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High-resolution vacuum ultraviolet spectroscopy of 5d-4f transitions in Gd and Lu fluorides

M. Kirm,[1] J. C. Krupa,[2] V. N. Makhov,[3,*] M. True,[1] S. Vielhauer,[1] and G. Zimmerer[1]
[1]*Institut für Experimentalphysik, University of Hamburg, Luruper Chaussee 149, D-22761 Hamburg, Germany*
[2]*Institut de Physique Nucléaire, 91406 Orsay Cedex, France*
[3]*P.N. Lebedev Physical Institute, Leninskii Prospect 53, Moscow 119991, Russia*

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Observation, investigation, and characterization of vacuum ultraviolet (VUV) (~10 eV) luminescence due to interconfigurational $4f^{n-1}5d$-$4f^n$ transitions in Gd^{3+} and Lu^{3+} are reported. High-resolution (~0.5 Å) VUV emission and excitation spectra as well as decay kinetics of VUV luminescence have been measured for $LiGdF_4$, GdF_3, $LiLuF_4$, and LuF_3 crystals using synchrotron radiation. The obtained results are the direct proof that the VUV luminescence observed from $LiGdF_4$ or GdF_3 crystals and $LiLuF_4$ or LuF_3 originates from $4f^6 5d$-$4f^7$ transitions in Gd^{3+} and $4f^{13}5d$-$4f^{14}$ transitions in Lu^{3+}, respectively. The fine structure due to zero-phonon and vibronic lines was well resolved in VUV emission and excitation spectra of $LiGdF_4$, whereas the spectra of GdF_3 and LuF_3 have a smooth shape because of stronger electron-lattice coupling between the $4f^{n-1}5d$ electronic configuration of the Gd^{3+} and Lu^{3+} ions and the lattice vibrations.

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Spectroscopy of parity-allowed interconfigurational $4f^n \rightarrow 4f^{n-1}5d$ transitions of trivalent rare earth (RE^{3+}) ions in a wide band-gap matrix requires a tuneable light source in the vacuum ultraviolet (VUV). In the pioneering work of Yen *et al.*,[1] the potential of synchrotron radiation as an excitation source for luminescence spectroscopy was demonstrated. It was first applied to $4f^n \rightarrow 4f^{n-1}5d$ excitations of RE^{3+} ions by Elias *et al.*[2] and Heaps *et al.*[3] The pioneering work, dealing with the $4f^{n-1}5d \rightarrow 4f^n$ VUV luminescence of Nd^{3+}, Er^{3+}, and Tm^{3+}, was published by Yang and DeLuca.[4] For the first half of the lanthanide series, transitions from the lowest level of the $4f^{n-1}5d$ electronic configuration into the $4f^n$ ground state are spin allowed with short lifetimes (a few ns to ≈50 ns). For ions in the second half of the lanthanide series, such transitions are spin forbidden (lifetimes in the μs range). Depending on the ion and the host, spin-forbidden, slow emission from the lowest high-spin $4f^{n-1}5d$ state, and fast spin-allowed emission from the lowest low-spin state coexist.[5,6] Up to now, VUV RE^{3+} luminescence has been detected only from Nd^{3+}, Er^{3+}, and Tm^{3+}.[4–8]

To the best of our knowledge, Gd^{3+} and Lu^{3+} VUV $d \rightarrow f$ emission has never been observed before. This may be partly due to experimental difficulties in luminescence spectroscopy in the VUV, in particular for photon energies ⩾10 eV (80 000 cm^{-1}) where the emission was expected.[9] On the other hand, for Gd^{3+} with its large number of $4f$ levels extending up to 150 000 cm^{-1},[10] it was generally accepted that the $d \rightarrow f$ luminescence would be quenched by energy transfer to $4f$ levels with subsequent non-radiative relaxation, populating the lower emitting $4f$ levels. Two photon spectroscopy has been applied in experimental studies for the lower $4f$ levels of Gd^{3+} by Dagenais *et al.*[11] and more recently up to 61 400 cm^{-1}.[12] But the onset of Gd^{3+} $4f^n \rightarrow 4f^{n-1}5d$ excitations in CaF_2 was found around 78 000 cm^{-1}.[13] The respective Lu^{3+} excitations have been identified only recently in experiments on the Ce^{3+} luminescence in $LiLuF_4:Ce^{3+}$.[14]

In the present Communication, high-resolution spectroscopic studies of VUV emissions from $LiGdF_4$, GdF_3, $LiLuF_4$, and LuF_3, nominally pure and doped with Ce^{3+} are reported for the spectral range around the edge of $4f^7$-$4f^6 5d$ transitions in Gd^{3+} and $4f^{14}$-$4f^{13}5d$ transitions in Lu^{3+}.

The VUV spectroscopy was performed at the SUPERLUMI station of HASYLAB at DESY.[15] High-resolution VUV emission was recorded using an open position sensitive microchannel-plate (MCP) detector coated with CsI in combination with a 1 m VUV monochromator, at resolutions up to 0.5 Å in second order.[8] The excitation spectra of VUV emission and decay curves were recorded using a Pouey type monochromator ($\Delta\lambda = 25$ Å) equipped with a CsI sensitized microsphere plate detector. A SpectraPro 308i spectrograph with a R6358P (Hamamatsu) photomultiplier tube (PMT) was applied for measuring excitation spectra of UV/visible emission. Due to the extremely weak luminescence intensity, the VUV emission from $LiLuF_4:Ce$ was investigated at the BW3 beamline of HASYLAB providing high-intensity excitation by XUV photons. In these measurements a high throughput 0.4 m VUV monochromator was used together with a MCP-PMT (Hamamatsu 1645 U-09) at a resolution of ~6 Å.

Single crystals of nominally pure $LiGdF_4$, $LiGdF_4$ doped with 0.05 at. % Ce^{3+}, $LiLuF_4$, and LuF_3, both doped with 0.1 at. % Ce^{3+}, were grown by the Czochralski method.[16] Powder samples of GdF_3 and LuF_3 were high-purity chemicals with a concentration of unwanted RE and other metals of 0.0005–0.001 %, and an oxygen concentration of 0.02–0.05 %.

The $d \rightarrow f$ emission spectrum from the $LiGdF_4$ crystal has a well-resolved fine structure which shows at least seven lines spread over ~500 cm^{-1} extending into a wide sideband centered at ~78900 cm^{-1} [Fig. 1(b)]. A striking similarity was observed between the VUV emission spectrum from $LiGdF_4$ [which is essentially the same for the $LiGdF_4:Ce(0.05\%)$ crystal] in the range of 78 500–79 500 cm^{-1} and the excitation spectrum of the

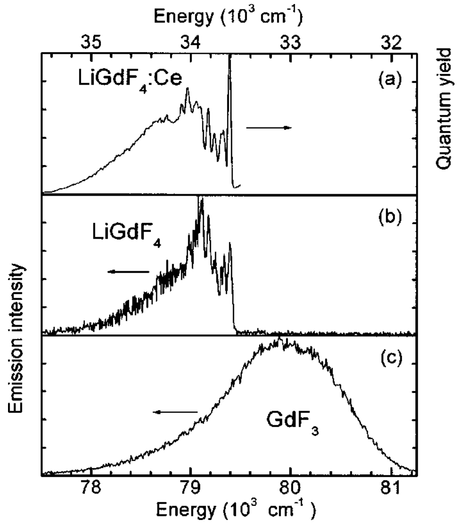

FIG. 1. (a) High-resolution excitation spectrum of LiGdF$_4$:Ce^{3+}(0.05%) monitoring 311 nm emission (upper energy scale). High-resolution emission spectra ($\Delta\lambda=0.8$ Å) of (b) LiGdF$_4$ and (c) GdF$_3$ excited by 119 (84 033 cm^{-1}) and 117 nm (85 470 cm^{-1}) photons, respectively (lower energy scale). $T=10$ K.

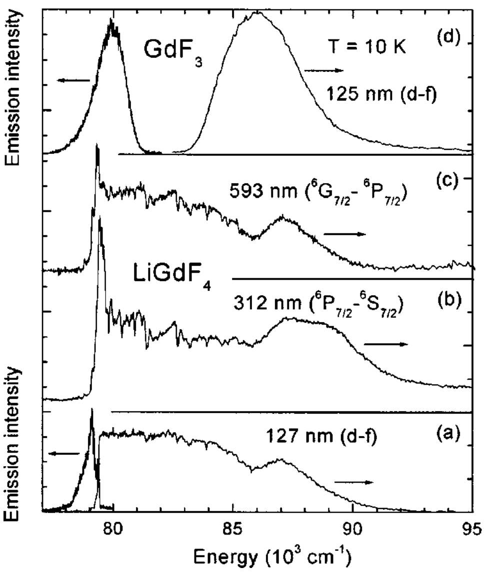

FIG. 2. (a) High-resolution excitation spectrum of $4f^65d$-$4f^7$ Gd^{3+} emission at 127 nm from LiGdF$_4$ crystal together with high-resolution emission spectrum from LiGdF$_4$ crystal excited by 119 nm (84 033 cm^{-1}) photons. High-resolution excitation spectra ($\Delta\lambda=0.8$ Å) of $4f^7$-$4f^7$ Gd^{3+} emissions monitoring (b) 312 nm ($^6P_{7/2}$-$^6S_{7/2}$) and (c) 593 nm ($^6G_{7/2}$-$^6P_{7/2}$) emission. (d) Excitation spectrum ($\Delta\lambda=2.9$ Å) of $4f^65d$-$4f^7$ Gd^{3+} emission at 125 nm from GdF$_3$ together with high-resolution emission spectrum from GdF$_3$ excited by 117 nm (85 470 cm^{-1}) photons. $T=10$ K.

311 nm emission from LiGdF$_4$:Ce(0.05%) in the range of 33 500–34 500 cm^{-1} [see Fig. 1(a)]. The VUV emission from GdF$_3$ is situated at higher photon energies and shows a single structureless band centered at ~80 000 cm^{-1} [Fig. 1(c)]. The excitation of VUV emission from LiGdF$_4$ has a well-pronounced onset at 79 000 cm^{-1} which overlaps only with shortest-wavelength line of the emission spectrum [Fig. 2(a)]. The orange (590–640 nm) luminescence, which is due to $4f^6G_{7/2}$-^6P_J transitions in Gd^{3+},[17] is also observed from LiGdF$_4$ under excitation to high-lying energy levels of Gd^{3+}. The most intense emission line at 311 nm is due to transitions from the lowest excited $4f^{7\,6}P_{7/2}$ level to the $^8S_{7/2}$ ground state of Gd^{3+}. Excitation spectra of UV/visible luminescence from LiGdF$_4$ have a well-pronounced fine structure and their onsets lie at energies slightly below that of the VUV emission [see Figs. 2(b) and 2(c)]. The structureless excitation spectrum of VUV emission from GdF$_3$ has its threshold near 83 000 cm^{-1} [Fig. 2(d)]. The decay times of VUV emission from both Gd compounds lie in the nanosecond range: 2.8 ns for LiGdF$_4$ and 0.97 ns for GdF$_3$ at 10 K. The complete thermal quenching of VUV emission observed from the LiGdF$_4$ crystal as well from the GdF$_3$ powder takes place near 200 K.

The methodology proposed in Ref. 18 allows the estimation of the energy for the lowest $4f^n$-$4f^{n-1}5d$ transition in the RE^{3+} ion doped into a particular host if the value of this energy is known for Ce^{3+}. In LiGdF$_4$ weakly doped with Ce^{3+} the intensity of Ce^{3+} $5d$-$4f$ luminescence is practically negligible because of very efficient energy transfer from Ce^{3+} to Gd^{3+} resulting in the 311 nm emission from Gd^{3+}. However, from the excitation spectrum of the 311 nm Gd emission [Fig. 1(a)], the energy of the zero-phonon line for the lowest $4f$-$5d$ transition of Ce^{3+} in LiGdF$_4$ can be determined as 33 615 cm^{-1}. The estimated energy for the zero-phonon line of the lowest $4f^7$-$4f^65d$ transition in Gd^{3+} is 79 415 cm^{-1}, that is very close to the observed threshold in excitation for VUV emission from LiGdF$_4$ as well as to the energy of the shortest-wavelength emission line from this crystal (79 377 cm^{-1}).

The above consideration allows us to ascribe the observed VUV luminescence from LiGdF$_4$ (and from GdF$_3$) to interconfigurational radiative transitions in Gd^{3+} from the lowest $4f^65d$ level to the $4f^7$ $^8S_{7/2}$ ground state. This conclusion is also confirmed by the following arguments. The decay time is expected to scale down to a few nanoseconds with increasing emission energy for the parity-allowed $4f^65d$-$4f^7$ radiative transitions in Gd^{3+}, which are also spin allowed because the lowest $4f^65d$ level of Gd^{3+} has the same spin as the $4f^7$ $^8S_{7/2}$ ground state, as for all RE^{3+} ions in the first half of lanthanide series. Only a single band of the fast emission, which is due to transitions from the lowest $4f^65d$ level to the $4f^7$ $^8S_{7/2}$ ground state is observed in the spectrum because of the absence of spin-orbit splitting for the ^8S ground term of Gd^{3+}. The Gd^{3+} $5d$ crystal-field splitting in GdF$_3$ is expected to be smaller than in LiGdF$_4$ because of the higher coordination number for Gd^{3+} (9 instead of 8), and accordingly the Gd^{3+} $4f^65d$-$4f^7$ luminescence is observed at higher energy in GdF$_3$.

As was mentioned before, the observation of VUV emission due to the $4f^65d$-$4f^7$ transitions in Gd^{3+} is a rather unexpected result because of the considerable number of closely spaced $4f^7$ levels in the same energy region as the $4f^65d$ states, enabling nonradiative relaxation from the lowest Gd^{3+} $4f^65d$ level. However the branching between radiative and nonradiative transitions favors the radiative decay at low temperatures. Most probably, the reason for this effect is that the respective non-radiative energy transfer is heavily spin forbidden, because the multiplicity of the lowest $4f^65d$ level of Gd^{3+} is eight, whereas the $4f^7$ levels of Gd^{3+} closest to this $4f^65d$ level are doublet or quartet.[19]

The crystal-field splitting of the ground state of Gd^{3+} is extremely small,[20] i.e., only a single zero-phonon line can be expected in the VUV emission spectrum of Gd^{3+}. Thus, the fine structure of VUV emission from $LiGdF_4$ should be due to one zero-phonon line corresponding to the electronic origin of the $4f^65d$-$4f^7\ {}^8S_{7/2}$ transition plus vibronic lines. The shape of the spectra with a zero-phonon line, a few narrow vibronic lines corresponding to different modes of lattice vibrations, and a wide lower-energy vibronic side band is typical for the case of intermediate electron-lattice coupling which is confirmed by the estimation of the Huang-Rhys parameter $S \sim 1$ from the energy difference between the zero-phonon line and the maximum of the wide side band, taking into account the phonon spectrum of scheelite crystals.[21]

The Stokes shift of $\sim 6000\ \mathrm{cm}^{-1}$ observed for $4f^7$-$4f^65d$ transitions in GdF_3 [Fig. 2(d)] is more than 10 times larger than the maximum phonon energy in RE trifluorides,[22] i.e., the Huang-Rhys parameter S exceeds 5 for all phonon modes of lattice vibrations, which corresponds to the case of strong electron-lattice coupling. As a result the Gd^{3+} $4f^65d$-$4f^7$ emission and $4f^7$-$4f^65d$ excitation spectra from GdF_3 have no vibronic fine structure. It should also be noted that the influence of oxygen contaminations in the powder sample on the spectrum of the VUV emission from GdF_3 cannot be significant because oxygen impurity luminescence in fluorides is known to be in the visible range.[23]

The structure observed in the excitation spectra of the 592 and 311 nm emission from $LiGdF_4$, which spreads over about $6000\ \mathrm{cm}^{-1}$, should correspond to features of $4f^7$-$4f^65d$ transitions in Gd^{3+}. The rectangular shape of the excitation spectrum for $d \rightarrow f$ emission [Fig. 2(a)] above the threshold confirms that the total absorption is observed for the stoichiometric $LiGdF_4$. Generally the penetration depth of exciting radiation is controlled by the absorption coefficient. Taking into account very different lifetimes of $5d$ and $4f$ excitations, the influence of well-known surface quenching is much stronger for the long-lived $4f$ excitations. So the dips in the excitation spectra [Figs. 2(b) and 2(c)] can be caused by absorption modulations.

Rather extensive studies have been performed earlier for $4f^7$-$4f^65d$ transitions in Eu^{2+} (see Ref. 24, and references therein), which is isoelectronic to the Gd^{3+} ion. The structure observed for $4f^7$-$4f^65d$ transitions in Eu^{2+} was well enough interpreted in first approximation as being due to the splitting of the $4f^6$ core in the $4f^65d$ state. We are not aware of any theoretical calculations describing $4f^7$-$4f^65d$ transitions in Gd^{3+}, and a detailed analysis of the structure of these transitions is beyond the scope of this communication. However, it should be noted that the energy range of this structure matches well the energy spread for the ground ${}^7F_J$ multiplet of $4f^6$ configuration of Eu^{3+}.

The VUV luminescence from the $LiLuF_4{:}Ce^{3+}$ crystal possesses both fast $(\sim 82\,600\ \mathrm{cm}^{-1})$ and slow $(\sim 80\,200\ \mathrm{cm}^{-1})$ emission bands with nanosecond and considerably longer lifetimes, respectively [Fig. 3(a)]. The VUV emission from this crystal was rather weak and the spectrum with moderate resolution was only measurable under intense XUV excitation at BW3. Due to the same reason the excitation spectrum of VUV emission from this crystal near the f-d threshold was not recorded. The VUV emission from both the Ce^{3+} doped single crystal and pure powder of LuF_3 consists only of a single band $(\sim 80\,500\ \mathrm{cm}^{-1})$ with a slow decay (longer than detectable range) [Figs. 3(b) and 3(c)]. The high-resolution measurements of both VUV emission and excitation spectra of LuF_3 did not reveal any fine structure showing practically identical behavior for single crystal and powder samples. The VUV emission from LuF_3 is thermally quenched near 200 K.

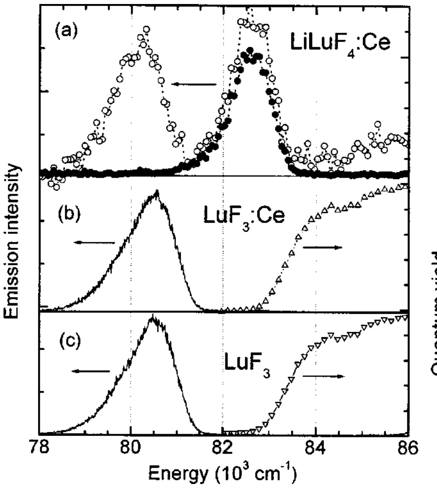

FIG. 3. (a) Emission spectra $(\Delta\lambda = 6\ \text{Å})$ from $LiLuF_4{:}Ce$ crystal excited by 130 eV photons at BW3. Time-resolved spectrum (●) was recorded within the time window of 0.8 ns after the excitation pulse. Time-integrated spectrum (○) is also shown. High-resolution emission $(\Delta\lambda = 0.8\ \text{Å})$ spectrum (solid line) excited by 116 nm photons and high-resolution excitation spectrum $(\Delta\lambda = 1\ \text{Å})$ of $4f^{13}5d$-$4f^{14}$ Lu emission (△) recorded at 124.5 nm from $LuF_3{:}Ce$ crystal (b) and LuF_3 powder (c). $T = 10$ K.

Following the approach of Ref. 18 for the prediction of the energy for the lowest $4f^{13}5d$ level of Lu^{3+} in a particular host, the energy of the Lu^{3+} low-spin (singlet) $4f^{13}5d$ level in $LiLuF_4$ is expected at $\sim 82\,300\ \mathrm{cm}^{-1}$, which is in relatively good agreement with the energy of the high-energy band in the VUV emission spectrum of $LiLuF_4$. Considering the kinetic properties of VUV luminescence from $LiLuF_4$, the two bands observed in the VUV emission spectrum of the $LiLuF_4$ crystal can be ascribed to spin-allowed (high-energy band, fast decay) and spin-forbidden (low-energy band, slow decay) interconfigurational $4f^{13}5d$-$4f^{14}$ transitions from the lowest singlet and triplet levels of the $4f^{13}5d$ configuration to the ${}^1S_0$ ground state of the $4f^{14}$ configuration of Lu^{3+}.

The VUV emission spectrum of LuF_3 consists only of a single wide band with a slow decay, which is ascribed to spin-forbidden $4f^{13}5d$-$4f^{14}$ transitions in Lu^{3+}. This is not an unusual observation since in many hosts the VUV emission of the $4f^{n-1}5d$-$4f^n$ transitions in RE^{3+} ions consists only of a spin-forbidden band because of the fast nonradiative relaxation from higher-lying low-spin states to the lower-lying high-spin state.[6,7]

The fine structure in the VUV emission spectrum of

$LiLuF_4$ was not resolved in our moderate-resolution measurements. However, in the excitation spectrum of the Ce^{3+} emission in $LiLuF_4:Ce^{3+}$ from Ref. 14 both sharp zero-phonon lines and structureless side bands are observed in the energy range corresponding to Lu^{3+} $4f^{13}5d$-$4f^{14}$ transitions, indicating intermediate coupling for the $LiLuF_4$ crystal. The Stokes shift between emission and absorption for $4f^{13}5d$-$4f^{14}$ transitions in Lu^{3+} is larger in LuF_3 than in $LiLuF_4$, which results in the absence of vibronic fine structure in both emission and excitation spectra of VUV luminescence from LuF_3.

In conclusion, we observed VUV luminescence from $LiGdF_4$, GdF_3, $LiLuF_4$, and LuF_3 crystals which was ascribed to radiative interconfigurational $4f^6 5d$-$4f^7$ and $4f^{13}5d$-$4f^{14}$ transitions in Gd^{3+} and Lu^{3+}, respectively. Only fast nanosecond VUV luminescence is observed from Gd crystals, which is typical for spin-allowed $4f^{n-1}5d$-$4f^n$ transitions in RE ions from the first half of lanthanide series. Both fast and slow emission was detected from $LiLuF_4$, corresponding to spin-allowed and spin-forbidden $4f^{13}5d$-$4f^{14}$ transitions in Lu^{3+}. Fine structure due to zero-phonon lines and vibronic lines was well resolved in VUV emission and excitation spectra of $LiGdF_4$ whereas the spectra of GdF_3 and LuF_3 have a smooth shape because of stronger electron-lattice coupling between the $4f^{n-1}5d$ electronic configuration of the Gd^{3+} and Lu^{3+} ions and the lattice vibrations.

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*Electronic address: makhov@sci.lebedev.ru

[1] W. M. Yen, L. R. Elias, and D. L. Huber, Phys. Rev. Lett. **24**, 1011 (1970).

[2] L. R. Elias, W. S. Heaps, and W. M. Yen, Phys. Rev. B **8**, 4989 (1973).

[3] W. S. Heaps, L. R. Elias, and W. M. Yen, Phys. Rev. B **13**, 94 (1976).

[4] K. H. Yang and J. A. DeLuca, Appl. Phys. Lett. **29**, 499 (1976).

[5] R. T. Wegh, H. Donker, and A. Meijerink, Phys. Rev. B **57**, R2025 (1998).

[6] R. T. Wegh and A. Meijerink, Phys. Rev. B **60**, 10 820 (1999).

[7] J. Becker, J. Y. Gesland, N. Yu. Kirikova, J. C. Krupa, V. N. Makhov, M. Runne, M. Queffelec, T. Y. Uvarova, and G. Zimmerer, J. Lumin. **78**, 91 (1998).

[8] Y. Chen, M. Kirm, E. Negodin, M. True, S. Vielhauer, and G. Zimmerer, Phys. Status Solidi B **240**, R1 (2003).

[9] E. Loh, Phys. Rev. **147**, 332 (1966).

[10] G. H. Dieke and H. M. Crosswhite, Appl. Opt. **2**, 675 (1963).

[11] M. Dagenais, M. Downer, R. Neumann, and N. Bloembergen, Phys. Rev. Lett. **46**, 561 (1981).

[12] P. Peijzel, Ph.D. thesis, University of Utrecht, Utrecht, 2004.

[13] M. Schlesinger, T. Szczurek, and G. W. F. Drake, Solid State Commun. **28**, 165 (1978).

[14] N. Yu. Kirikova, M. Kirm, J. C. Krupa, V. N. Makhov, E. Negodine, and J. Y. Gesland, J. Lumin. **110**, 135 (2004).

[15] G. Zimmerer, Nucl. Instrum. Methods Phys. Res. A **308**, 178 (1991).

[16] M. Louis, E. Simoni, S. Hubert, and J. Y. Gesland, Opt. Mater. (Amsterdam, Neth.) **4**, 657 (1995).

[17] R. T. Wegh, H. Donker, A. Meijerink, R. J. Lamminmäki, and J. Hölsä, Phys. Rev. B **56**, 13 841 (1997).

[18] P. Dorenbos, J. Lumin. **91**, 91 (2000).

[19] A. Meijerink (private communication).

[20] W. T. Carnall, P. R. Fields, and R. Sarup, J. Chem. Phys. **57**, 43 (1972).

[21] S. Salaün, M. T. Fornoni, A. Bulou, M. Rousseau, P. Simon, and J. Y. Gesland, J. Phys.: Condens. Matter **9**, 6941 (1997).

[22] M. M. Lage, A. Righi, F. M. Matinaga, J. Y. Gesland, and R. L. Moreira, J. Phys.: Condens. Matter **16**, 3207 (2004).

[23] U. Rogulis, S. Schweizer, and J. M. Spaeth, J. Phys.: Condens. Matter **14**, 6949 (2002).

[24] A. Ellens, A. Meijerink, and G. Blasse, J. Lumin. **59**, 293 (1994).