Correlation between Crystal Size and Photo Luminescence Intensity of SiV Centres in HTHP Nanodiamonds
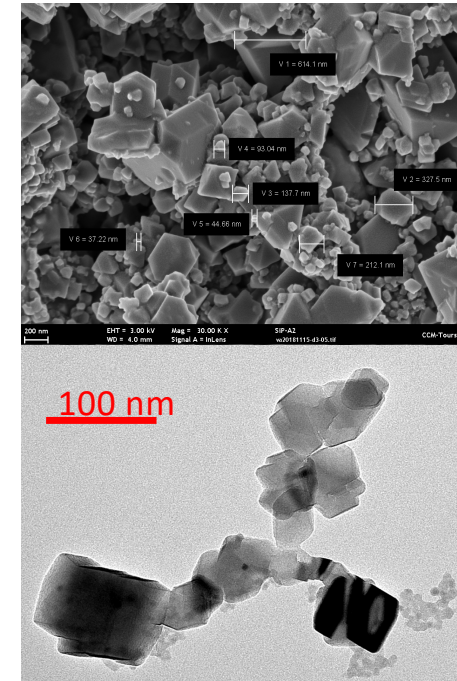
Taras Plakhotnik

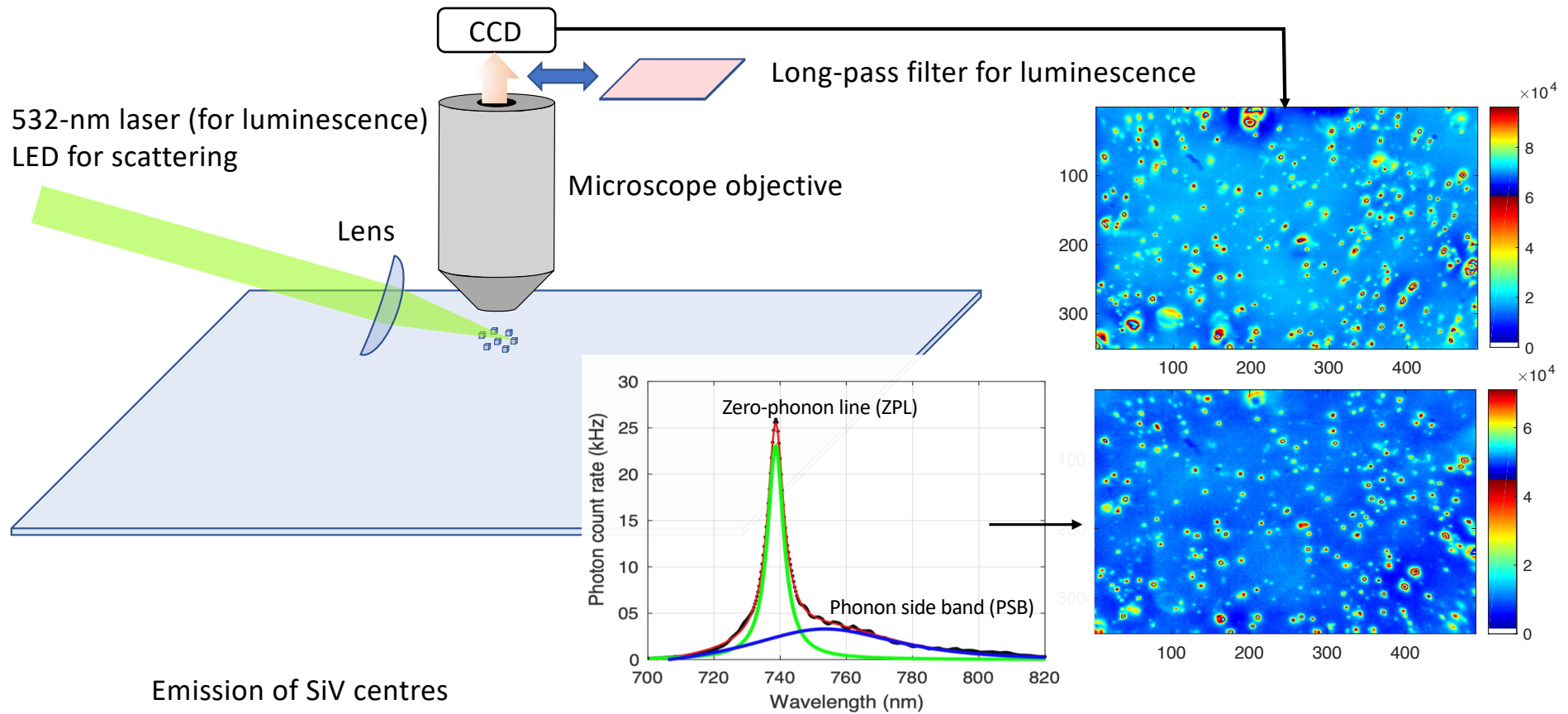School of Mathematics and Physics, The University of Queensland

Motivation:
Understand formation of SiV centers in nanodiamonds produced by HTHP method

- Application of nanodiamonds for optical sensing is expanding.

- Large number of luminescent defects in a crystal is needed for higher luminosity of each crystal.

- Higher luminosity results in higher sensitivity (more photons are emitted per unit time).

- High temperature high pressure (HTHP) is one of two methods producing artificial diamonds

- HTHP process generates a wide distribution of crystal sizes and crystal luminosity

Setup and experimental data

CCD

Long-pass filter for luminescence

532-nm laser (for luminescence)
LED for scattering

Microscope objective

Lens

Emission of SiV centres
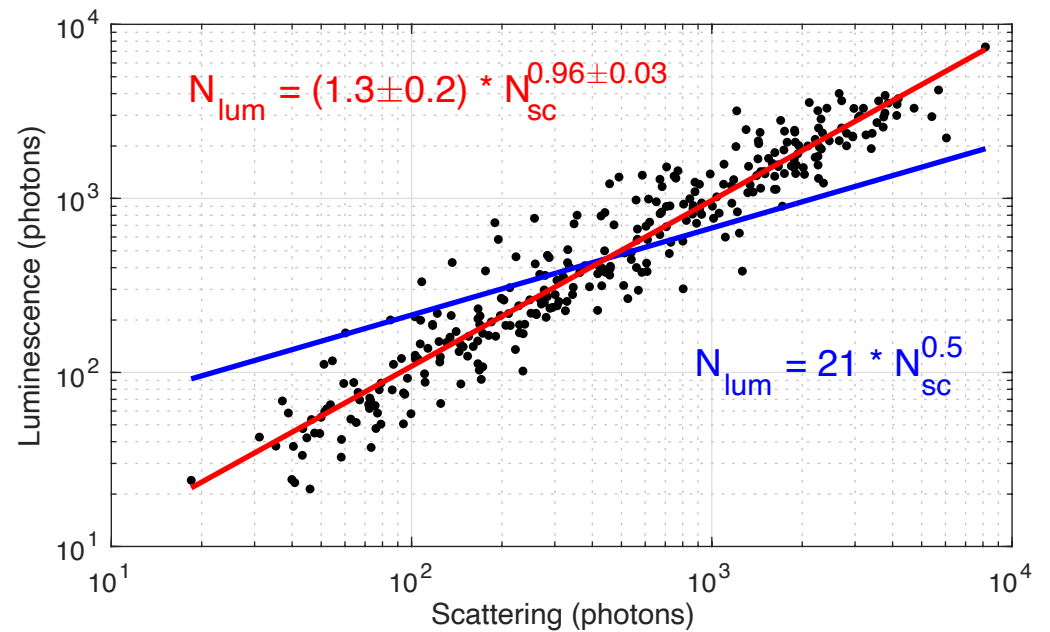
Zero-phonon line (ZPL)

Phonon side band (PSB)

Results of preliminary data analysis
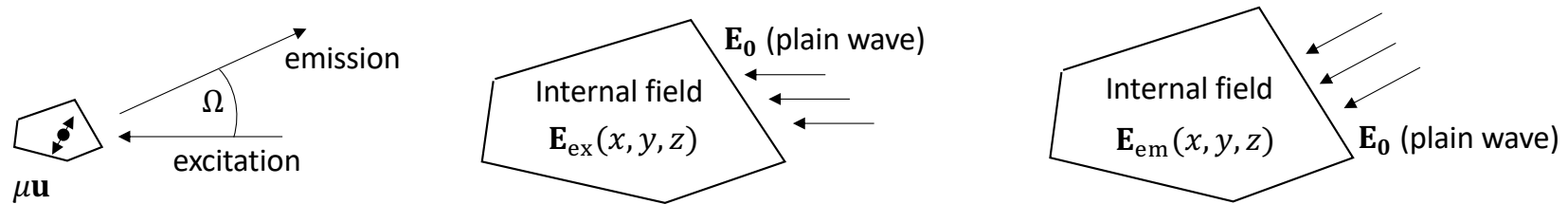
Scattering is expected to be $\propto r^6 \propto V^2$

Luminesce is expected to be $\propto r^3 \propto V$
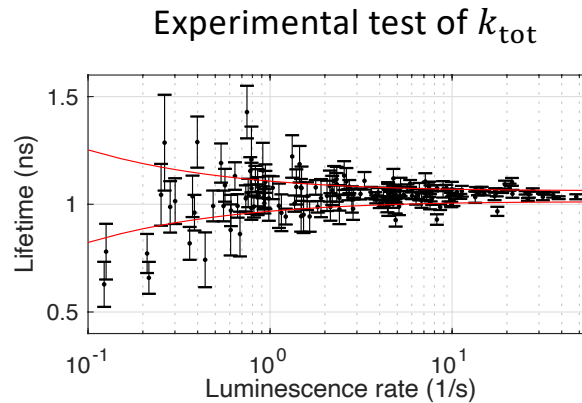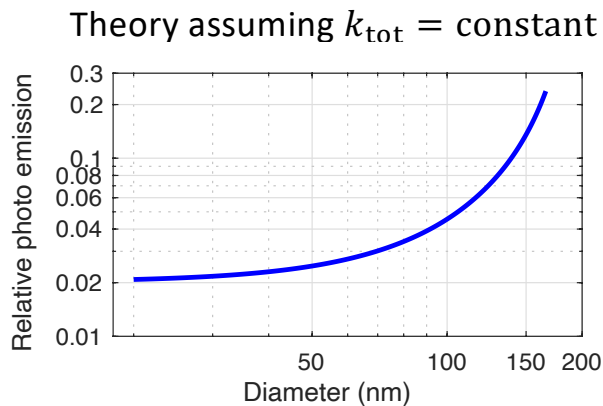
But it seems luminescence $\propto$ scattering

Number of photons (per second) detected from each particle

$N_{lum} = (1.3\pm0.2) * N_{sc}^{0.96\pm0.03}$

$N_{lum} = 21 * N_{sc}^{0.5}$
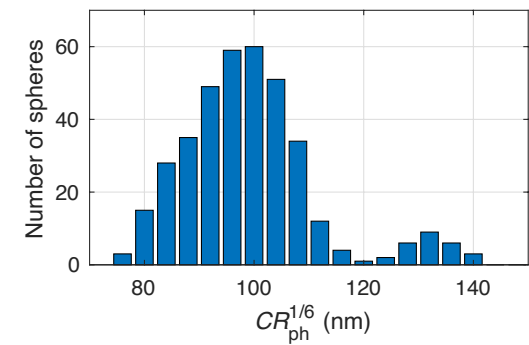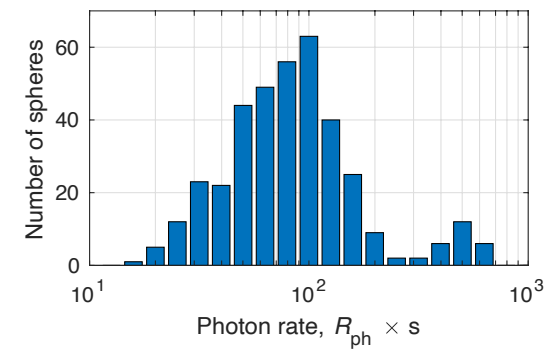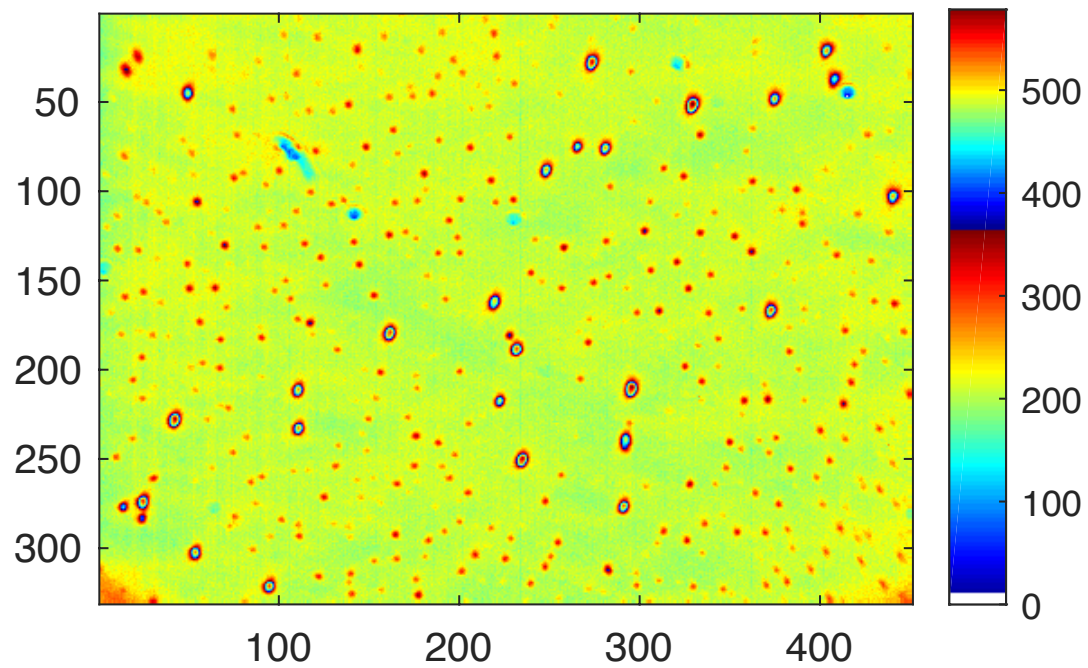
Electrodynamic effects and photo emission rates

One can use Lorentz reciprocity theorem and obtain:

$$\frac{\mathrm{d}R}{\mathrm{d}\Omega} \propto \sum \frac{|\mu\mathbf{u}_n \cdot \mathbf{E}_{\mathrm{ex}}(x,y,z)|^2 \, |\mu\mathbf{u}_n \cdot \mathbf{E}_{\mathrm{em}}(x,y,z)|^2}{k_{\mathrm{tot}}}$$

Theory assuming $k_{\mathrm{tot}} = $ constant

Experimental test of k_{tot}
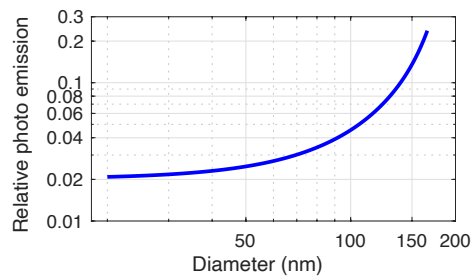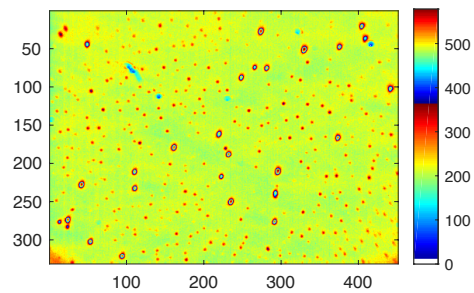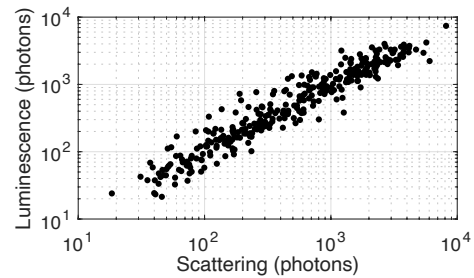

$$k_{\mathrm{tot}} = k_{\mathrm{rad}} + k_{\mathrm{nr}}$$

In agreement with literature:
$k_{\mathrm{rad}} \ll k_{\mathrm{nr}}$
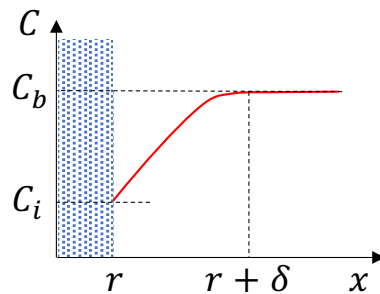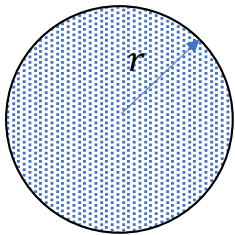
Calibration with silica nanospheres (100 nm)

Correlation corrected for electrodynamic effects
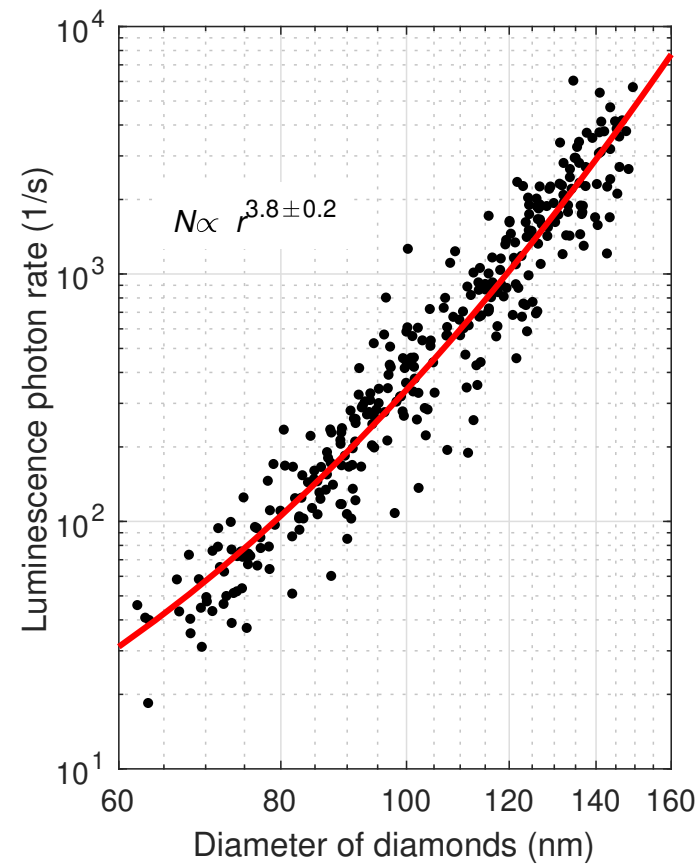
Growth of a nanocrystal depends on three factors

1) Formation of a seed crystal

2) Transport of monomers to the surface of the growing crystal

3) Chemical reaction on the surface

1) We assume that seeds (a few nm across) are formed

2) Flux: $j = D\frac{r+\delta}{r\delta}(C_b - C_i)$

3) Flux consumed by the chemical reaction: $j = k(C_i - C_e)$

4) Crystal growth: $\frac{dr}{dt} = jV_m$

If diffusion is the limiting factor in the crystal growth (that is $D \ll kr$) then $\frac{dr}{dt} = \frac{r+\delta}{r\delta}DV_m(C_b - C_e)$

If inequality $r \ll \delta$ holds, then $\frac{dr}{dt} = \frac{DV_m(C_b - C_e)}{r} \equiv \frac{\alpha}{r}$

Dynamics of crystal growth by diffusion

- HTHP is a complex process at high pressure (up to 8GPa) and temperature (up to 1500 K).
- Crystal growth is mediated by low weight and volatile molecules (typically hydrocarbon radicals).
- Such molecules transport carbon by diffusion to the cites of active growth.

$$\frac{\mathrm{d}r}{\mathrm{d}t} = \frac{\alpha}{r} \qquad (1)$$

SiV formation is limited by the reaction rate

- Concentration of Si relative to carbon is on the order of 10^{-2} in the initial mixture but only 10^{-6} in the crystal

- Concentration of Si is much larger than the crystals can accept.

$$\frac{\mathrm{d}N}{\mathrm{d}t} = \beta r^2 \qquad (2)$$

Combination of (1) and (2) results in $\frac{\mathrm{d}N}{\mathrm{d}r} = \frac{\beta}{\alpha} r^3 \rightarrow N \propto r^4$

In agreement with experiment!

Conclusions

- HTHP diamond growth is determined by diffusion of carbon while formation of defect centres is limited by the chemical reaction (its rate is proportional to the surface area of the crystal).

- The number of the defects is proportional to the fourth power of the crystal size.

- In combination with electrodynamic effects, this results in brightness being approximately proportional to the sixth power of the size.

- This is an unfortunate result if synthesis of ultra small diamonds with a high number of defects is required (this is a frequent case).

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