excitation peak around 1200 Å diminishes rapidly when the excitation energy exceeds 11 eV. This may be caused by an excitonic absorption as is observed for alkali halides[13] or may be a surface effect associated with the trifluoride hosts. The absorption constant

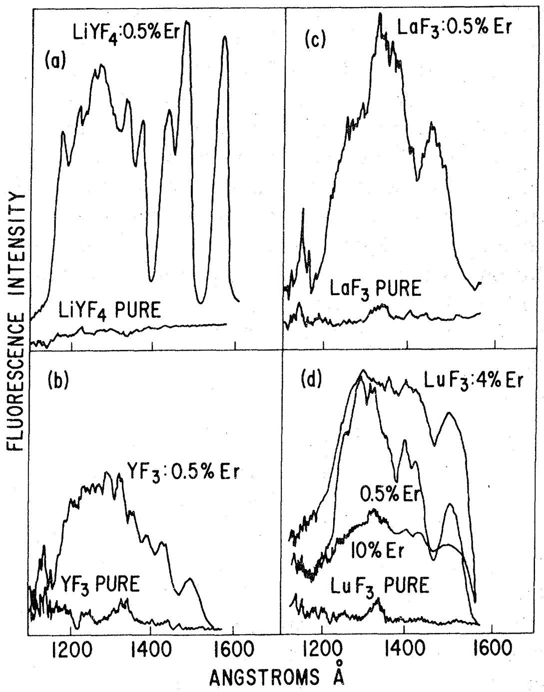

FIG. 4. Vacuum-uv excitation spectra of vacuum-uv fluorescence due to transitions from $5d^14f^{10}$ to $4f^{11}$ of Er-doped trifluorides.

for the incident vacuum-uv radiation is very large (usually in the order of $10^6$ cm$^{-1}$ for direct band-gap crystals) when the energy of the incident photon is considerably larger than the onset of host-lattice absorption. In this case most of the incident vacuum-uv photons are absorbed near the surface of the crystallites of the powder sample. If there exist surface recombination centers[14] or surface fluorescence "killer" centers, the electron-hole pairs or excitons are recombined at those centers before they can transfer their energy to impurity ions. The higher the energy of excitation, the closer are the created electron hole pairs or excitons to the crystal surface, and the higher the probability of surface recombination. The single excitation peak of intraconfiguration transitions in LuF$_3$ samples shows concentration quenching when the neodymium concentration is increased from 0.1 to 1 mol %. This observed behavior of concentration quenching is different from the excitation spectrum of interconfiguration transitions of the LuF$_3$ sample shown in Fig. 2 (b).

Vacuum-uv excitation spectra of the vacuum-uv fluorescence resulting from interconfiguration transitions of Er-doped trifluorides are shown in Fig. 4. The number of excitation peaks resolved differs for each host. Four peaks are observed for the LuF$_3$ sample, three for the LaF$_3$ sample, and more than five for both the LiYF$_4$ and YF$_3$ samples. Crystal-field splitting of the $5d$ state which should result in five peaks obviously cannot account for these results. Since the $5d^14f^{10}$ configuration contains one electron in the $5d$ orbits and ten electrons in the $4f$ orbits, interconfiguration mixing is likely to be extensive. The total perturbation due to the crystal field, spin-orbit interactions, and interconfiguration mixing is un-

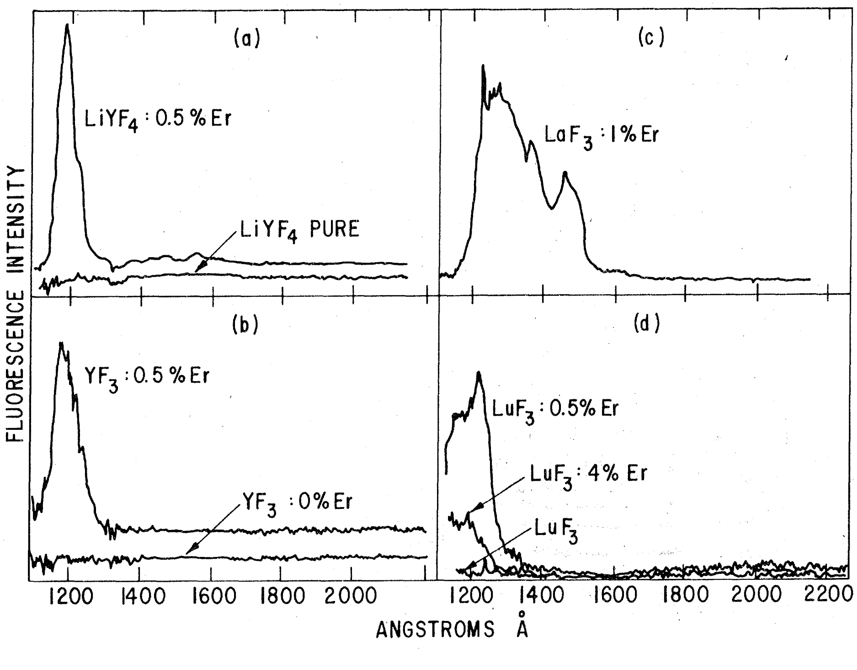

FIG. 5. Vacuum-uv excitation spectra of an emission line centered around 4660 Å caused by transitions within the $4f^{11}$ configuration of Er-doped trifluorides.

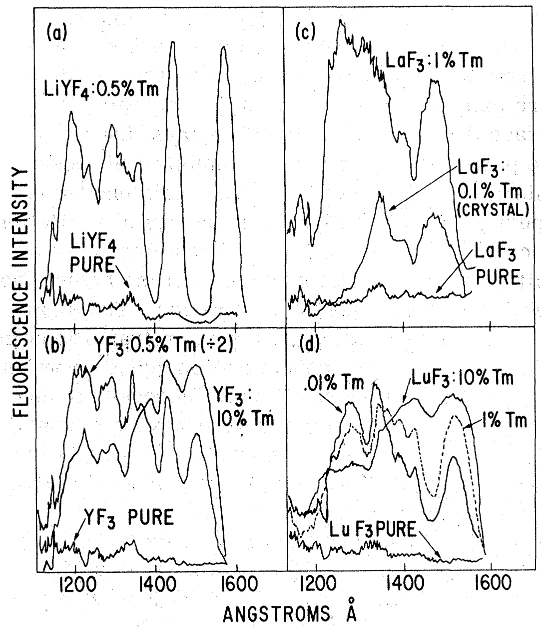

FIG. 6. Vacuum-uv excitation spectra of vacuum-uv fluorescence due to transitions from $5d^14f^{11}$ to $4f^{12}$ of Tm-doped trifluorides.

doubtedly complicated. In Fig. 4(d) concentration quenching is apparent in $LuF_3$:10-mol % Er. Figure 5 shows excitation spectra of the intraconfiguration transitions in the Er-doped trifluorides. The interference filter used in these measurements had a transmission peak at 4700 Å and a bandwidth of 93 Å at 50% of peak transmission. The $Er^{3+}$ emission line lies at ~4660 Å. Again, an excitation peak at ~1200 Å was observed. Comparing Fig. 4 with Fig. 5, we see that, similar to the Nd-doped samples, Er-doped $YF_3$ and $LuF_3$ each exhibit a single strong excitation peak corresponding to the intraconfiguration transition that is completely different from the corresponding excitation spectrum associated with interconfiguration transitions. However, in the Er-doped $LaF_3$ samples the two excitation spectra are similar except that, as shown in Fig. 5(c), one peaks at shorter wavelengths. In the $LiYF_4$ sample, in addition to a large single peak ~1200 Å, there are many smaller peaks from 1400 to 1600 Å which correspond to transitions involving the energy levels of the $5d^14f^{10}$ configuration. Evidence of concentration quenching for $LuF_3$:4-mol % Er can be seen in the excitation spectra shown in Fig. 5(d).

Figure 6 shows the vacuum-uv excitation spectra of vacuum-uv fluorescence arising from interconfiguration transitions in Tm-doped trifluorides. As above, the spectra cannot be explained simply by crystal-field splitting of a single $5d$ state. In both $YF_3$ and $LuF_3$ concentration quenching is not apparent even at a thulium concentration of 10 mol %. Figure 7 shows the vacuum-uv excitation spectra of intraconfiguration transitions in Tm-doped trifluorides. An interference filter (trans-

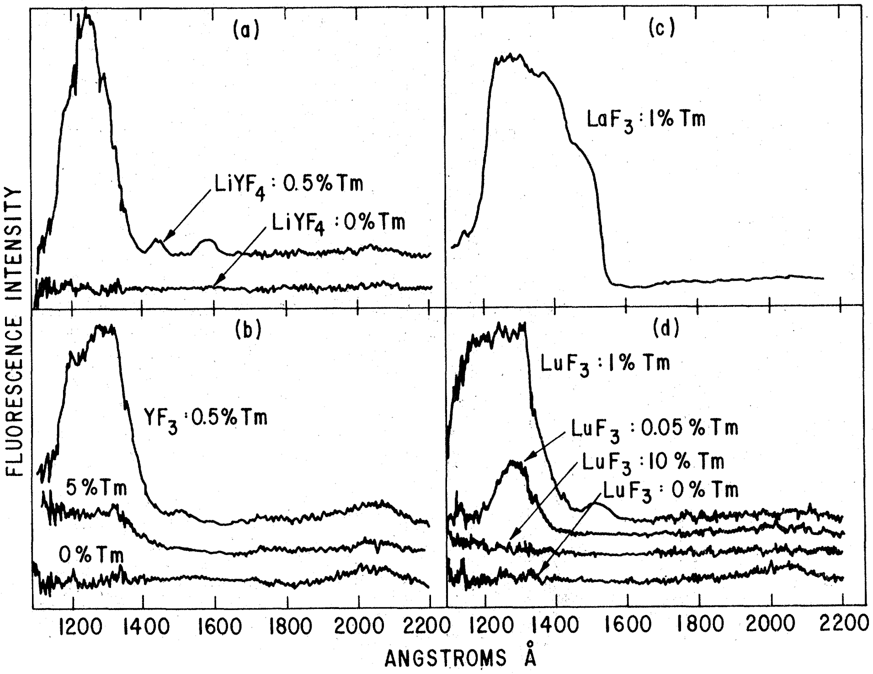

FIG. 7. Vacuum-uv excitation spectra of an emission line centered around 3600 Å resulting from transitions within the $4f^{12}$ configuration of Tm-doped trifluorides.

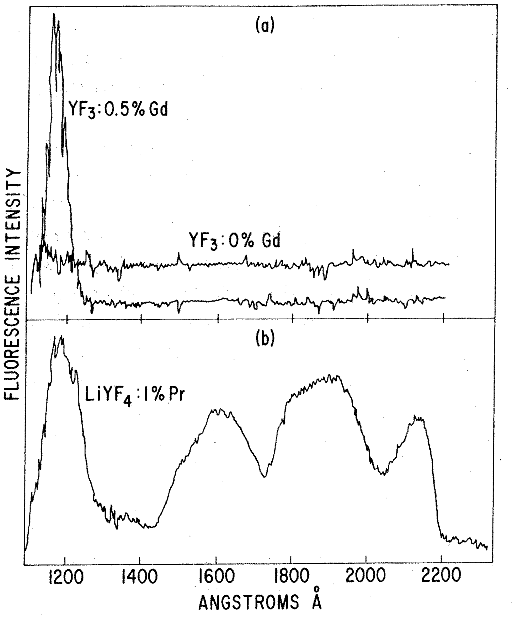

FIG. 8. (a) Vacuum-uv excitation spectra of an emission line centered around 3140 Å resulting from transitions within the $4f^7$ configuration of $Gd^{3+}$ in $YF_3$. (b) Vacuum-uv excitation spectra of an emission line centered around 4840 Å resulting from the transitions within the $4f^2$ configuration of $Pr^{3+}$ in $LiYF_4$.

mission peak at 3604 Å, bandwidth of 30 Å at 50% of peak transmission) was used to isolate the emission line at ~3600 Å. As in the previous two cases, a strong peak was observed around 1200 Å. Comparing Fig. 6 with Fig. 7, we conclude that the excitation spectra of interconfiguration transitions are remarkably different from those of intraconfiguration transitions. In Fig. 7(b) concentration quenching is apparent at 5-mol % Tm concentration, while in Fig. 7(d) it is also apparent at 10-mol % Tm concentration. These results are different from those of Fig. 6(b) and Fig. 6(d). Also, in both Er- and Tm-doped trifluorides the excitation spectra of intraconfiguration diminishes in the shorter-wavelength region beyond the onset of host-lattice absorption.

In order to verify that the strong excitation peak of intraconfiguration transitions around 1200 Å is a characteristic phenomenon of trivalent rare-earth-doped trifluorides, we measured the excitation spectrum of $YF_3$:0.5-mol % Gd sample at the emission wavelength of 3140 Å (transition from ${}^6P_{7/2}$ to ${}^8S$). As seen in Fig. 8(a), a single peak was observed. We also measured the excitation spectrum of the emission at 4840 Å for $LiYF_4$:1-mol % Pr. The result is shown in Fig. 8(b) where a peak around 1200 Å is also present.

If this peak results from a host-lattice absorption, with a subsequent transfer of the absorbed energy to the trivalent rare-earth ions, then any postulate of the lattice relaxation mechanism characterizing the energy transfer must take into consideration the large Stokes shift observed. We postulate that the strong lattice relaxation occurs via the formation of self-trapped holes such as have been observed in the alkaline-earth fluorides,[14] $CaF_2$ and $BaF_2$. The vacuum-uv radiation is absorbed by the trifluoride host, creating electron-hole pairs (excitons). The hole becomes self-trapped immediately after creation and transfers a large amount of energy to the lattice. When the electron recombines with a self-trapped hole, the recombination energy is transferred to nearby trivalent rare-earth ions. The recombination energy is only large enough to excite the trivalent rare-earth ions from ground state to the energy levels within the $4f^n$ configuration.

It might be possible to detect the recombination emission of the self-trapped holes in pure trifluoride hosts. It is well known that the recombination radiation[15] of self-trapped holes in $BaF_2$ extends from 2600 to 4000 Å. We measured the vacuum-uv excitation spectrum of the recombination radiation of self-trapped holes of $BaF_2$ powder sample (crushed from single crystals obtained from the Harshaw Chemical Company). The result is shown in Fig. 9(b). An interference filter

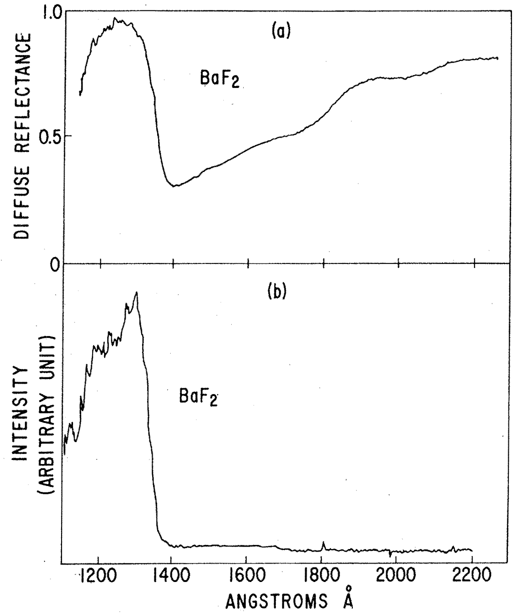

FIG. 9. (a) Diffuse reflectance of a powdered Harshaw $BaF_2$ crystal. The signal detection system has equal response from 1100 to 3600 Å. (b) The excitation spectra of the emission of self-trapped excitons in the $BaF_2$ sample.

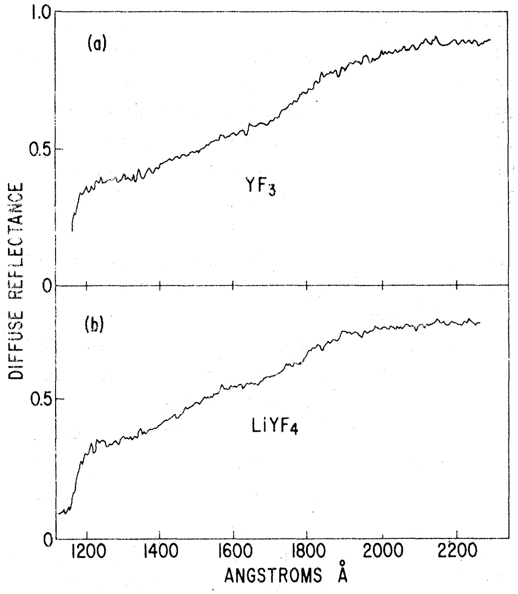

FIG. 10. (a) Diffuse reflectance of a pure $YF_4$ powder sample. The signal detection system has equal response from 1100 to 3600 Å. (b) Same as (a) except for $LiYF_4$.

centered at 3110 Å (bandwidth of 103 Å at 50% of peak transmission) was used to transmit part of the spectrum of the recombination radiation. We obtained the diffuse reflectance measurements on powder samples using the double-beam monochromator. The Pyrex window on the signal channel facing the powder sample was coated with a layer of sodium salicylate to convert the radiation from 1150 to 3600 Å into a broad band radiation centered around 4400 Å which was detected by the EMI 9635 Å photomultiplier (S-11 response). The experimental results for $BaF_2$ are shown in Fig. 9(a), and for pure $YF_3$ and $LiYF_4$ are shown in Figs. 10(a) and 10(b), respectively. In Figs. 9(a) and 9(b) we have verified that a single excitation peak of the recombination radiation of self-trapped excitons in $BaF_2$ exists at a position overlapping with the band-gap absorption of $BaF_2$ (onset at 1340 Å) and that the excitation peak also falls off on the high-energy side. However, in pure $LiYF_4$ and $YF_3$, as shown in Fig. 10, there is no evidence of the existence of the recombination radiation of self-trapped excitons having radiation with wavelength in the region from 1200 to 3600 Å. For some alkali halides[16] the recombination radiation of self-trapped holes are observed at low temperatures only, since at room temperature the self-trapped holes are mobile and are easily annihilated by nonluminescence processes. We have measured the diffuse reflectance of $YF_3$ and $LiYF_4$ sample at a temperature of approximately 110 K. The results are similar to that shown in Fig. 10 and offer no evidence of the existence of self-trapped holes. Note that in Fig. 10 the rapid drop of the diffuse reflectance around 1200 Å corresponds to the onset of a large host-lattice absorption.

We also measured the diffuse reflectance of "pure" $LuF_3$. The result is shown in Fig. 11(b). We have observed five peaks: one around 1200 Å, one around 1600 Å, and three in the region from 1900 to 2200 Å. We then excited the sample with an $E$ beam and measured the fluorescence spectrum. The observed fluorescence spectrum[2] shows two overlapping peaks of broad bandwidth from 2800 to 3220 Å. We have established that these two peaks are due to a cerium impurity by measurement of $LuF_3$ intentionally doped with different concentrations of cerium. The final confirmation[2] of the presence of cerium impurity was based on the excitation spectrum of the cerium emission. The excitation spectrum shows five peaks that are inconsistent with the crystal-field splitting of a

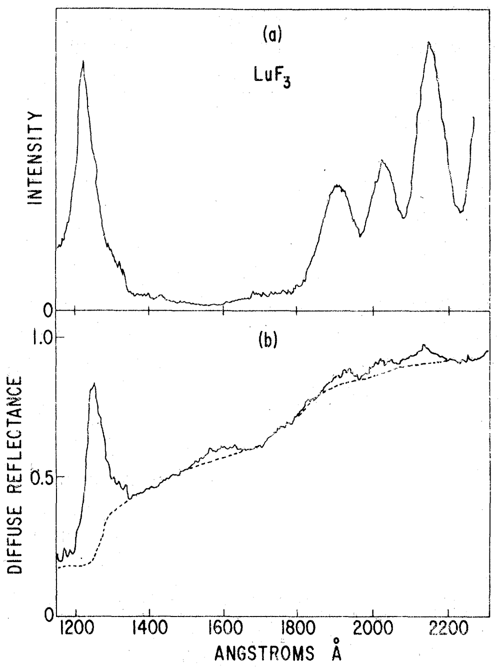

FIG. 11. (a) Vacuum-uv excitation spectrum of $Ce^{3+}$ emission using a narrow-band interference filter centered at 3110 Å. The cerium impurities are present in the supposedly pure $LuF_3$ sample. There are two excitation peaks extending from 2200 to 2700 Å which are not shown in the figure. (b) Diffuse reflectance of the same sample as in (a). The signal detection system has equal response from 1100 to 3600 Å. The dashed curve represents the result of the diffuse reflectance measurements if the emission of $Ce^{3+}$ impurities is excluded from the signal. The rapid drop on the dashed curve around 1300 Å indicates the onset of $LuF_3$ lattice absorption.

single $5d$ electron. The excitation spectrum of the "pure" $LuF_3$ using the interference filter centered at 3110 Å is shown in Fig. 11(a), where five excitation peaks are evident in the region from 1900 to 2700 Å (the last two peaks in the low-energy side are not shown in Fig. 11). A peak around 1200 Å was also observed. We believe that this peak is caused by energy transfer from the $LuF_3$ lattice to cerium impurities. We have measured also the diffuse reflectance of two $LaF_3$ samples (one obtained from Optovac). A strong peak around 1200 Å was observed for both samples which we believe is caused by rare-earth impurities.

## IV. CONCLUSIONS

In conclusion, we have measured the vacuum-uv excitation spectra of interconfiguration and intraconfiguration transitions in Nd-, Er-, and Tm-doped $LaF_3$, $YF_3$, $LuF_3$, and $LiYF_4$. The observed vacuum-uv excitation spectra of intraconfiguration transitions are entirely different from those of interconfiguration transitions in neodymium-doped samples, and remarkably different in both the erbium- and thulium-doped samples. While the excitation spectra of interconfiguration transitions in Nd-doped samples can be explained by the crystal-field splitting of a $5d$ state, the corresponding excitation spectra for Er- and Tm-doped samples are more complicated and cannot be explained by crystal-field effects alone.

The vacuum-uv excitation spectra of intraconfiguration transitions in Nd-, Er-, and Tm-doped trifluorides show a strong excitation peak around 1200 Å which overlaps the host-lattice absorption. This peak falls off rapidly as the excitation energy exceeds 11 eV and exhibits concentration quenching behavior different from that observed for the interconfiguration transitions. This excitation peak was also observed in Ce-doped $LuF_3$, Gd-doped $YF_3$, and Pr-doped $LiYF_4$. We believe that this excitation peak is a common phenomenon characteristic of rare-earth-doped trifluorides. The location of this excitation peak indicates that it is associated with a process involving energy transfer from the host lattice to the doped rare-earth ions. The observed large Stokes shift (~6 eV) of the emission resulting from this excitation suggests that the transfer process is accompanied by a strong lattice relaxation mechanism other than direct phonon emission. We believe that this relaxation process is similar to that observed in $BaF_2$ for self-trapped exciton emission excited by host-lattice absorption. Attempts to observe the recombination radiation of self-trapped excitons in pure $YF_3$ and $LiYF_4$ hosts at room temperature and at a temperature of 110 K have been unsuccessful. Similar attempts with $LaF_3$ and $LuF_3$ are complicated by the presence of rare-earth impurities which generate an excitation peak around the band-gap energy of the corresponding trifluoride host.

## V. DISCUSSION

The properties of self-trapped holes (halogenic molecular ions embedded inside the crystal) have been investigated in doped and undoped crystals of alkali halides and alkaline earth halides. Their existence as well as the existence of other color centers in trifluoride crystals have not been observed. The application of experimental techniques, such as x-ray luminescence, photoluminescence, and thermoluminescence, polarization studies of emission and absorption bands, EPR spectrum and related thermally annealed properties on doped or undoped trifluoride crystals, may lead to the demonstration of self-trapped holes in rare-earth trifluoride hosts. Direct proof of the energy transfer from the rare-earth trifluoride host to doped trivalent rare-earth impurities accompanied by a lattice relaxation by a self-trapped hole mechanism is necessary to establish the nature of the ~1200 Å excitation peak of the intraconfiguration transitions. More experimental data might be obtained by extending the excitation spectrum into the extreme uv region.

The vacuum-uv or uv fluorescence resulting from the transition from the $5d^1 4f^{n-1}$ to $4f^n$ transition in trivalent rare-earth ions doped into trifluorides usually has a broad bandwidth, large Stokes shift, and high fluorescent quantum yield. These properties are highly desirable for the construction of tunable lasers[2,5] in the vacuum-uv or uv region which could be pumped by $H_2$ or noble-gas-halide lasers. Systematic studies of the interconfiguration fluorescence of other rare-earth (except Nd, Er, and Tm) doped trifluorides will probably be quite fruitful in this respect.

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