

# Structural origins of light emission in Germanium quantum dots

Andrei V. Sapelkin

Center for Condensed Matter and Materials  
Physics, School of Physics and Astronomy



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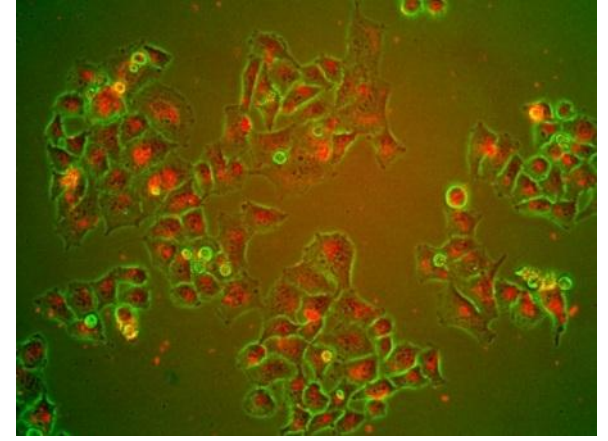
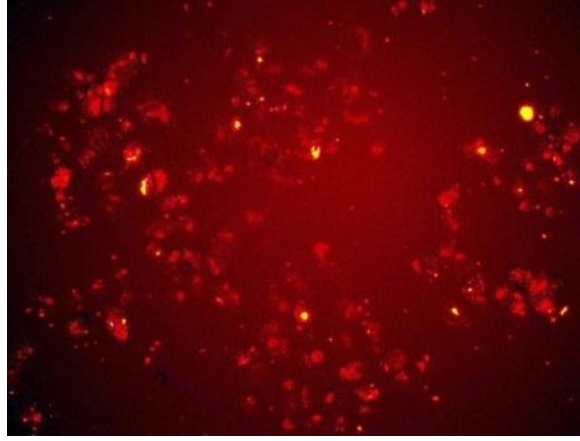
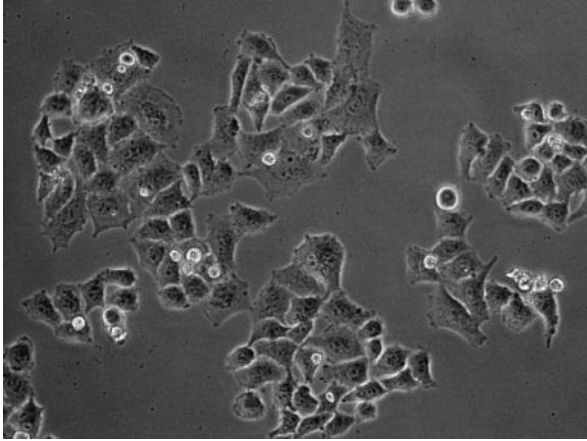
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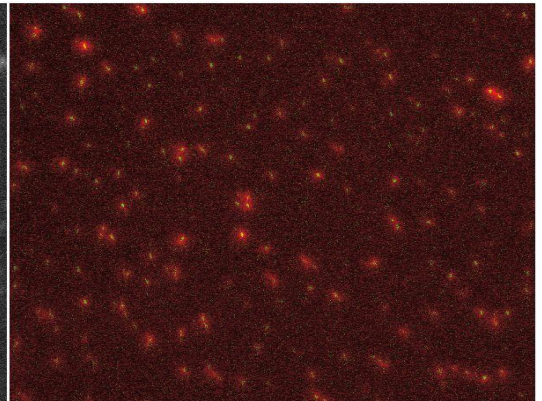
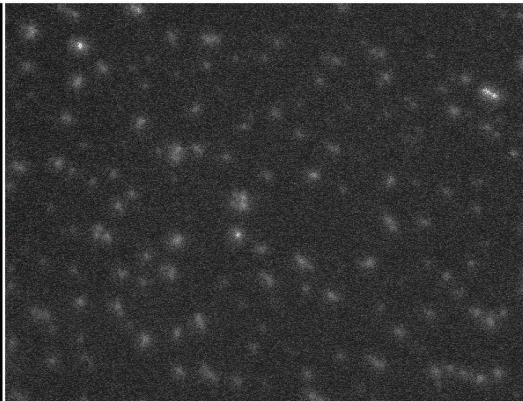
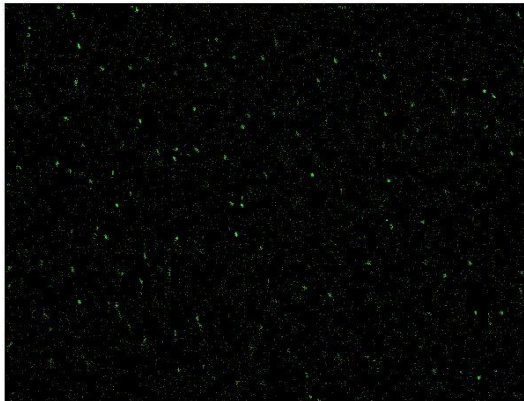


# Motivation

- Morphological super-resolution imaging
- Cell signal imaging

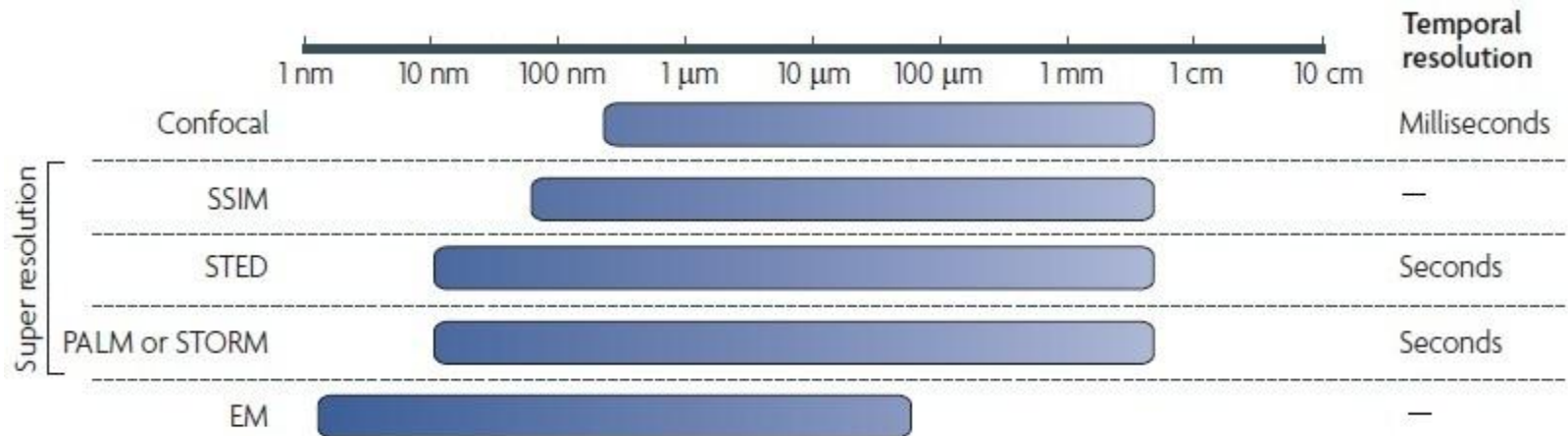
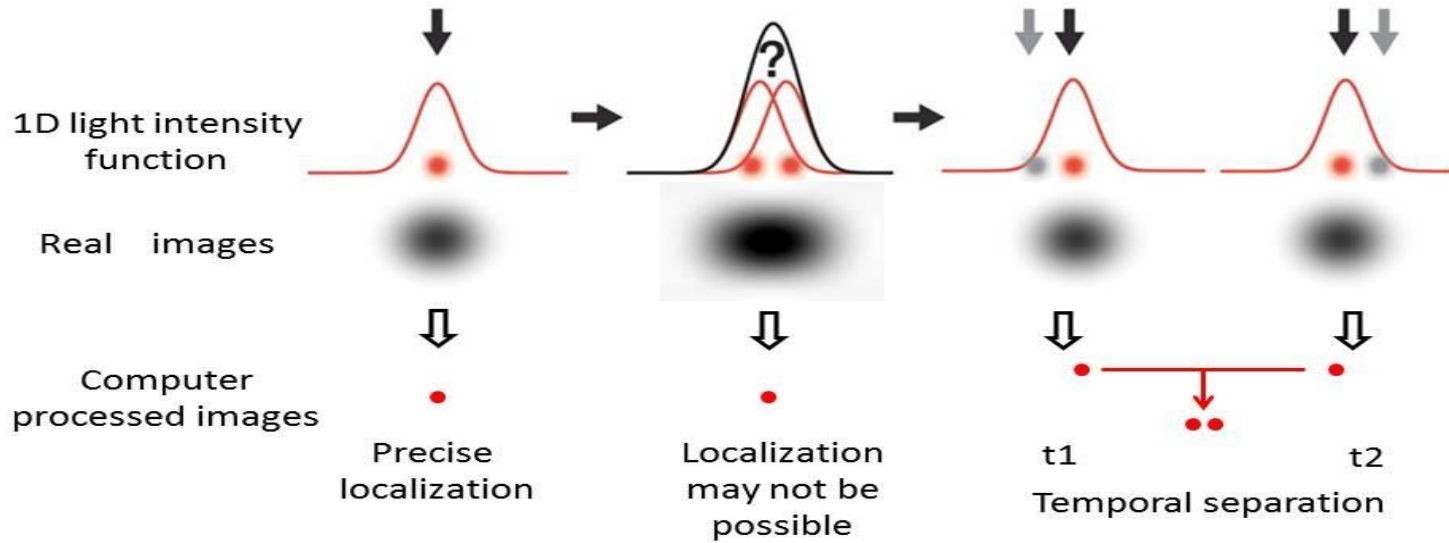


CdSe

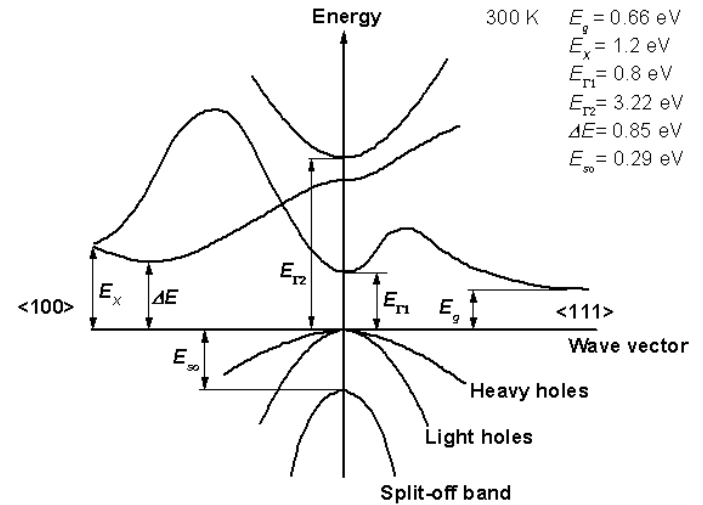
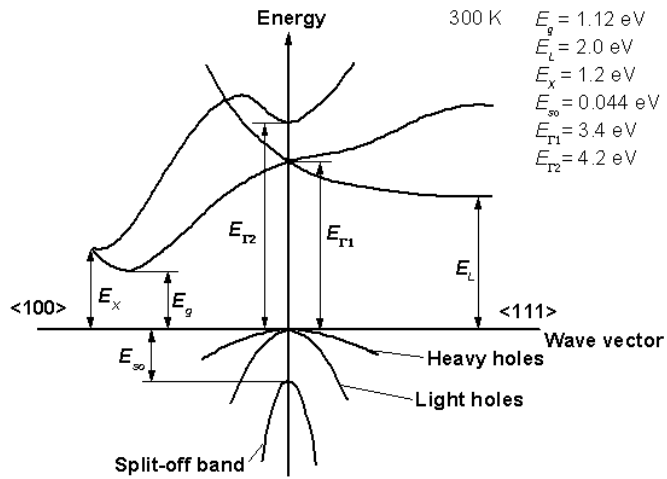


nc-Si

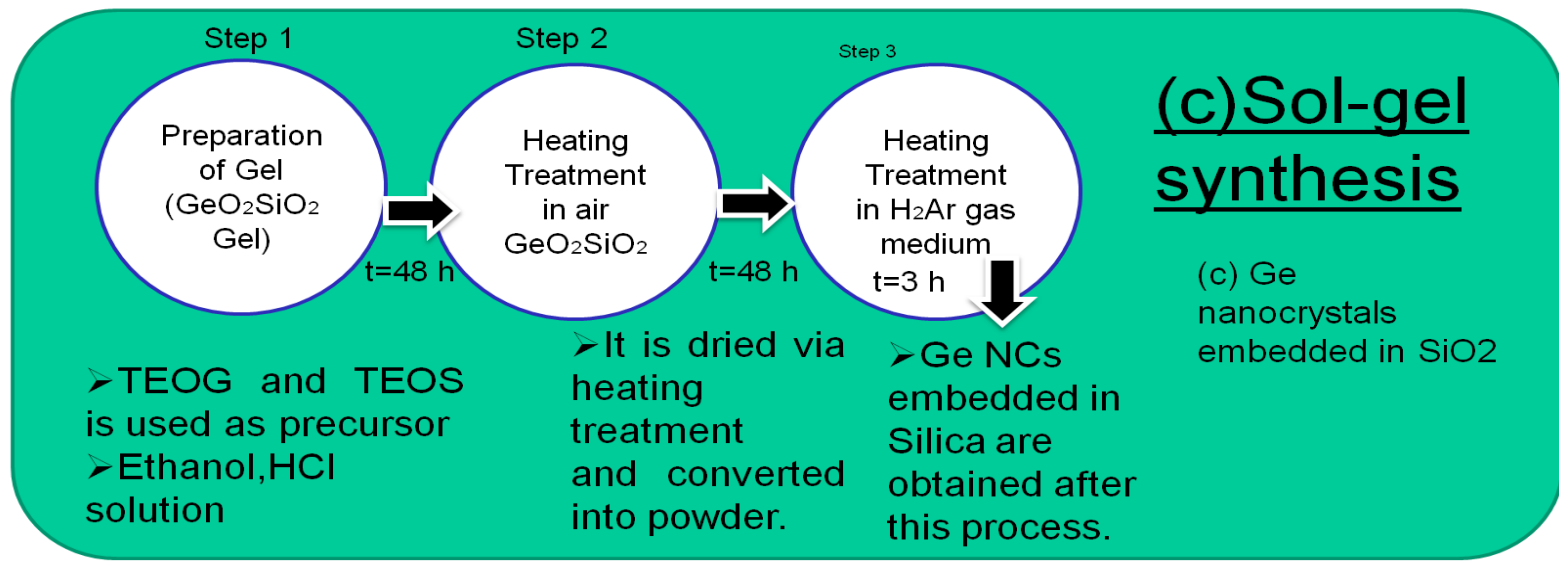
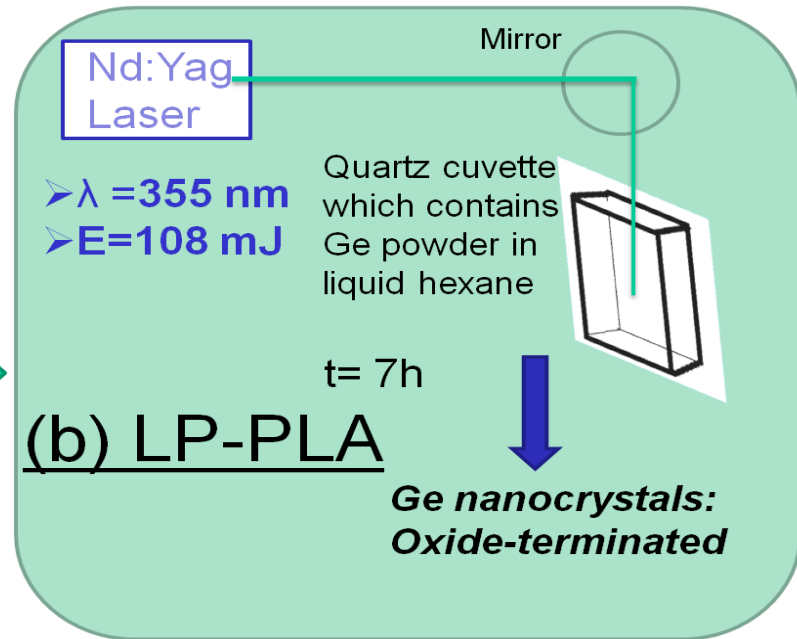
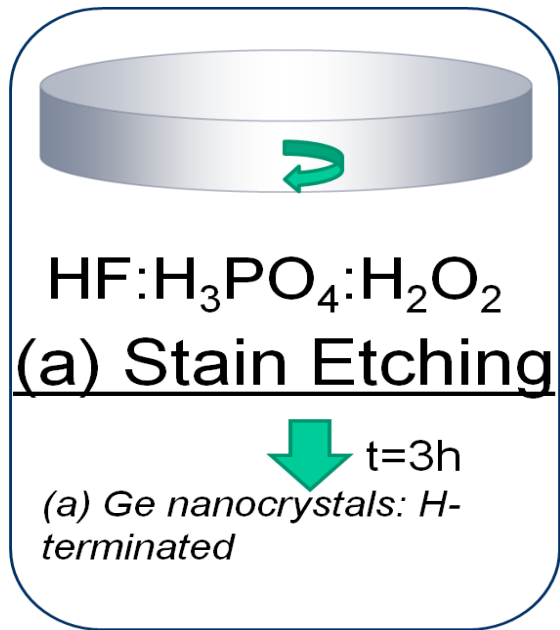
# Super-resolution



# Si vs Ge



# Sample Preparation



# Characterisation

## CHARACTERISATION TECHNIQUES:

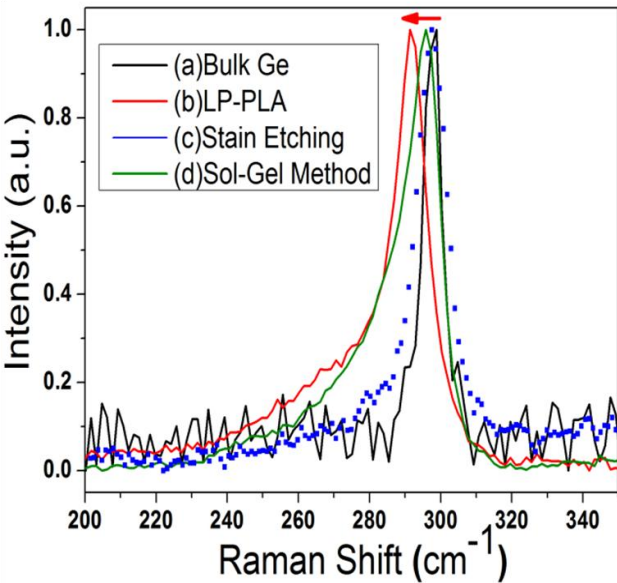
- ✓ Raman
- ✓ PL
- ✓ TEM



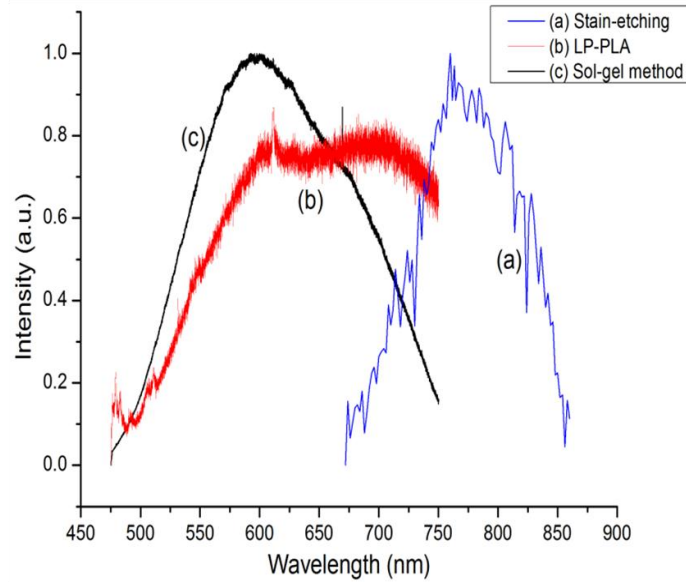
- ✓ OD-XAS
- ✓ EXAFS
- ✓ XEOL

beamline B18 at  
Diamond Light  
Source

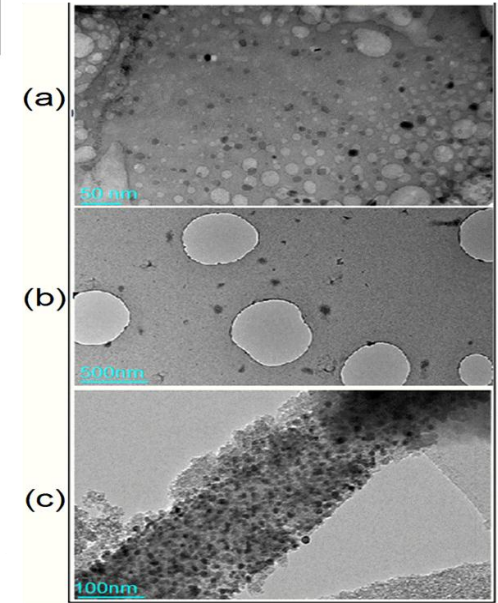
# Characterisation



**Figure 1** Normalised Raman Shift from right to left (a) bulk Ge and Ge nanoparticles formed by using (b) stain etching, (c) Sol-gel method and (d) LP-PLA.



**Figure 2** PL spectra of Ge nanoparticles formed by (a) stain etching (b) LP-PLA, (c) sol gel synthesis. Photoluminescence (PL) spectrum has been recorded from the each of the samples with excitation at 473 nm.

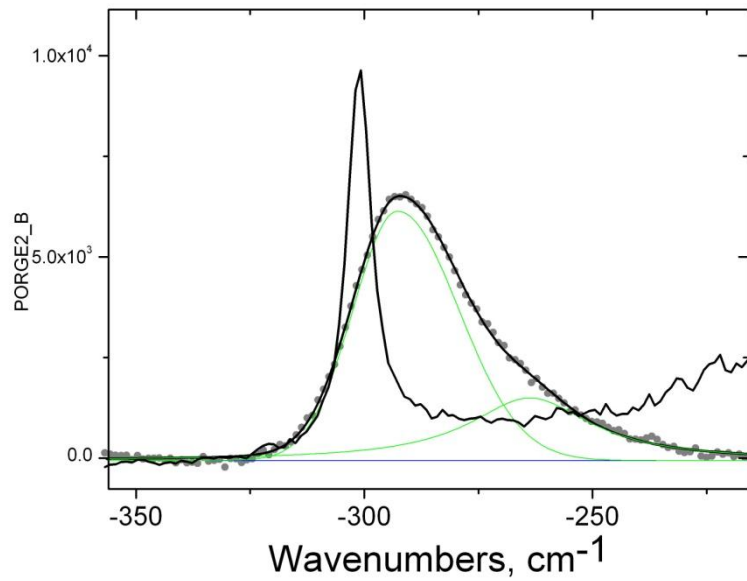


**Figure 3** TEM micrograph of Ge nanoparticles from top to down prepared by (a) stain etching (b) LP-PLA and (c) Sol-Gel Method.

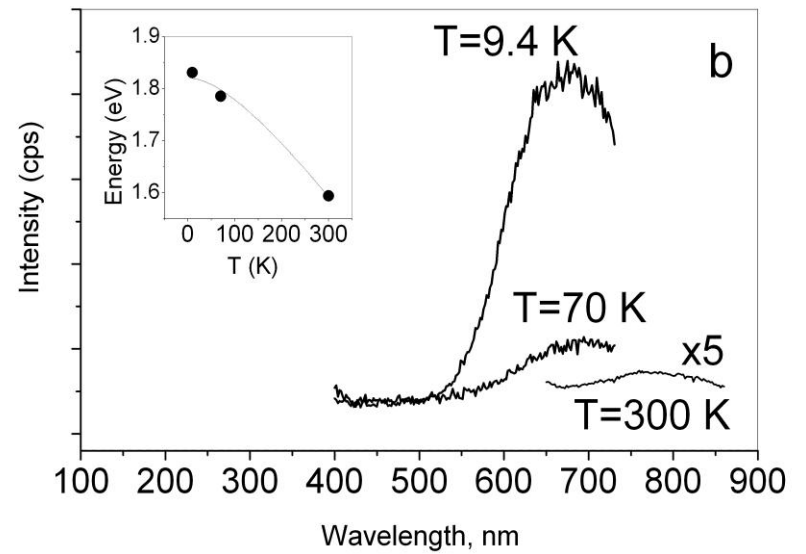


# Characterisation

## Raman



## Photoluminescence



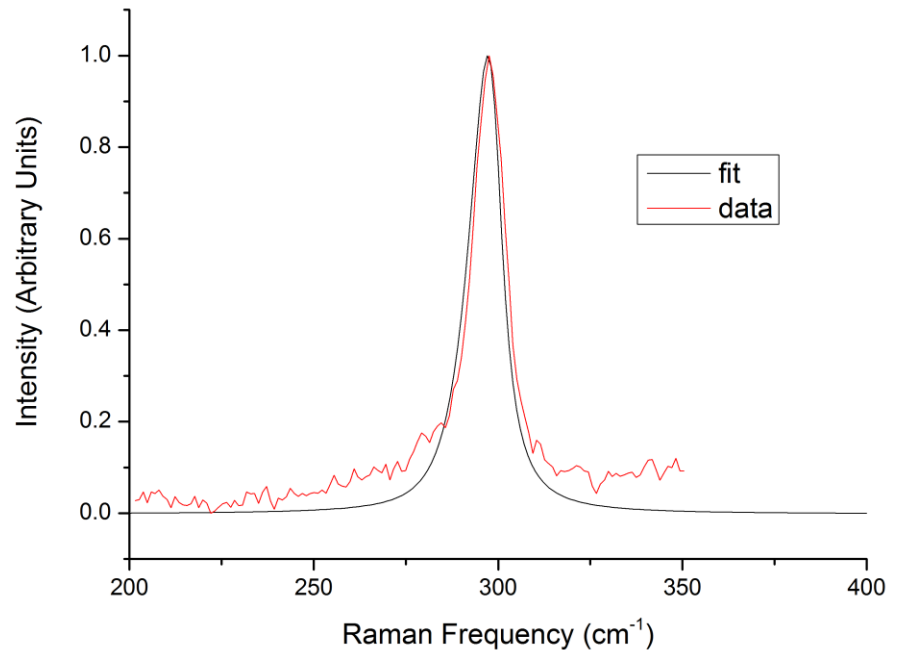
# Raman Spectroscopy: the model for particle size evaluation

The Raman signal line shape can be described by the following expression, which includes phonon dispersion and natural line width:

$$I(\bar{\nu}) = I_0 \int \frac{d^3 \vec{q} |C(0, \vec{q})|^2}{[\bar{\nu} - \bar{\nu}(\vec{q})]^2 + \left(\frac{\Gamma_0}{2}\right)^2}$$

The phonon confinement function which defines the area in the nanoparticle where phonons can exist.  $r$  is the radial position and  $L$  is the particle diameter.

$$|C(0, \vec{q})|^2 = e^{-\frac{q^2 L^2}{4}}$$



# Size analysis results

Method	Technique	Transmission Electron Microscopy (nm)	Raman Spectroscopy	
			Size (nm)	FWHM (cm <sup>-1</sup> )
(a) Stain Etching		10 ± 4	6.9	10
(b) LP-PLA		41 ± 22	6.2	12
(c) Sol-Gel Method		10 ± 6	5.3	14

# Structure of nanoGe

## SYNCHROTRON LIGHT

### 1. Electron production

Electrons are generated in the same way as in a television tube. Subsequently, they are pre-accelerated by electric fields in a *Linear Accelerator*.

### 2. Acceleration

In a *Booster Ring* the electrons are further accelerated with the aid of powerful magnetic (20,000 times greater than the magnetic field of the Earth) and electric fields, until they reach velocities greater than 99.999% of the speed of light.

### 3. Storage

The electrons are then injected into a *Storage Ring*, where they are maintained in a circular orbit by strong magnetic fields. Velocity is kept constant by compensating for the energy lost as light emission with electric fields from a radio-frequency source.

#### Magnets in a Storage Ring

- > Bending Magnets: essentially dipoles that bend the
  - > Quadrupoles: focus the electron beam onto a nomin
  - > Sextupoles: reduce the energy dispersion (chromatic
  - > Correctors: small dipoles that correct the electron tr
  - > Dipoles, Quadrupoles and Sextupoles are activated
  - > Pulsed Magnets (*Septums, Kickers and Bumpers*) are
- They produce strong magnetic fields in a short period magnetic materials.

### 4. Beam-lines

Synchrotron Light is propagated through a *Beam-line*, placed tangentially to the ring. There are two types of beam-lines, depending on whether *Insertion Devices* or *Bending Magnets* are used for light production.

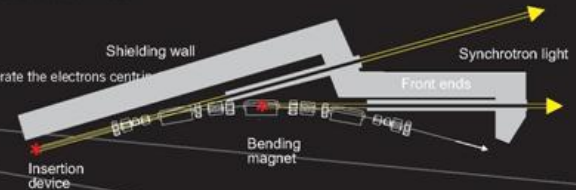
In the *Insertion Devices* Synchrotron Light is generated when the electrons are accelerated into a sinusoidal trajectory by a periodic magnetic structure. The light thus obtained is very intense and collimated.

The light then generated is white (polychromatic), albeit less collimated and intense than that from the *Insertion Devices*.

### 5. Light condition

In an optical "hutch" one selects certain wave-lengths, i.e., a small portion of the white electro-magnetic spectrum, by means of a monochromator. These photons are transported and focused onto the sample by, for example, bent X-ray mirrors.

sample



### Data reduction and analysis

In the control "hutch" the experimental set-up and data collection is under computer control. Data are extracted, reduced, processed and prepared for analysis and/or storage.

# ODXAS measurements

## SCHEMATIC OF DETECTION SYSTEM AT DIAMOND LIGHT SOURCE (BEAMLINE B18)

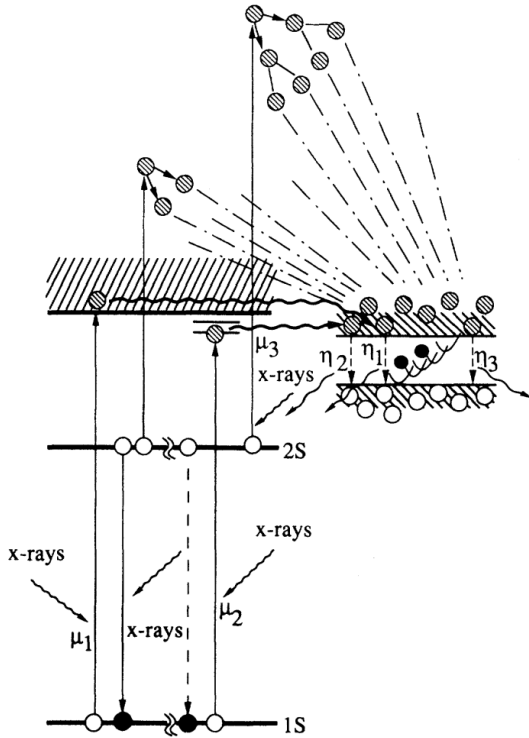
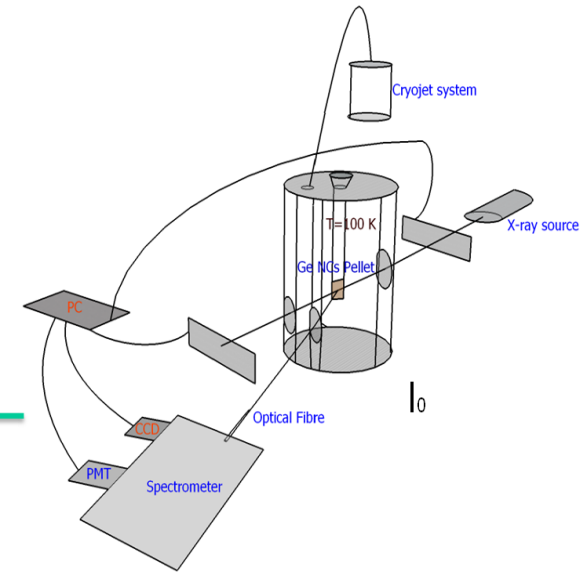
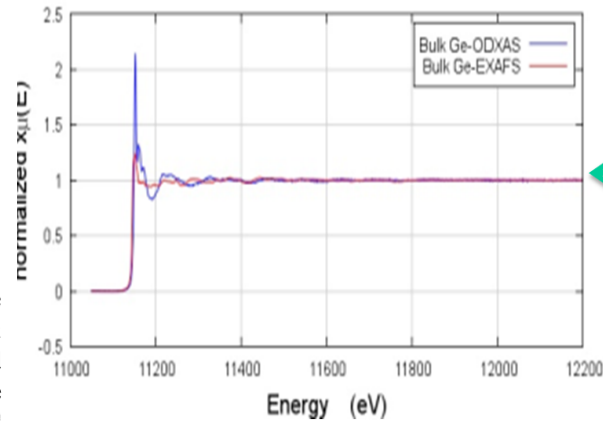
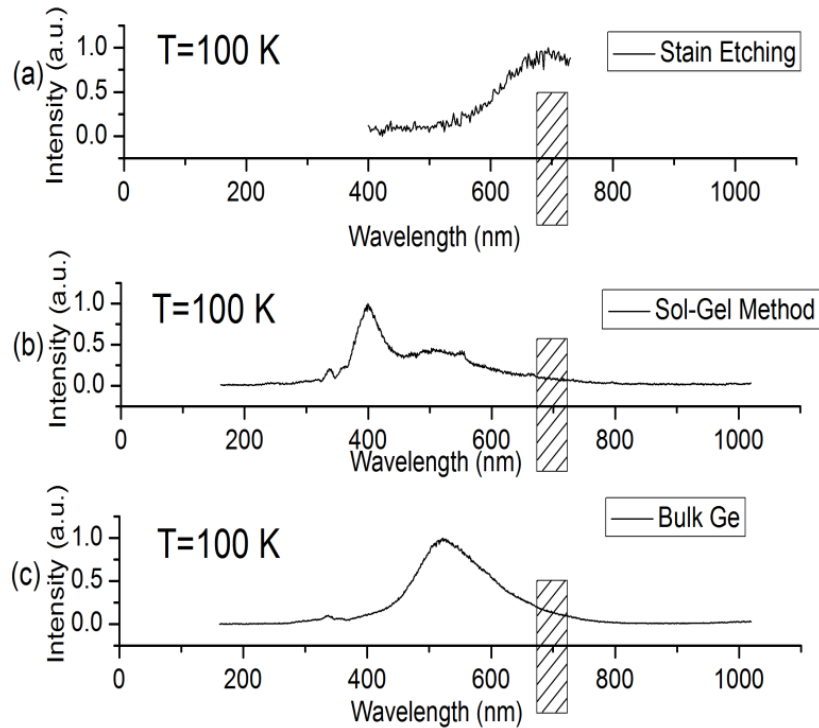


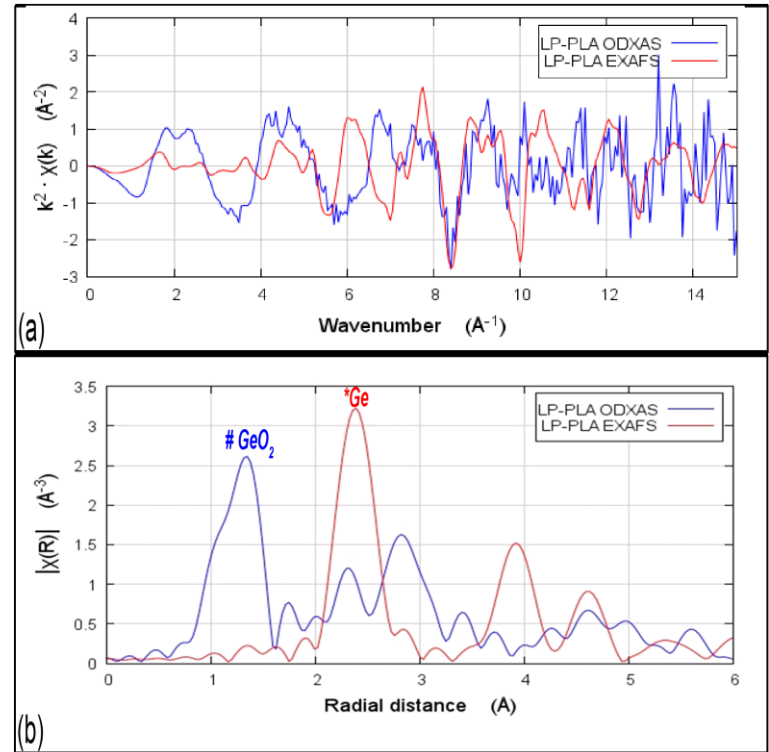
FIG. 1. A schematic diagram of the excitation-luminescence cycles. Three different excitations—from a  $1s$  state (absorption coefficient  $\mu_1$ ) to a continuum state, a  $1s$  state ( $\mu_2$ ) to a bound state, and a  $2s$  ( $\mu_3$ ) to a continuum state—give rise to a single luminescence with the respective luminescence yields  $\eta_1$ ,  $\eta_2$ , and  $\eta_3$ . The events of an x-ray fluorescence, a *KLL* Auger, electron multiscatterings, a nonradiative decay due to electron-phonon scattering, and radiative transitions are schematically depicted.



# ODXAS and EXAFS

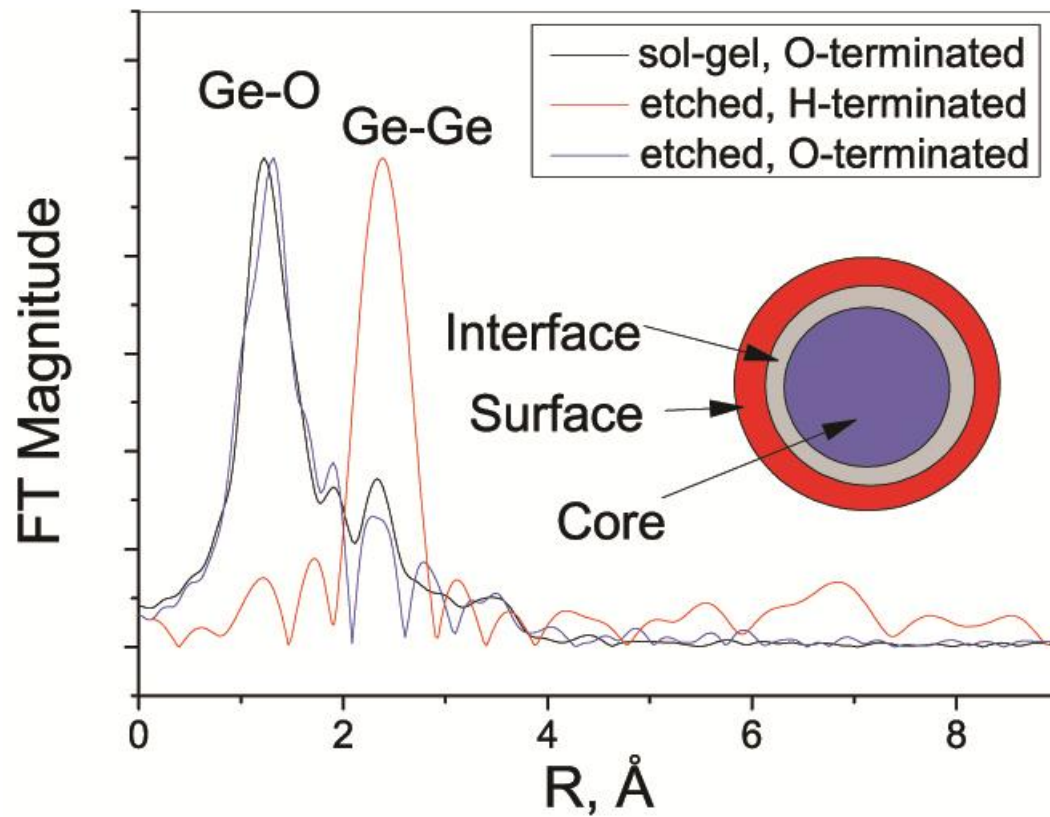


XEOL measurements of the Ge nanoparticles at 100 K.



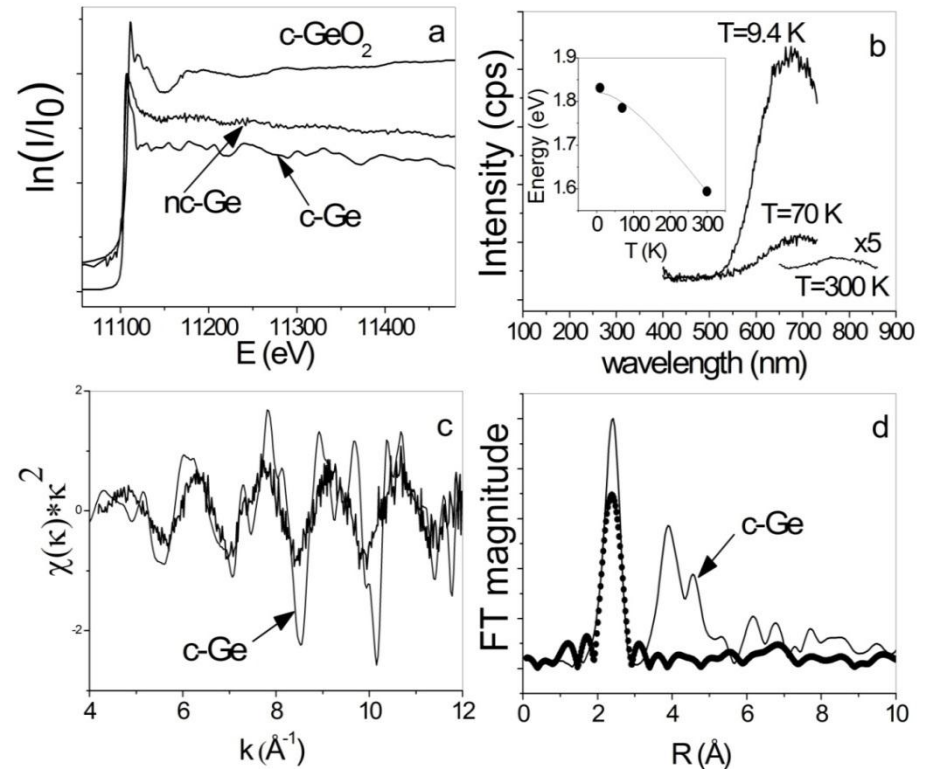
Comparison of OD-XAS and EXAFS of Ge K edge of LP-PLA (a) in k space (b) in R space.

# ODXAS and Structure



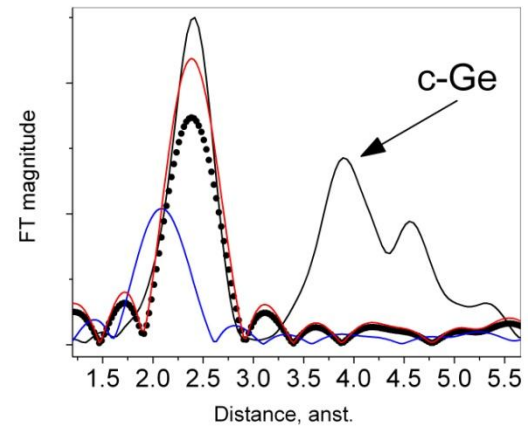
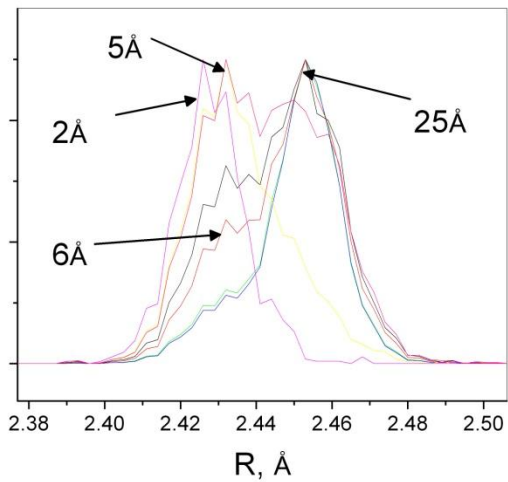
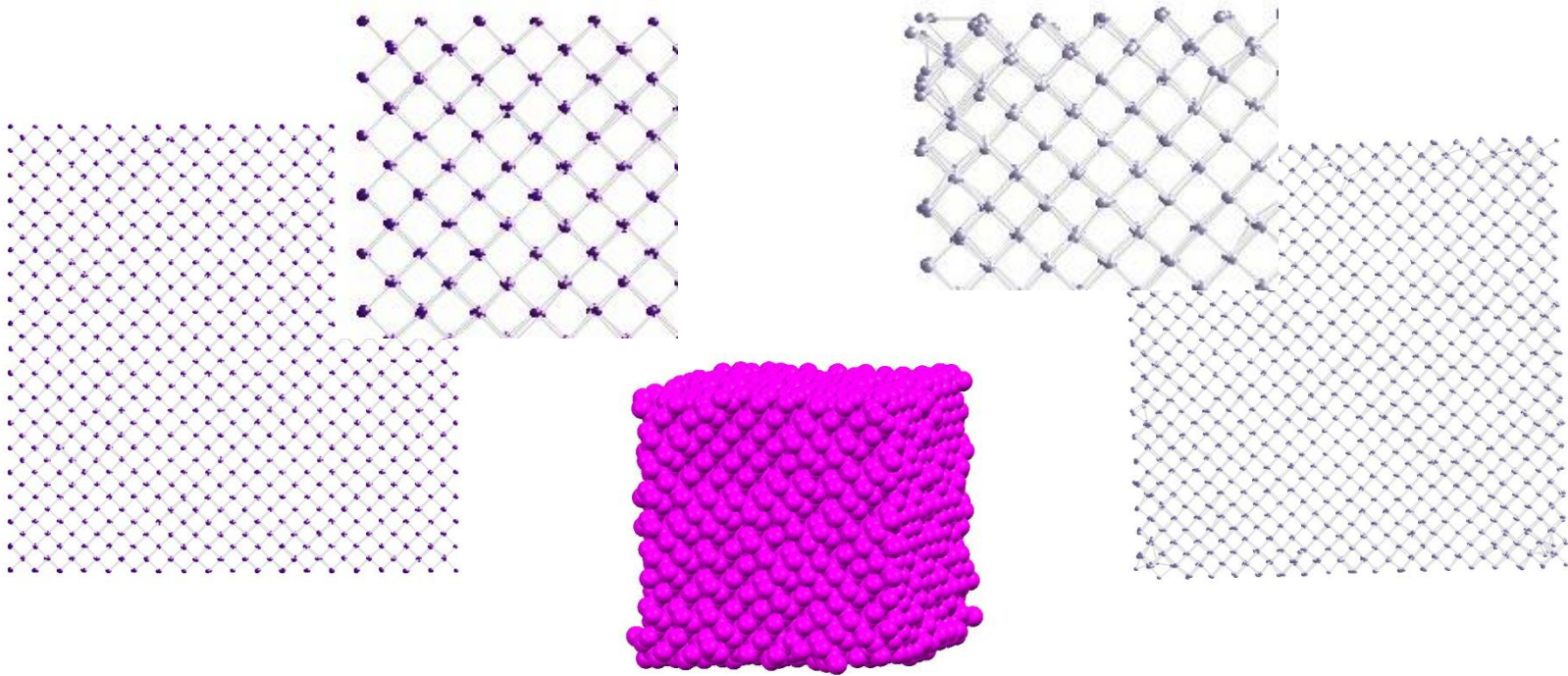
# Structure: EXAFS and ODXAS

- $R = 2.44(1) \text{ \AA}$  - consistent with the corresponding value for the diamond structure of *c*-Ge
- Debye-Waller factor (mean square relative displacements of atoms) of  $0.0044(15) \text{ \AA}^2$  ( $0.0027(2) \text{ \AA}^2$  for *c*-Ge at this temperature).
- The coordination number was found to be reduced ( $2(0.7)$  against 4 in *c*-Ge).





# Structure: EXAFS and MD



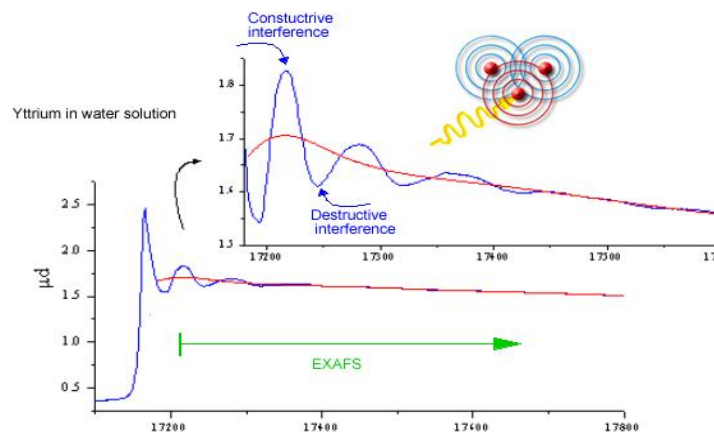
## Conclusion

- Comparison of OD-EXAFS, EXAFS and Raman shows that various sub-structures can be responsible for light emission.
- PL in Ge nanocrystals synthesised by various routes can be of different origin depending on the surface termination.
- We show that for a given nano-particle set OD-EXAFS can show sub-nanoparticle resolution.

## Future work

- Surface/strain effects in PL and Raman.
- Improving photon yield and controlling peak wavelength.
- Blinking.
- In-vitro bio-stability and toxicity
- Magnetic semiconductor nanoparticles

# ODXAS and EXAFS



**Debye-Waller term**

$n_X = \# \text{ of X atoms in shell}$

amplitude function  $\sigma^2 = \sigma_{\text{stat}}^2 + \sigma_{\text{vib}}^2$   
 $\sigma < 0.10 \text{ \AA}$

phase function

$$\chi = \sum_{\text{shells}} \frac{n_X \cdot S_0^2 \cdot f_X(k) \cdot e^{-2k^2\sigma^2}}{k \cdot r^2} \sin(2kr + \alpha_{MX}(k))$$

amplitude reduction factor

$r = (\text{average}) \text{ MX distance}$