

VUV spectroscopy of BaF₂:Er

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Abstract

Luminescence and luminescence excitation spectra of BaF₂:Er in UV and VUV have been measured at Superlumi station in Hamburg, in search for fast and efficient VUV scintillator materials. Although, under selective VUV excitations, we observe the 4f¹⁰5d–4f¹¹ VUV emission, it is relatively slow and is not efficiently excited at VUV wavelengths below 124 nm. The structure observed in the VUV excitation spectra reflects rearrangement of ten 4f electrons left behind by transition promoting one of the 4f electrons of the original 4f¹¹ configuration to the lowest energy d-orbital. Other emission bands, excited at complementary VUV wavelengths, are due to the 4f¹¹ intra-configuration transitions. The VUV excitation mechanism of these transitions involves a bound exciton at Er³⁺ ion. Subsequent large energy relaxation leading to the F–H pair associated with the Er³⁺ ion prevents energy transfer to the higher lying states of the 5d4f¹⁰ configuration. Even when the 5d4f¹⁰ configuration is reached directly, the coupling between the 5d and 4f¹⁰ electrons generating the high and low spin (HS and LS) excited states of the 5d4f¹⁰ configuration is responsible for relatively slow d–f emission in BaF₂:Er.

In summary, the Er³⁺ activated BaF₂ fails to provide fast and efficient emission under ionizing excitation, expected of new scintillating materials.

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1. Introduction

UV (ultraviolet) and VUV (vacuum ultraviolet) emissions from rare earth activated broad bandgap materials are very interesting for applications such as fast scintillator materials and lasers [1,2]. Decay time of Ce³⁺ emissions in different materials is usually between 20 and 60 ns, whereas the decay times of shorter wavelengths emitters such as Pr and Nd, typically at about 250 and 190 nm, are about 8–15 and 5–10 ns, respectively. An efficient scintillator material possessing such a short scintillation decay time would be of major interest in a number of applications that require high counting rates and/or a high timing resolution, such as PET and time-of-flight PET.

Since VUV emissions from Er and Tm have been found to peak at about 165–168 nm (in YF₃) their decay times have been expected to be even shorter [3].

Unfortunately these estimates ignore the possibility that the lowest energy d–f transition is spin-forbidden and, consequently, much slower [4]. There are, nevertheless, other applications such as VUV lasers and quantum-cutting phosphors that are not critically dependent on the speed of the transition, justifying the interest in studies of these ions [5].

Synchrotron radiation has been used to study d-levels and energy transfer processes since the early seventies [6]. In particular it has been noted that the large energy loss during the hole self-trapping could be responsible for apparent differences in host sensitized excitation of inter- and intra-configurational transitions on lanthanide ions in fluorides [7].

The positions of the high energy d and f levels in Er activated fluorides (LiYF₄ and LaF₃) have been studied by

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Wegh et al. [8]. They have identified luminescent high lying $4f^{11}$ levels ($^4D_{1/2}$, $^2F(2)_{5/2}$) that are responsible for a number of emission lines in VUV and UV.

In this paper, we shall present results of the VUV experiments performed on $BaF_2:Er$ at the Superlumi station of HASYLAB located at the DESY synchrotron in Hamburg, Germany.

2. Crystals and experimental

The crystals of Er-doped BaF_2 were grown by Optovac Inc., (North Brookfield, MA, USA) using the Bridgman method. The crystal was cut from the boule grown from the melt containing 0.2 mol% of Er. It was of high optical quality, clear, displayed no color, no inclusions and no indication of oxygen contamination.

Luminescence and excitation spectra were measured at the Superlumi station, described by Zimmerer [9] (see also [10]).

In most cases the excitation spectra have been corrected using a salicylate standard. The emission spectra have not been corrected for spectral sensitivity of the experimental set-ups.

3. Experimental results and discussion

3.1. VUV excited UV and VIS luminescence of $BaF_2:Er$

In Figs. 1 and 2 we present emission spectra of $BaF_2:Er$. The spectrum shown in Fig. 1 was measured with the excitation wavelength set at 132 nm. The spectrum shows a number of well known emission lines (322, 381, 405, 471, 523 and 547 nm), mostly in the visible (VIS emissions) starting at energy levels due to the $4f^{11} Er^{3+}$ states such as $^2P_{3/2}$, $^4G_{11/2}$, $^2G(1)_{9/2}$, $^4F_{7/2}$, $^2H_{11/2}$ and $^4S_{3/2}$.

Interestingly, a relatively small change of the excitation wavelength (to e.g., 134, 144, 154 and 164 nm, see Section

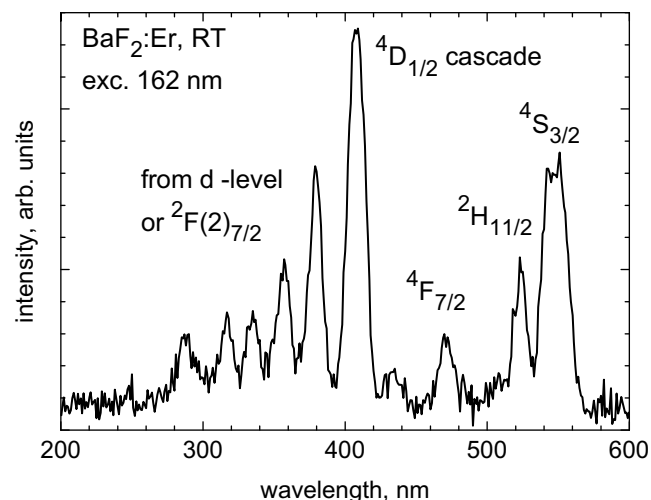


Fig. 2. Uncorrected UV and VIS emission spectrum of $BaF_2:Er$ at RT. The excitation wavelength was set at 162 nm (resolution 6.4 nm, step 1 nm).

3.2) produces very different emission spectra such as the one shown in Fig. 2 (162 nm). In these spectra, in addition to the VIS lines characteristic of the spectrum shown in Fig. 1, we find a number of additional lines, at 223, 242, 289, 317, 335, 357, 379 and 409 nm, mostly at UV (UV emissions). These lines originate, probably, in the lowest d-level, or in highly lying $Er^{3+} 4f^{11}$ levels such as $^2F(2)_{5/2}$, $^2F(2)_{7/2}$ and $^4D_{1/2}$, terminating at various levels of the same configuration situated between 15,000 and 40,000 cm^{-1} [8].

3.2. Excitation processes leading to STE, VIS and UV emissions

In Fig. 3 we show the excitation spectra of the VIS and VUV/UV emissions at 5 K. The first spectrum (broken

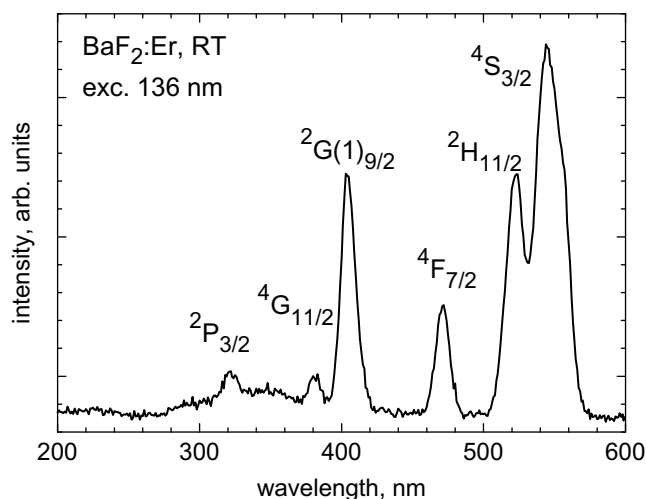


Fig. 1. Uncorrected VIS emission spectrum of $BaF_2:Er$ at RT. The excitation wavelength was set at 136 nm (resolution 6.4 nm, step 1 nm).

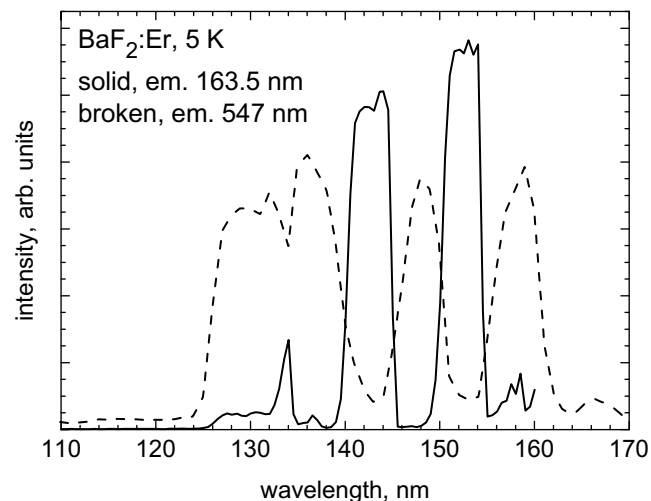


Fig. 3. Corrected excitation spectra of VIS and UV emissions of $BaF_2:Er$ at 5 K. Solid line, emission wavelength set at 163.5 nm, broken line, emission wavelength set at 547 nm. Resolution was 0.28 nm, step 0.5 nm.

line) was measured at 547 nm (VIS emission), while the second (solid line), at 163.5 nm (the shortest wavelength VUV line, see Section 3.3).

Unfortunately excitation efficiency of the VIS and VUV/UV emissions at VUV wavelengths below 124 nm is strongly reduced and the emission spectra reveal no VUV/UV and almost no VIS emission lines. Instead the spectrum (not shown) is dominated by the well known, single broad band peaking at about 325 nm and due to decay of self-trapped excitons (STE) [11].

We conclude that there must be three different excitation channels; the first channel feeding STEs (below 124 nm), the second higher levels (for selected wavelengths above 124 nm) and the third feeding lower levels of the $4f^{11}$ configuration of the Er^{3+} ions.

The competition between two Er-targeting channels is nicely visualized in Fig. 3. We note that the wavelengths, for which VUV/UV emissions are excited efficiently, coincide with the minima in the excitation spectrum of VIS emissions (134, 144, 154 and 164 nm) providing a direct evidence of competition between the two spectrally overlapping excitation channels.

It is reasonable to assume that the channel targeting the lower VIS emission levels of Er^{3+} is represented by a broad, relatively weak band covering wavelengths from, say, 125 up to about 166 nm. This band is then distorted by the three stronger bands producing “dents” at 134, 143 and 152.5 nm, due, most likely, to d-levels of the Er^{3+} ion. We will discuss the energy levels of the $\text{Er}^{3+} 4f^{n-1}5d$ configuration later on.

The amount of energy transferred eventually to the Er^{3+} ion via a weak band excitation is not enough to excite the $\text{Er}^{3+} 4f^{11}$ higher energy levels although it must be enough to excite its lower levels such as $^2P_{3/2}$ or $^4S_{3/2}$. We conclude therefore that the excitation into this band must be followed by a large energy relaxation, as suggested earlier by Yang and DeLuca [7] and then followed by energy transfer to the ion. This energy relaxation process is, apparently, similar to that of the self-trapped hole; note that the $^2P_{3/2}$ level at 322 nm lies in the middle of the STE emission band demonstrating the feasibility of radiative or nonradiative energy transfer from the STE to Er^{3+} ion.

Nevertheless the excitation energy is not efficiently transferred from STE to Er^{3+} as there is almost no Er emission for VUV excitations below 124 nm (see Fig. 3). The final unrelaxed state reached by a weak band excitation above 125 nm must be due to the Er-bound exciton. The large relaxation of the Er-bound exciton is likely to involve both electron and hole components, so that the relaxed state is represented, probably, by a complex consisting of the Er^{3+} ion and the pair of F–H centers [12]. VUV excitation of the levels responsible for the VIS emissions would then be due to the F–H recombination followed by energy transfer to the Er^{3+} ion. In contrast, the relaxation after excitation of d-levels stops at the lowest d-level with no large relaxation characteristic of the F–H complex.

3.3. VUV emissions and excitations

To identify shorter wavelengths Er^{3+} emissions that follow the d-states excitation we have switched to the VUV monochromator in detection [10].

In Fig. 4 we present the emission spectrum of $\text{BaF}_2:\text{Er}$ under 144 nm excitation at 5 K. In addition to the UV lines identified previously (see Fig. 2) there are additional VUV lines at 163.6, 176 and 183.9 nm. We have not, however, detect any emission at shorter wavelengths down to 150 nm, well below the edge of the lowest d-band identified so far, at 155 nm (see Fig. 3). We also note that the energy difference between bands at 163.6 and 183.9 nm, at about 6700 cm^{-1} is only slightly higher than the energy difference between the two lowest energy levels of the $\text{Er}^{3+} 4f^{11}$ configuration, $^4I_{15/2}$ and $^4I_{13/2}$ (6500 cm^{-1} , from the Dieke's diagram reproduced in [13]). So it well could be that these two emissions originate from the same, so far undetected energy level and should have, in principle, the same excitation spectrum. We were unable to identify this level by measurement of the excitation spectrum of the 163.6 nm emission, shown in Fig. 3, because of the excitation stray light leaking into detection monochromator but it could be done by monitoring the longer wavelength emission at 184 nm.

We note also that if we assume that the third line, at 176 nm, is due to transition that terminates at $^4I_{13/2}$, then the energy of the corresponding upper level should be equal to $63,270\text{ cm}^{-1}$, reasonably close to the calculated energy of the $^2F(2)_{5/2}$ level at $\sim 63,400\text{ cm}^{-1}$ ($\sim 157.8\text{ nm}$).

In Fig. 5 we present the excitation spectrum of the 184 nm emission. The spectrum shows a new band, peaking at 161.6 nm, close to the emission band at 163.5 nm. Thus we have four bands, at 133.9, 142.7, 152.5 and 161.6 nm, which we assign to intra-configurational f–d transitions at Er^{3+} ions in BaF_2 . The energy separations between centers of these bands are about 4600, 4500 and 3700 cm^{-1} .

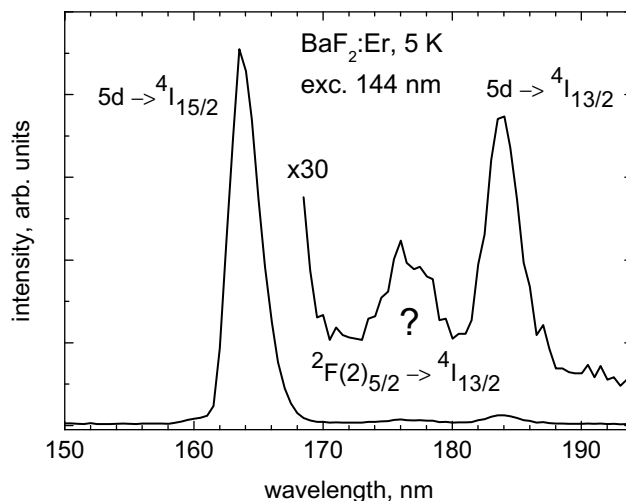


Fig. 4. Uncorrected VUV emission spectrum of $\text{BaF}_2:\text{Er}$ at 5 K. Excitation wavelength was set at 144 nm. Resolution, 4 nm, step 1 nm. Labels indicate the origin of emission bands (see text).

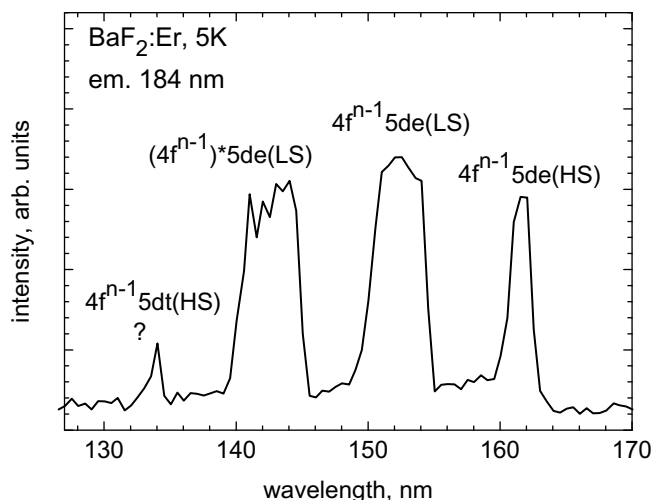


Fig. 5. Corrected excitation spectrum of VUV emission of BaF₂:Er at 5 K. The emission wavelength was set at 184 nm. Resolution was 0.28 nm, step 0.5 nm. Labels indicate the origin of transitions assigned to given bands (see text). (4fⁿ⁻¹)^{*} indicates the excited state of the 4fⁿ⁻¹ configuration.

The upper bound of the d(e)–d(t) energy separation (10 Dq) in BaF₂ cubic field can be estimated at 14,300 cm⁻¹ as the positions of the d(e) and d(t) bands in the excitation spectra of the Ce emission in BaF₂ are about 290 and 206 nm, see e.g. [14], and the higher energy e-level is undetectable [15]). Thus it is impossible to interpret the reported structure as due to the low symmetry crystal field since the dominant crystal field component must be cubic (8 fluorine ligands) with a relatively high value of 10 Dq.

To understand the spectrum shown in Fig. 5 we refer to some earlier papers of Meijerink and coworkers [4,16,17] on Er in LiYF₄ and CaF₂. According to their interpretation the low intensity band at 161.6 nm must be due to the spin-forbidden transition terminating at the high spin (HS) 4f¹⁰5d(e) energy state of the Er³⁺ ion, while the next band, at 152.5 nm is due to the low spin (LS) 4f¹⁰5d(e) energy state. The 3700 cm⁻¹ energy difference between these two bands comes from the exchange interaction between d and f electrons of the higher energy 4f¹⁰5d configuration with the d-electron placed in the lowest energy e-orbital.

We also infer that the third band, at 142.7 nm, is due to the spin-allowed transition in which one f-electron is promoted to the lowest energy e-level, but the remaining ten f-electrons assume the next, higher energy state, ⁵I₇, of the 4f¹⁰ configuration (Ho³⁺). Note that the energy difference between these bands, at 4510 cm⁻¹ is, as expected, only slightly lower than the 4800 cm⁻¹ energy difference between ⁵I₈ and ⁵I₇ states of the Ho³⁺ ion (estimated roughly from the Dieke's diagram reproduced in [13]).

We propose, nevertheless, a different interpretation of the fourth band, at 133.9 nm. First of all, unlike in CaF₂ [17], the energy gaps between the consecutive bands are not consistent with the energy gaps between the relevant levels of the 4f¹¹ configuration, ⁵I₈, ⁵I₇ and ⁵I₆. We also

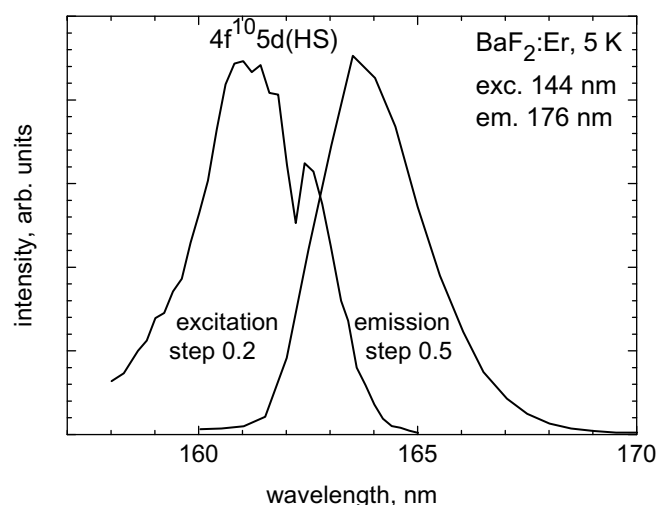


Fig. 6. Emission and excitation spectra of BaF₂:Er at 5 K. For the emission spectrum, the excitation wavelength was set at 144 nm, resolution was 4 nm, step 0.5 nm. For the excitation spectrum the emission wavelength was set at 176 nm, resolution was 0.28 nm, step 0.2 nm.

observe that this band is even lower in intensity than the spin-forbidden band at 161.6 nm. Consequently, we assume that this band is due to a spin-forbidden transition to the HS state in which electron is promoted to the t-, not e-orbital and the 4f¹⁰ core remains in the lowest energy state (⁵I₈). The crystal field parameter 10 Dq would then be about 12800 cm⁻¹, in agreement with the previous estimate. This interpretation explains the weakness of the 133.9 nm band.

Finally in Fig. 6 we compare the shortest wavelength VUV emission band (shown previously in Fig. 4), peaking at 163.6 nm, and the lowest energy excitation band, peaking at 161.2 nm. Note that this excitation spectrum has been measured with the emission set at 176 nm and that the step is smaller.

The spectrum shows some additional, relatively sharp feature at 162.5 nm. The sharp feature could be a zero-phonon line; this assumption is consistent with distortions at the higher energy side of the emission band that are typical of the relatively highly doped samples. We also note that the Huang Rhys factor must be 1–1.5, consistently with the relatively narrow emission and absorption bands.

4. Summary

We have identified a number of emission lines and bands in VIS, UV and VUV from Er activated BaF₂. The VIS lines correspond to transitions from the lower energy levels of the Er³⁺ 4f¹¹ configuration excited by VUV wavelengths forming a broad band adjacent to the bandgap of undoped BaF₂ (Er-bound exciton). This broad band shows “dents” caused by two spin-allowed and two spin-forbidden Er³⁺ 4f¹¹ → 4f¹⁰5d transitions.

Consequently, because of the Hund's rule, the lowest d-level has a total spin of 5/2 and the final 4f¹¹ state of Er³⁺ is

characterized by a spin of 3/2, the d–f emission is spin-forbidden and slow.

Excitation into any of the four f–d bands generates d–f emission (at 161.2 and 184 nm) and a number of UV lines that correspond to transitions starting, most likely, at highly positioned $^2F(2)_{7/2}$ and $^4D_{1/2}$ levels of the $4f^{11}$ configuration and terminating at various levels with energies between 15,000 and 40,000 cm^{-1} . At VUV wavelengths we have identified three bands at 163.6, 176 and 183.9 nm. Two of these bands correspond to spin forbidden d–f transitions terminating at $^4I_{15/2}$ and $^4I_{13/2}$, while the origin of the third line is unclear ($^2F(2)_{5/2} \rightarrow ^4I_{13/2}$?).

Finally, the excitation below 124 nm generates mostly STE emission characteristic of undoped BaF_2 , no VUV and UV and almost no VIS emissions. This observation suggests that Er ions are not efficient recombination centers of electrons and holes in BaF_2 .

Summarizing $\text{BaF}_2\text{:Er}$ fails to generate, under ionizing excitation, fast and efficient emission expected of new scintillating materials. Complex scheme, involving various excitation processes generating various emissions at VUV, UV and VIS may be, nevertheless, interesting for other applications.

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References

- [1] A. Lempicki, A.J. Wojtowicz, J. Lumin. 60–61 (1994) 94.
- [2] R.W. Waynant, P.H. Klein, Appl. Phys. Lett. 46 (1985) 14.
- [3] K.H. Yang, J.A. DeLuca, Appl. Phys. Lett. 29 (1976) 499.
- [4] R.T. Wegh, A. Meijerink, Phys. Rev. B 60 (1999) 10820.
- [5] L. van Pieterse, M.F. Reid, R.T. Wegh, S. Soverna, A. Meijerink, Phys. Rev. B 65 (2002) 045113; L. van Pieterse, M.F. Reid, G.W. Burdick, A. Meijerink, Phys. Rev. B 65 (2002) 045114.
- [6] L.R. Elias, Wm.S. Heaps, W.M. Yen, Phys. Rev. B 8 (1973) 4989.
- [7] K.H. Yang, J.A. DeLuca, Phys. Rev. B 17 (1978) 4246.
- [8] R.T. Wegh, E.V.D. van Loef, G.W. Burdick, A. Meijerink, Mol. Phys. 101 (2003) 1047.
- [9] G. Zimmerer, Nucl. Instr. Meth. Phys. Res. A 308 (1991) 178.
- [10] <http://hasylab.desy.de/facilities/doris_iii/beamlines/i_superlumi/index_eng.html>.
- [11] K.S. Song, R.T. Williams, Self-Trapped Excitons, Springer, Berlin, 1993.
- [12] C.R.A. Catlow, J. Phys. C: Solid State Phys. 12 (1979) 969.
- [13] B. Henderson, G.F. Imbush, Optical Spectroscopy of Inorganic Solids, Clarendon Press, Oxford, 1989.
- [14] A.J. Wojtowicz, P. Szupryczynski, J. Glodo, W. Drozdowski, D. Wisniewski, J. Phys.: Condens. Matter 12 (2000) 4097.
- [15] W.J. Manthey, Phys. Rev. B 8 (1973) 4086.
- [16] R.T. Wegh, H. Donker, A. Meijerink, Phys. Rev. B 57 (1998) R2025.
- [17] L. van Pieterse, M.F. Reid, A. Meijerink, Phys. Rev. Lett. 88 (2002) 067405.