Experiments on random lasers

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5. Narrow peaks in fluorescence from scattering systems

Recently, several articles have appeared reporting on the observation and interpretation of narrow peaks in the emission spectrum of random lasers. The phenomenon was said to be a manifestation of Anderson localization. This is a bold claim, needing a solid experimental backing. We performed a series of experiments trying to replicate the results and to investigate these peaks more quantitatively and systematically than in the published research. The outcome of our experiments can be explained in terms of material properties, and we assert that this explanation can be generalized to the literature results.

The combination of Anderson localization and amplification has been appealing since the idea was brought up [71]. The picturesque view of Anderson localized light being captured in “loops” suggests the possibility of random ring laser cavities [52, 105], providing resonant feedback, i.e. light experiences a phase shift of an integer times $2\pi$ in a round trip. This would permit a “coherent random laser”, a third, qualitatively different regime in scattering amplifying systems (first and second being the single, post-ASE scattering as in section 2.3.2, and multiple scattering as in the other experiments described in this thesis). The suggestion that Anderson localization might be facilitated by the presence of gain—localization being destroyed by absorption, and gain being negative absorption, in a way—has been present for a long time, but up to today nobody has theoretically pursued the idea to its full (3D) extent.

Experimentalists have put a tremendous amount of effort into achieving localization of light, until now without undisputed success. Furthermore, the knowledge about the phenomenology of the localized state in an actual measurement is very limited. These considerations call for wariness when interpreting experimental results in terms of Anderson localization. Fluorescence is sensitive to microscopic changes
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in the electronic structure of the sample (e.g. specific defects, surface adsorption). For this reason material parameters should only be ruled out as an explanation for a spectroscopic phenomenon after very careful inspection.

5.1 Critical review

5.1.1 Observations and interpretations from the literature

In this section we present an overview of relevant results and interpretations from the literature, followed by a discussion. The reported phenomena are summarized in figure 5.1: sharp peaks appear in the emission spectrum of a random laser, on top of the narrowing ASE spectrum, near the maximum of the emission spectrum. Such observations have been made in multiply scattering samples made of ZnO and GaN powders [52, 106–110], and dye solutions with ZnO scatterers [53], but also in transparent samples, such as thin films of nanocrystalline ZnO [105, 110–113], dye-doped gel, active polymer, or index-matched opal [114, 115]. A distinction has to be made between the multiply scattering materials and thin films, that have become part of the same discussion. The observations are similar for both types of samples, although the optical properties differ strongly.

The measurements have been explained in terms of resonant feedback induced by disorder. A dominant idea is that of microscopic ring cavities, light trajectories that return to the same scatterer with a round trip phase lag of $n \cdot 2\pi$, with $n$ an integer. Recurrent scattering events (loop paths of any length) have been shown to exist as a single-scattering-like contribution to the backscattered intensity [116] for $k\ell \lesssim 10$. We will discuss this interpretation in some more detail in section 5.1.2.

Recently some results were reinterpreted [108] in terms of the system’s electromagnetic eigenstates, characterized by a spectral width $\delta\omega$ and a spacing $\Omega$. The eigenmodes overlap in frequency, $\delta\omega > \Omega$, for less than very strong disorder—said to result in the incoherent-feedback multimode random laser as in our chapter 2—to decouple for strong disorder, $\delta\omega < \Omega$—allowing a coherent random laser working in a single electromagnetic mode of the system. See also our discussion of the random laser vs. cavity laser $\beta$-factor, section 3.3.1. $\delta\omega/\Omega < 1$ for the transport eigenstates of a disordered medium is the Thouless criterion for Anderson localization [88], implying that a random laser exhibiting the narrow peaks should be in the localized regime.

To substantiate the proposal of a disorder-induced resonant feedback, one has attempted to reduce the amount of disorder and so make the effect disappear. One method is already mentioned in figure 5.1: to change the amount of scatterers in the dye solution, which indeed has an effect on the occurrence of the frequency peaks.
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Figure 5.1 Narrow frequency spikes (FWHM≈ 0.2 nm) appearing in the emission spectrum of a random laser consisting of ZnO powder, from ref. 52. The particle size is ≈ 50 nm, the refractive index \( \eta = 2.2; \) \( k\ell = 5 \) is claimed. The pump intensity increases (bottom to top) from 400 to 1387 kW/cm\(^2\). Narrow peaks appear at 763 kW/cm\(^2\). Pump data: \( \lambda = 355 \) nm, beam diameter \( \approx 45 \) \( \mu \)m, pulse duration 15 ps.

The phenomenology: microscope images [107] show the field at the frequency of the peaks to be concentrated in small spots (\( \sim 0.5 \) \( \mu \)m). The spectrum varies with emission angle, and the pump intensity at which the peaks appear decreases for larger pump spots. The number of peaks grows with pump intensity and the pump area. A measurement in a system of Rhodamine 640 perchlorate dye with ZnO scatterers [53] investigates the dependence on \( \ell \), or scatterer density. The peaks are absent for the largest \( k\ell \approx 70 \), but do appear for \( k\ell = 47 \) and smaller. The photon statistics of the peaked emission exhibit the Poisson distribution of coherent light [108].

Another method is to anneal the powder film [106], increasing the particle size. This either eradicates the peaks or increases the amount of pump light needed to produce them by up to factor 10.

In both methods—changing scatterer density and annealing the sample—the disorder is not the only varying quantity. Besides the question whether one actually reduces the disorder when the grain size changes from 50 nm to 150 nm by annealing, the effect of the reducing number of (surface) defects could be much more important, if defects play a role. The influence of defects on ZnO luminescence is an active area of research [117, 118]. Many semiconductor excitations, related to the surface,
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![Diagram](image)

**Figure 5.2** Illustration of Anderson localization in loops. (a) The probability to go from A to B via path 1 (amplitude $P_1$) or path 2 ($P_2$) is $\alpha P_1^2 + P_2^2$, without interference terms because all contributing fields have a random phase. (b) Only paths returning to A always interfere constructively with their reversed counterparts, resulting in a return probability $\alpha (P_1 + P_1')^2 = 4P_1^2$.

... defects, or microscopic disorder (i.e. non-crystallinity) are optically active, possibly exhibit a nonlinear response, and could influence the emission spectrum [109, 119]. A cleaner way to change the mean free path in ZnO powders is to reduce the refractive index contrast by filling them with a transparent liquid [27, 120].

For varying the scatterer density in a dye a similar remark can be made: it also changes the surface area of the scatterers in contact with the solution. If the dye adsorbs to the surface of the scatterer, its electronic structure may change, affecting its optical properties in hardly predictable ways, especially on semiconductors [121].

The influence of material properties has not been ruled out with these experiments. In fact, the evidence presented for an explanation of the data in terms of multiple scattering is debatable: the scattering strengths in different samples vary widely. All reported values of $k\ell$ indicate classical diffusive transport.

### 5.1.2 Localization and random ring cavities

Localization is an inhibition of transport due to interference, we said on page 22. The current discussion necessitates a little more detail. The criterion for localization is $D = 0$. The principle of Anderson localization is usually illustrated with the following picture [122], see also figure 5.2.

The probability $P(r_A, r_B)$ to get from a position $r_A$ to $r_B$ is the squared sum of all contributing probability amplitudes $P_i$. For all points $r_B$ but one, each random path $i$ starting at $r_A$ has a random phase, and so the interference terms do not contribute in the ensemble average; $P(r_A, r_B) = \sum_i P_i^2$. The one exception is $r_B = r_A$, where every path is in phase with its time-reversed counterpart $-i$ (of course $P_i = P_{-i}$), so the interference terms do contribute: $P(r_A, r_A) = \sum_i (P_i + P_{-i})^2 = 2 \sum_i P_i^2$, like in EBS. The higher resultant intensity at $r_A$ can not have gone somewhere else and so the transported intensity is smaller than given by diffusion theory. The diffusion
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**Figure 5.3** Comparison between a ring cavity contracted with prisms (a) and the closed loop light paths (b) proposed as an explanation for the narrow peaks observed in random laser fluorescence. In (a) the losses at every prism, at the dispersive frequency selection \( S \) and the gain cell \( G \) are \( \sim 1\% \) due to reflection losses. In (b), however, light emitted in a scatterer (★; depicted is the case of amplifying scatterers, as in ZnO powder) is radiated from every scatterer in a spherical wave (bottom right) the amplitude of which is modified by the differential scattering cross section (top right). The result is a huge loss, resulting in a very broad frequency profile.

The path constant is reduced by interference, and when \( D = 0 \) at \( k\ell \sim 1 \), transport stops and the system is in the localization regime.

The paths featuring in this handwaving picture for localization are the supposed random ring cavities, proposed as a mechanism providing coherent feedback in a random laser. However, these trajectories in localization are not actual, traceable light rays from scatterer to scatterer. It is not possible to construct such paths in wave diffusion; a propagation line drawn in multiple scattering is the normal to the spherical wavefronts emanating from the scatterers. The lines are rather the curves along which the propagation of the field amplitude is evaluated, not unlike the multiple scattering approach to the refractive index [123]. Each individual path has measure zero. The inhibition of transport only emerges in the summation of the infinite number of possible paths. A localized wave is better regarded as an exponentially decaying field state [124] with an extent that is the localization length.

One can assess the probability of a loop to function as a random ring micro-laser, by resorting to a classical wave propagation picture between scatterers and trying to create the threshold condition in such a ring cavity. The estimation is illustrated in figure 5.3. Imagine a short path of \( N \) scatterers, starting on scatterer 1 and meeting \( N - 1 \) other scatterers before returning to 1. Every scatterer \( j \) radiates a spherical wave subject to its differential scattering cross section \( \frac{d\sigma_j}{d\Omega} \), which together with the solid angle spanned by scatterer \( j + 1 \) determines the fraction \( R_j \) of the wave continuing in the ring. The round trip loss factor of such a ring “cavity”
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is \((\prod_{j=1}^N R_j)^{-1}\), which is an enormous number for any realistic estimate for the \(R_j\). Two consequences: firstly, the threshold condition in this ring with a length of a few \(\lambda\) is only satisfied by an impossibly large gain. Secondly, with such a large loss the frequency spectrum is so broad that one cannot speak of a resonant wavelength for which a round trip shifts the phase by \(n \cdot 2\pi\). Of course, a rare event with smaller loss may exist, but the major characteristic of such a random laser is unlikelihood. The essence is not that the loops do not exist, it is that they are a scarce and unimportant subclass of all possible events.

Incidentally, the picture just sketched also shows that the proposed mechanism is an amplitude property, since only one propagating field is needed to demonstrate it. Localization is an intensity effect. Contributions to it always arise out of interference between two or more paths.

5.1.3 Thin film "random" laser

Since the optical properties of the semiconductor, polymer, and dye-doped gel thin films, in which the phenomena of figure 5.1 have been observed, differ strongly from the multiply scattering systems, we discuss them separately. The measurements were explained [105, 110–112, 114] in terms of the same random ring cavities, but now supposed to occur in-plane. We will present a different interpretation for the observations in ZnO thin films.

First, it is important to realize that the samples essentially do not scatter. Estimated scattering lengths range up to 0.5 mm [109, 114], compared to thicknesses of 0.1–1.0 \(\mu m\). The films are transparent, and homogeneous in the direction normal to the plane. The ZnO films are polycrystalline, consisting of “columnar” grains (reaching from substrate to top), with sizes of 20–150 nm. Experiments are done by illuminating the film with a stripe of pump light, imposing a preferred direction for the amplification process.

The role of the transparency is exemplified by the sensitivity to external feedback [112], the difference in characteristics in directions in the plane of the film and normal to it [111] and the importance of the stripe excitation. The narrow peaks of stimulated emission can only be caused by direct optical feedback, for instance by reflection off the film edges or even off external objects, known to influence the mode structure in high-gain semiconductor lasers [125]. The variability of the output spectrum can be attributed to details of the film, such as (macroscopic) imperfections or edge structure [114]. However, we can be a little more specific, at least for the ZnO films.

In ZnO layers with a known hexagonal morphology of the grains, Tang et al. [126] have shown that the film microstructure induces laser action upon pumping with a stripe, without external mirrors. They measure an emission spectrum consist-
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Figure 5.4 Spectrum produced by superposition of the fields (in all modes) of 4 amplifying Fabry-Pérot cavities of nearly equal length, 50 ± 5 μm, calculated for a film of ZnO. The phenomenology of the spectrum is the same as measured in the emission spectrum of disordered ZnO thin films.

We contend that this mechanism is at work in the disordered ZnO films in which the emission spectrum shows peaks at irregular distances. In a disordered layer like the one described above, parallel facets can occur, and if they do near the ends of the pump stripe, they set up a FP-type cavity, with ends reflecting due to the refractive index change induced by the high exciton density along the pump stripe. One cavity produces a comb of peaks, one for each longitudinal mode, but since the pump stripe is wide enough to contain a number of cavities of similar length, the sum of the fields can produce a spectrum that has lost its regular aspect.

We calculate the resonance spectra of such FP cavities, formed by the combination of free carrier generation and film microstructure. The real part of the refractive index of ZnO \( n(\lambda_e = 385 \text{ nm}) = 2.285 \) [127, 128], which in the pumped region (i.e. in the cavity) is reduced to 1.90, the value far from resonance [129]. The imaginary part \( \zeta \) contains gain and absorption: gain is only in the pumped region, a Lorentzian spectrum with a FWHM of 10 nm centered on \( \lambda_e \); \( \zeta(\lambda_e) = -0.019 \), from the measured gain coefficient in this kind of ZnO films [126]. The absorption rises steeply on the blue side of \( \lambda = 378 \text{ nm} \) [127]. The resulting intensity of four such cavities is in figure 5.4. Its features are remarkably similar to those of the spectra in e.g. ref. 105.

There is no carrier transport through the grain boundaries, providing a truly
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Figure 5.5 EBS cone of ZnO powder (CW, no gain), measured with the off-centered rotation technique [130], measurement by J. Gómez Rivas. The sample thickness is ≈ 1 mm. With this wavelength (λ = 632.8 nm) the best fit indicates $k\ell = 25$, including internal reflection correction. This number is to be compared with data in ref. 52, where the same measurement was done on a thin sample, on the basis of which $k\ell = 5$ was claimed. See also ref. 131.

discontinuous refractive index step. The refractive index contrast between pumped and unpumped grains is quite small, resulting in a small 1.5% reflectance of the “mirrors”. The result is a lossy cavity with an correspondingly large threshold gain, i.e. a high carrier density, exerting a large effect on the refractive index.

5.2 Experimental results

In this section we present our experimental results on the luminescence of ZnO powder films and scattering dye solutions. We try to reproduce the results of refs. 52 and 53, to do more quantitative measurements and so to establish whether multiple scattering has a role in the occurrence of the narrow peaks.

5.2.1 ZnO powders

We measure the luminescence spectrum of ZnO powder upon excitation with a UV pulse. The samples are commercially obtained ZnO, supplied by Aldrich [132] (ZnO-A) and Nanophase [133] (ZnO-N). These powders differ in the methods of synthesis, particle size distribution and morphology. The mean free paths as determined by EBS, however, are similar: $\ell \approx 2.5$ μm at $\lambda = 632.8$ nm ($k\ell = 25$), see figure 5.5. At the ZnO emission wavelength ($\lambda_e = 385$ nm) the refractive index of the scatterers $\eta_1 = 2.28$ instead of 2.0 at the wavelength of the EBS measurement, and probably also the average particle scattering cross section $\sigma_s$ is larger at $\lambda_e$. We estimate the reduction of $k\ell$ to be at most a factor 2 [131, 134].

Samples are made from a thick suspension in chloroform. A drop is put on a glass slide and the liquid is let to evaporate. This method produces smooth samples of a uniform density.
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![Graph showing emission intensity vs. wavelength for different pump energies.](image)

**Figure 5.6** Narrow features in the emission spectrum of ZnO. For low pump energies only the broad fluorescence band is seen, which develops narrow frequency structure if the pump energy is increased. For the highest pump energy shown the narrow features have merged. The rep. rate is 2 Hz, the pump energy increases from bottom to top. The instrument resolution is 0.3 nm.

Both powders fluoresce upon illumination with the UV pump beam, though the ZnO-A does so more readily than the ZnO-N, compare figures 5.6 and 5.7. For this reason most measurements were done on ZnO-A, and all data shown are obtained from this sample, unless otherwise noted. Single-shot fluorescence spectra of ZnO-A for different pump energies are shown in figure 5.6. The pump spot is focused to a diameter of \( \approx 50 \mu m \).

The pump source is a frequency-tripled (355 nm) Nd:YAG laser (Coherent Infinity 40–100), with a pulse duration of 1.7 ns and a variable pulse repetition rate. The fluorescence is picked up by an Ocean Optics 200 \( \mu m \) core UV-silica fiber, positioned at a distance of 5 cm from the pump spot on the sample, so the collection angle is 4 mrad (smaller than a speckle spot). The directions of incident pump light and detection make an angle of \( \approx 30^\circ \). The fluorescence is analyzed using an Oriel MS-257 0.25 m, f/4 single grating spectrometer, using a 2400 lines/mm grating, and detected with a Princeton Instruments Intensified CCD camera. The instrument resolution is 0.3 nm. The image intensifier on the camera amplifies not only the signal, but also the relative uncertainty in the signal: at the gain setting we use the error in a count \( c \) is \( 2\sqrt{c} \).

As shown in figure 5.6, narrow frequency structure is observed in the fluores-
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![Fluorescence spectra from ZnO-N](image)

**Figure 5.7** Fluorescence from ZnO-N. The pulse energy is (a very high) 0.58 mJ, different spectra are taken from different locations on the sample. Again, the gray curve is the camera dark count level. The instrument function is also shown. The broad fluorescence background is not observed (see figure 5.6), but the variability of the luminescence yield precluded a systematic study in this sample. The rep. rate is 1 Hz.

The cent emission of ZnO powder upon excitation with a UV pulse. It appears only for pump intensities higher than a certain threshold, low pump intensities only give the broad spontaneous emission spectrum. The peaks are not as pronounced as those of Cao and coworkers [52,107], which we attribute to limitations in the resolution and detection efficiency of our setup. Our pump intensities (in W/m²) are approximately 20 times higher than in ref. 52. The explanation for this strange discrepancy is given in figure 5.8 and the accompanying discussion.

For comparison the luminescence of the ZnO-N powder is shown in figure 5.7. This powder has the same scattering characteristics as ZnO-A, but differs in other material parameters. The threshold for narrow peaks is much larger here, and the spectra show more pronounced structure. The spectrum is redshifted by ≈ 3 nm with respect to the data shown in figure 5.6, possibly because the luminescence originates from an electron-hole plasma (EHP), formed at this high excitation pulse energy. At lower pump energies no reliable signal could be obtained, so a systematic study of the peaks on power dependence could not be done in this sample.

Both series of data (figures 5.6 and 5.7) were measured with low pulse repetition rates of 2 and 1 Hz. Changing the pulse rate \( f_p \) to higher values turns out to have a profound effect on the emission spectrum, see figure 5.8. It displays two spectra,
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**Figure 5.8** Effect of the pulse repetition rate $f_p$ on the ZnO emission. At a pulse energy of 2 $\mu$J, vastly different spectra are produced with $f_p = 10$ Hz (broken line) and $f_p = 50$ Hz (solid line). The number of spectra averaged in each curve is 50, all spectra (10 Hz and 50 Hz) are taken on the same location of the sample. Individual spectra at 50 Hz show the narrow peaks, averaging out to some degree in the accumulated data, although at this pump energy the count rates are too low to make out fine details. The camera dark counts for both exposure times are shown as broken (5 s) and solid (1 s) gray lines.

consisting of multiple shots, one taken at $f_p = 10$ Hz, the other at $f_p = 50$ Hz, with the same pulse energy (2 $\mu$J), at the same location on the sample, accumulating the same number of shots. The low $f_p$ spectrum is basically the spontaneous emission spectrum of ZnO, while the high $f_p$ spectrum has a narrowed intensity distribution, with narrow features in the single-shot spectra that partially average out in the sum of 50. The integrated intensity at $f_p = 50$ Hz is 16% lower than at $f_p = 10$ Hz.

The pump intensity is much lower than in figures 5.6 and 5.7, and now also a factor 2 smaller than in ref. 52. Cao et al. used $f_p = 10$ Hz. We find that the threshold for the narrowing and the onset of the frequency spikes decreases with increasing pulse rate. We currently do not have an explanation for this remarkable influence of the repetition rate on the emission spectrum. Speculations are postponed until the discussion in section 5.3.1.

A more elaborate study of the emission spectrum as a function of pump energy exposes the strong nonlinearity of the response of the luminescence to an excitation pulse. In figure 5.9 a series of spectra is shown, taken at 50 Hz, each containing the accumulated emission of 50 shots. This procedure again washes out finer details of the individual spectra, but it allows us to concentrate on the overall features.
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Figure 5.9 Peak intensity decrease, blueshift and rebroadening of ZnO fluorescence with increasing pump energy. $f_p = 50$ Hz, exposure 1 s. The averaging of many spectra washes out the details of the single-shot response. Pulse energies are indicated in the figure. The spectra obtained with the highest pump energies are shown as broken lines to avoid confusion where the lines cross.

At low pump intensities the system responds as expected: it emits a spectrum corresponding to the energy distribution of spontaneous emission. Increasing the excitation energy above 2 $\mu$J narrows the spectrum, with frequency spikes visible in the individual spectra (the pulse energy at which the spectral narrowing occurs, differs from that in figure 5.8 because the location on the sample was changed). Above 3 $\mu$J the peaks begin to merge, like in figure 5.6, but at 5 $\mu$J the fluorescence starts to decrease in intensity, to shift to higher energies and to broaden, finally resulting in a blueshifted spontaneous-emission-like spectrum at 8 $\mu$J.

The peak intensity decrease, blueshift and rebroadening of the fluorescence spectrum is not an effect of radiation damage. 8 $\mu$J is still a low excitation energy compared to the pump energies of figure 5.6, which produced reliable and reproducible fluorescence for extended periods of time. Also, the effect seen in figure 5.9
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<table>
<thead>
<tr>
<th>dye</th>
<th>scatt.</th>
<th>$kl$</th>
<th>$n$ (cm$^{-3}$)</th>
<th>comment</th>
<th>shorthand</th>
</tr>
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<tbody>
<tr>
<td>SRB</td>
<td>TiO$_2$</td>
<td>15</td>
<td>$1.8 \cdot 10^{13}$</td>
<td>good quality</td>
<td>ST</td>
</tr>
<tr>
<td>SRB</td>
<td>ZnO</td>
<td>70</td>
<td>$8.7 \cdot 10^{14}$</td>
<td>good quality</td>
<td>SZ</td>
</tr>
<tr>
<td>R640</td>
<td>TiO$_2$</td>
<td>–</td>
<td>–</td>
<td>inhomogeneous</td>
<td>RT</td>
</tr>
<tr>
<td>R640</td>
<td>ZnO</td>
<td>70</td>
<td>$8.7 \cdot 10^{14}$</td>
<td>low fluorescence</td>
<td>RZ</td>
</tr>
</tbody>
</table>

Table 5.1 Samples made for the investigation of the narrow peaks in scattering dye solutions. SRB is Sulforhodamine B, R640 is Rhodamine 640. Dyes are 5 mM solutions in spectroscopic methanol, scatterers are colloidal particles [44,133]. Both powders are suspended in densities of 320 mg powder per ml dye solution. $kl$ is measured by EBS with $\lambda = 632.8$ nm, $n$ is the scatterer density. The shorthand is used for reference in the text.

is insensitive to whether the series is measured with increasing or decreasing pump energy. At high pump energies, the spectrum does take some time to equilibrate. Suddenly switching on the pump at an energy of 8 $\mu$J initially produces a narrowed spectrum, which subsequently relaxes, in about 2–3 s, into the spectrum shown as the dotted line in figure 5.9. A sudden decrease from 8 $\mu$J back to $\approx 3$ $\mu$J only makes the peaks reappear after a similar amount of time. This slow response suggests a thermal origin.

5.2.2 Scattering dye solutions

The role of scattering in random lasing can be tested if the scattering and amplification are independent, e.g. in a dye solution with scatterers. To also test a possible material dependence of the narrow peaks in a dye-based random laser, we test different combinations of dye—5 mM Sulforhodamine B or Rhodamine 640 in methanol—and scatterers—320 mg/ml TiO$_2$ or ZnO-N colloid. We do not use ZnO-A because it is not suspended well in methanol. The samples are listed in table 5.1.

The high dye concentration is chosen to facilitate the comparison with the work by Cao et al. [53], although the results of chapter 3 indicate that the above-threshold gain does not increase substantially, but the reabsorption does. Also, the thickness of the amplifying layer decreases.

As a pump source we use a frequency-doubled Q-switched mode-locked Nd:YAG laser (Quantel YG-501 30), pulse duration < 40 ps, wavelength 532 nm, maximum pulse energy 0.7 mJ, pulse rate 10, 20 or 30 Hz. The pump beam is focused to a spot of $\approx 20 \mu$m diameter (barely out of, or still in, the small-spot limit of figure 2.10, depending on the $t$ of the material). The detection setup is the same as in the ZnO experiments, see page 99. The fiber is positioned 1 cm from the sample.

The energy stability of the pump laser is poor: the relative standard deviation from the mean pulse energy is 30–35%. We do use this laser as excitation source,
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Figure 5.10  Single-shot fluorescence spectra from ST sample (see table 5.1). (a) Low to medium pump energies; medium ≈ 180 nJ. Increasing pump (signal) intensity is accompanied by the emergence of peaks in the spectrum. The gray line is the dark count level. (b) At high pump intensities (up to ~7 μJ), the peaks’ relative intensity decreases. The middle spectrum is shown with a broken line for clarity.

because the use of picosecond excitation pulses turns out to be essential for the observation of the narrow peaks. With a nanosecond pump laser only the smooth spectra as shown in figure 2.1(a) are observed. With picosecond excitation, however, some of the spectra do show evidence of narrow frequency structure. Figure 5.10 contains an example, obtained with the ST sample.

As the pump energy increases from zero to ≈ 180 nJ, we see sharp peaks appearing on top of a broad (FWHM ≈ 9 nm) background of “normal” amplified fluorescence in figure 5.10. The peaks are not as pronounced as in the data in ref. 53, owing to a limited resolution. At higher pump energies the intensity in the peaks decreases with respect to the broad background: they either disappear or merge. The exact pump energies are unknown because of the pulse-to-pulse energy variation in the laser. We assume the usual correspondence between fluorescence intensity and pump pulse energy, in accord with the input-output power relation in a laser as measured in figure 2.2. The relatively large spectral width of the background (all measurements with an appreciable signal are above threshold) and the redshift compared to other fluorescence data of the same sample are consequences of the large dye concentration.

The large noise level makes it difficult to say whether the positions of the peaks are correlated between different spectra. This would be a sure sign of a material excitation. The positions are certainly not the same in the emission spectra of all shots, but a comparison of, for instance, the upper solid and broken lines of figure

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5.10(b), does suggest that the peak positions are not completely random.

The spectra in figure 5.10 differ in the position of the center of the broad fluorescence band. It shifts randomly over a range of 2–3 nm. We did not observe this kind of shift with nanosecond excitation. The differences are possibly chemical in origin, stemming from an interaction of the dye with the surface of the scatterers [135]. Note that the TiO$_2$ particles are surface treated with an (insulating) alumina/silica layer. The scatterer surface is amorphous, hence many specific adsorption sites exist. A small shot-to-shot variation at the onset of the emission-amplification process could persist in the resulting measured spectrum due to the nonlinearity of the ASE process at high gain. Owing to the large intrinsic emission linewidth of the dye, such a process does not seem a likely candidate as an explanation for the narrow peaks.

Repeating this experiment with the SZ sample—same dye, different scatterer, larger $\ell$—yields qualitatively the same outcome. Compared to the ST measurements, the emission spectrum is redshifted by 6 nm, the recorded intensities are a factor 1.5–2 lower at the same pump intensity, and the number of peaks is smaller. The lower intensity is a consequence of the higher threshold in this sample, caused by a larger $\ell$. An interaction of the dye with the ZnO surface is readily apparent as the sample is prepared: upon addition of the scatterers the dye solution changes color from bright red/pink to deep purple. No change of color is observed if the coated TiO$_2$ scatterers are used. This interaction of the dye with the scatterer surface could influence the emission spectrum.

The scatterers in the RT sample aggregate, and even after ultrasonic shaking the suspension remains inhomogeneous. The RZ sample is identical to the material used by Cao et al. [53]. We find that it luminesces weakly, and does not produce any convincing peaks at pump energies up to 50 $\mu$J; above this energy the pump pulse damages the glass of the sample container. We do not have an explanation for the discrepancy between our measurements and those of ref. 53. The stability of the suspension is markedly worse than the ST and SZ samples.

The pump pulse repetition rate profoundly influenced the ZnO emission. A variation from 10 to 30 Hz is, however, found to have no effect on the appearance of the spikes in the dye-based ST and SZ samples.

5.3 Discussion and conclusions

In the previous section we have presented measurements, augmenting the data from the literature reviewed in section 5.1. Here we discuss how the additional experiments fit in or modify the picture sketched in earlier publications. We do not try to answer the question whether or not the narrow peaks in ZnO are related to lasing; in ref. 108 they were shown to be. The issue we address is the role of multiple
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scattering in the laser process.

First, we remark that all samples studied, by us and by others, are far from localization: the smallest values for \( k\ell \) are achieved in the ZnO powder samples [131] and the dye samples with TiO\(_2\) scatterers, \( k\ell \approx 14 \). Considering that materials with \( k\ell = 3-4 \) still show predominantly diffusive behavior [26, 27], it is hasty to attribute any observation in less strongly scattering materials to localization. Even if the hand-wavingly substantiated hunch that gain facilitates localization (see page 91) turns out to be legitimate, the gap from \( k\ell \geq 14 \) to the transition is huge, and observable effects are at best improbable.

5.3.1 ZnO powders

The two ZnO powder samples react very differently to UV excitation, while their \( k\ell \) values are the same. ZnO-N only emits at high pump energy with an EHP-like spectrum. ZnO-A shows many narrow peaks in the exciton luminescence band.

In ZnO-A, we observed a surprisingly strong dependence of the emission spectrum on the pump pulse repetition rate (figure 5.8) and an extreme nonlinearity as a function of pump pulse energy (figure 5.9). Both phenomena are reversible, and both respond slowly, with a time constant of 2–3 s. The only likely candidate to produce such a slow response is a thermal process. The absorbed pump energy is partly converted into heat, producing a local temperature increase. This effect should be more pronounced in a powder than in any other phase, on account of the poor thermal conductivity of an inhomogeneous structure.

Underlying process? What the elevated temperature might effectuate is a matter of speculation, which we will pursue only briefly. Narrow sub-gap peaks in photoluminescence spectra have been observed in disordered or alloy II–VI semiconductors [136], and even lasing has been reported [137]. The intensity in the peaks shows the characteristic laser-like nonlinearity as a function of pump power. These narrow spectral features have been attributed to complex states consisting of an exciton bound to a localized defect. The peaks are observed only up to a maximum temperature, depending on the material, above which the exciton dissociates thermally from the defect and the emission disappears.

The stability of excitons in II–VI semiconductors under lasing conditions, however, is disputed [138]. Exciton absorption is seen to bleach above the laser threshold in quantum well lasers [139, 140]. Electron-hole recombination across the energy gap, that is renormalized due to the Coulomb interaction, produces gain and luminescence at the exciton energy, without an actual exciton population [141]. At room temperature, excitons are shown to be always unstable in these materials, owing
5.3 Discussion and conclusions

to the large coupling to other (continuum) states. On the other hand, the theory is
done for materials with a perfect crystal lattice, so defect-related excitations can not
be reproduced. Localized (bound) excitons have a much smaller coupling to other
states, with dephasing times up to 4 orders of magnitude larger than extended (free)
excitons [118].

Our experiments do not contain sufficient detail to decide whether the emission
we see is excitonic or free carrier recombination across a renormalized energy gap,
nor is this our prime interest. We do see a nonlinearity with a thermal-like time
response. Temperature-dependent excitations may seem peculiar in semiconductors
at room temperature, since most features are only observed at low temperatures. Two
energy scales in ZnO are larger than the thermal energy $k_B T = 25 \text{ meV}$: the bulk
exciton binding energy $E_b = 60 \text{ meV}$, and the Urbach tailing parameter $E_U = 40
\text{ meV}$ [142], describing the exponential decay of the electronic density of states at the
band edge due to defect states.

We propose that the pumping of the sample populates luminescent levels, and
that this process is facilitated by the heating of the powder by the pump absorption,
enhancing the luminescence at high rep. rates, cf. figure 5.8. The narrow linewidths
observed suggest a role for localized defect states. An increase of the pulse energy or
rep. rate raises the temperature further, thermally dissociating the luminescent state,
which we assume consists of one or more charge carriers bound to a lattice defect.
Consequently, the emission vanishes.

Stimulated emission from a compound defect state is possible by the narrow
linewidth and concomitant large gain. ref. 108 shows the light to be coherent, so
a resonant (amplitude) feedback mechanism is present. At these high gain levels,
however, even a weak external reflection can be sufficient to provoke lasing.

An example of defect-exciton complex luminescence is donor-acceptor pair
(DAP) emission. In this process an electron on a donor recombines with a hole
on an acceptor nearby [109, 143]. The result is a regular series of peaks at fixed
positions due to the $1/r$ Coulomb energy term contributing to the emitted photon
energy, with $r$ on the lattice. This regularity could not be established by an inventory
of literature data or our own. On the other hand, a signature of DAP emission is a
blueshift with increasing pump energy, as clearly observed in figure 5.9.

Above, we have presented a speculative proposal for an origin of the narrow peaks
in ZnO powders. The optics of highly excited semiconductors is a rich and complex
field of research [144], and especially the nature of the gain mechanism in II–VI
materials is a matter of debate, that we do not aspire to settle here. To summarize,
we remark that we did not find evidence for a crucial role for multiple scattering
in the occurrence of the narrow peaks in ZnO powder luminescence, and that our
Narrow peaks in fluorescence from scattering systems

results suggest a thermally activated mechanism with a strongly nonlinear response. Which semiconductor electronic process produces these spectral features, and has a compatible temperature or intensity dependence, remains speculative. Similar peaks have been seen in homogeneous alloy semiconductors.

5.3.2 Dye suspensions

The results of the experiments on dyes with scatterers are not as conclusive, or suggestive, as those on ZnO, partially on account of the lesser data quality. Based on the observations presented in section 5.2.2, the most straightforward conclusion is that the narrow peaks in this system are caused by scattering. The most strongly scattering (ST; cf. table 5.1) sample shows the strongest peaks, the scatterers in which happen to have a surface coating, reducing the interaction of the surface electronic structure with the dye. We tried to test the influence of the material more stringently by increasing the scatterer concentration in the SZ sample but found that a denser ZnO suspension is unstable and the colloid aggregates.

On closer inspection of the data in section 5.2.2, and comparing with the article by Cao and coworkers [53], two issues arise:

- The peaks are only observed with a picosecond excitation pulse, only the normal narrowed spectrum appears with a nanosecond pump.

- The RZ sample on which the published experiments by Cao et al. were performed showed no peaks in our experiments, and low luminescence. Even though its $k\ell$ is large, the absence of a convincing signal up to these high pump energies is surprising. On the other hand, the SZ sample does show peaks, but has the same $k\ell$ (from EBS) as a sample where Cao et al. did not observe any. The difference is the dye, the turbidity is the same.

The latter point only seems to indicate, if anything, a very sensitive dependence of the narrow-peak appearance on material and preparation. The former is an observation that needs to be explained if the phenomenon is to be given a theoretical backing in multiple scattering. If multiple scattering is to be responsible for the narrow peaks, we must find a process causing the peaks, that happens on a time scale $\gtrsim 50$ ps, because the peaks do not average out with this excitation pulse length, but $\lesssim 500$ ps, because there is no trace of the peaks with a nanosecond pump pulse.

In a nanosecond, a scattering medium is essentially static: particle motion in a colloidal suspension has a typical time scale of milliseconds. There are two processes in a diffusive random laser with time constants of the correct order. The longest detectable paths in a multiply scattering liquid medium dephase at a rate in the GHz range; these dynamics are used in DWS. Constructive interference between
long paths is a particular speckle, which is not sufficiently wavelength specific. Another process at a 10–100 ps time scale is the relaxation oscillation. This is not spectrally selective either.

Material-related processes with subnanosecond dynamics exist in great variety in a system of dye on an oxide surface. It is not always clear whether these are accompanied by narrow spectral features. Dye-like excitations have a large intrinsic linewidth, maybe a combination with the surface electronic structure of the scatterer can give rise to narrow features. Our experiments are not sufficient to decide whether a particular type of excitations causes the sharp peaks.

5.3.3 Conclusions

We find a striking difference in luminescence properties of the two ZnO powders, differing in method of synthesis, particle size distribution, and surface properties, but not in purity or scattering characteristics. The light transport is undoubtedly diffusive at $k\ell \approx 14$.

Furthermore, we measure a strong nonlinearity with a thermal-like time response in the fluorescent emission of ZnO powders. These observations lead us to an interpretation of the narrow peaks in terms of material excitations, rather than one based on the random laser concept. The explanation is compatible with, and even supported by [109, 117] the data on these samples in the literature, and could be applied to ZnO thin films. However, for the occurrence of narrow peaks in thin films there is another, more elegant candidate, that is supported by direct experimental evidence [126]: the formation of Fabry-Pérot cavities by grain boundaries between pumped and unpumped material, proposed in section 5.1.3. The only data that lack a consistent interpretation are those on scattering dye suspensions. Our findings partially contradict the results in the literature.

Superfluous as it may seem, there could be three different mechanisms at work, producing very similar-looking narrow peaks in different materials. One can also resort to the semi-skeptical statement that it must be some electronic excitation in all cases, the nature of which can be speculated on in ZnO, and is left unspecified in the dye materials. We opt for two processes: the cavities in the transparent films and an electronic excitation in the multiply scattering materials. The latter explanation is adopted for the dye suspensions only because the alternatives must be discarded; for the ZnO powders it is quite firmly supported by experimental data.