凝聚态物理-北京大学论坛
2012年第4期

由拉曼光谱学揭示的
纳米半导体的新物理特性

NOVEL PHYSICAL NATURE of NANO-SEMICONDUCTORS EXPOSED by RAMAN SPECTROSCOPY

北京大学 张树霖

北京大学　物理大楼 212

2012-03-15

周五论坛

低维／纳米半导体的曼光谱学与物性

北京大学 张树霖

第一讲

第一部分 拉曼光谱学基础

第二部分 低维结构及其拉曼光谱

第二讲

纳米半导体的拉曼光谱学与物性

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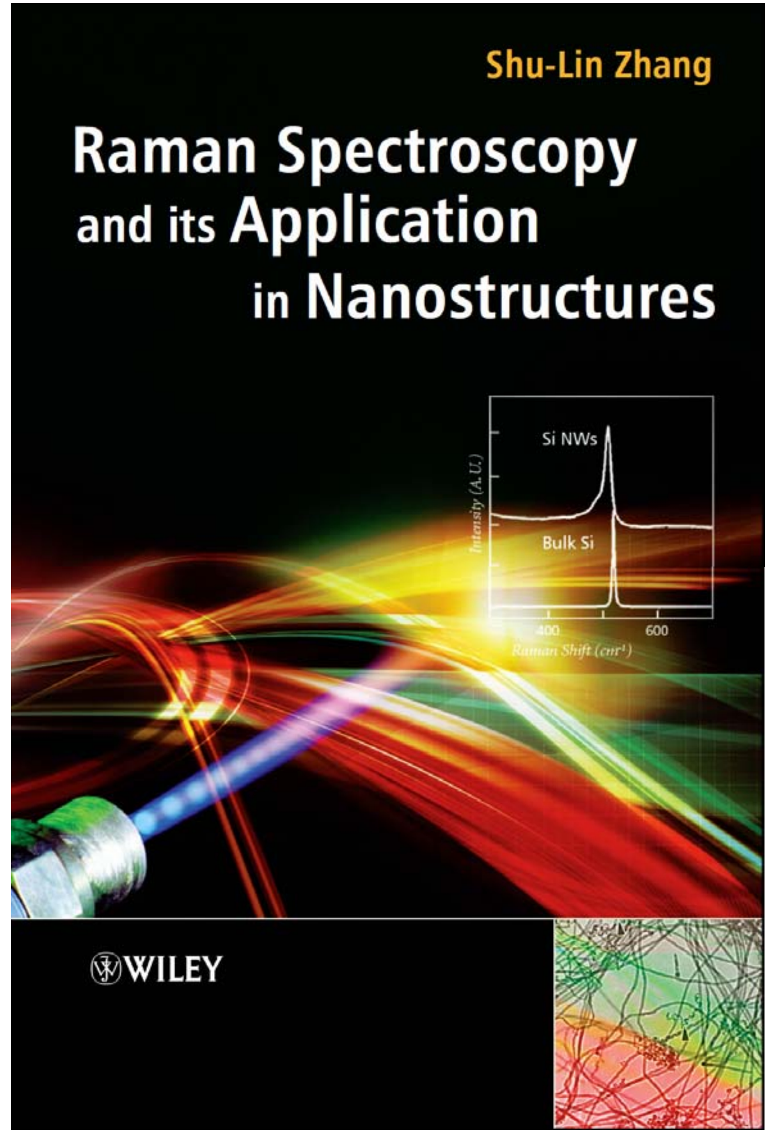

John Wiley & Sons Ltd, Chichester UK, 2012

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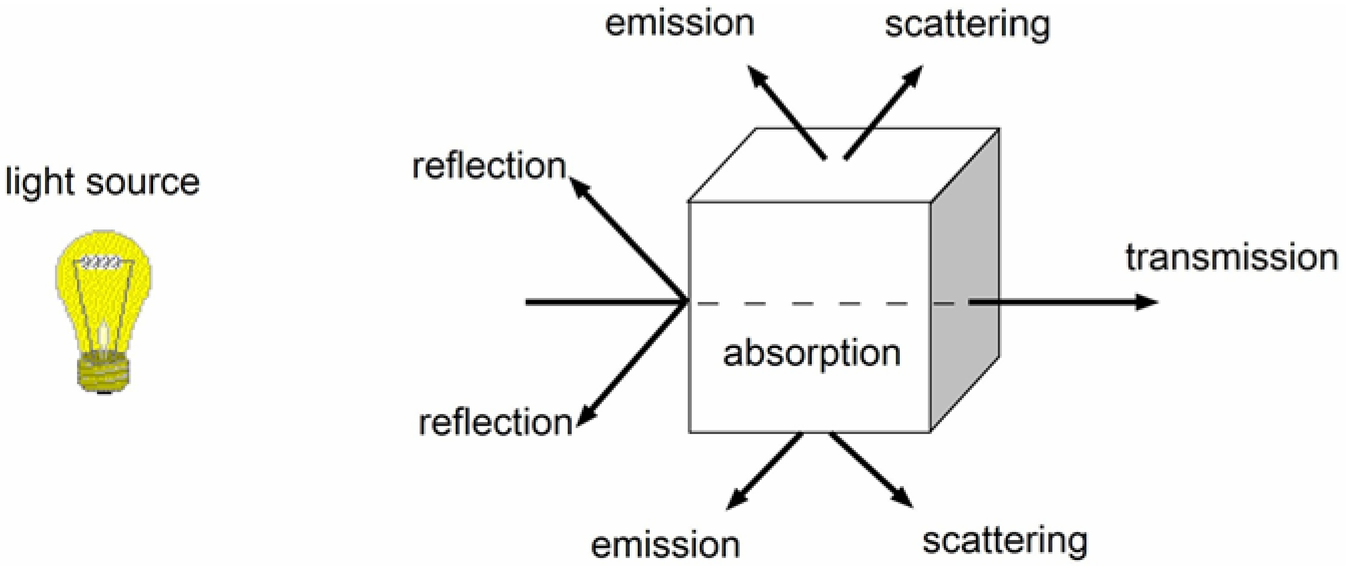
I-1 Fundamentals of Raman Spectra

(I) Production of Spectrum

The spectrum is induced by the light irradiation on medium.

It produces some types of light:



(1) Scattering light is one of many types of light induced by irradiation

The Light induced
by monochromatic light irradiation

- Reflected and transmitted light:

  The frequency must be same with that of monochromatic light.

- Scattering light:

  The frequency can be different from monochromatic light .

(2) Under monochromatic light irradiation:

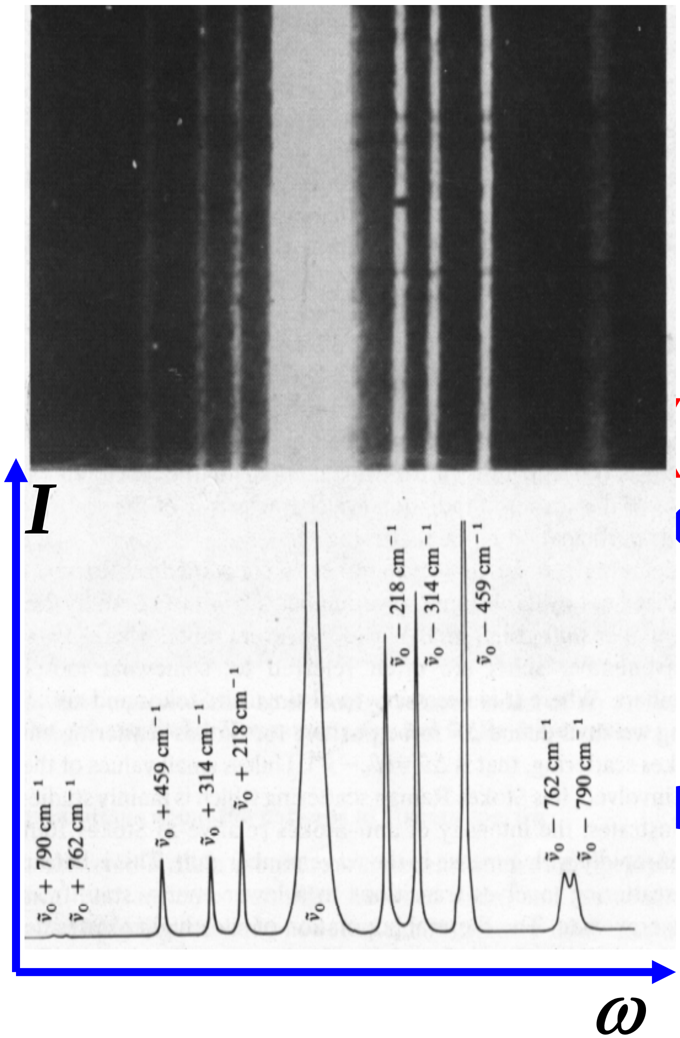
The scattering light can behave as a spectrum, while other two are impossible.

The frequency/energy of scattering light spectra

$\omega_S - \omega_{Rad} = \Delta\omega$	*Name*	*Property*
> 1 cm^{-1}	Raman	Non-elastic
< 1 cm^{-1}	Brillouin	Elastic
<10^{-5} cm^{-1}	Rayleigh	Elastic (~ 0)

(3) Raman scattering spectrum is one type of light scattering spectra.

(II) Features of Raman scattering spectra



(1) Intensity I

- $I_{Raman}/I_{Incident} < 10^{-6\sim12}$
  ($I_{Rayleigh} / I_{Incident} < 10^{-3}$)
- $I_{Stokes} / I_{Anti\text{-}Stokes} \approx exp(\hbar\, \omega_k/kT)$

>>

(2) Frequency ω_S

- ω_S Independent of ω_i

Energy conservation

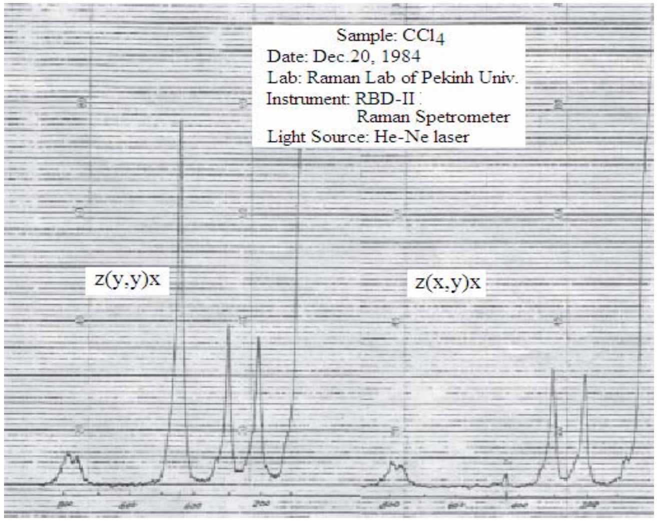
- $\omega_{Stokes}| = |\omega_{Anti\text{-}Stokes}|$

Time inversion symmetry

(3) Polarization *P*

Raman scattering light is polarized light,
If the orientation of the molecular or crystals is fixed.

- That is the Reflection of the symmetry properties of molecules or crystals;
- The information of symmetry of objects can be obtained from polarized Raman spectra.



(4) Spread direction *K*

As no relevance
between the phases of different Raman beams
The spread in space is isotropic.

Raman spectral features

- Raman spectrum is a non-elastic light scattering spectra with
  the energy/frequency > 1 ~ 2 cm^{-1}.

- Raman spectrum is one of the spectra with unique spectral features in frequency, intensity, polarization and spread direction, such as, its frequency ω_S:

1. ω_S Independent of ω_i

2. $|\omega_{Stokes}| = |\omega_{Anti\text{-}Stokes}|$

I-2 Introduction to nanostructure/nanomaterial

1. The influence of size on physical law

The size of the object has a significant influence to the properties and movement rules of matters.

- A macro-scale (> light wavelengths ~ μm) material is generally considered to be an infinite system and comply with classical physics law;

- A micro-scale (subatomic scale) material is described by quantum physical law.

2. Definition of nanostructure/nanomaterial

- Ones usually define a structure/material with a small size of a sub-micron ~ 1 nm (1 ~ 100 nm) in geometry as the nano-materials/nanostructures.

- For such defined nanostructure/nanomaterial, it is unable to determine which type of physical law will be complied, as its size is between the macroscopic and microscopic scales

- A scientific definition of the nano-structure/material:

  macroscopic in geometrical size;

  But appears the quantum mechanical phenomena.

3. Characteristic Length

- Following length called as 'Characteristic Length', such as

  Dephasing length,
  Diffused length
  Bohr radius r_{e},
  de Broglie wavelength
  ....

- The scale of same characteristic lengths might be different under different case. For example,
  The de Broglie wavelength of electrons in the conduction band bottom can be from 10-100nm and
  the Bohr radius of the electrons in hydrogen atoms and conduction electrons Bohr radius are 0.05nm and 10 nm, respectively.

4. Essential effect of small sizes

(1) The small size of nanostructures/nano-materials induces a finite size effect (FSE).

The influence of FSE is more concerned in physics.

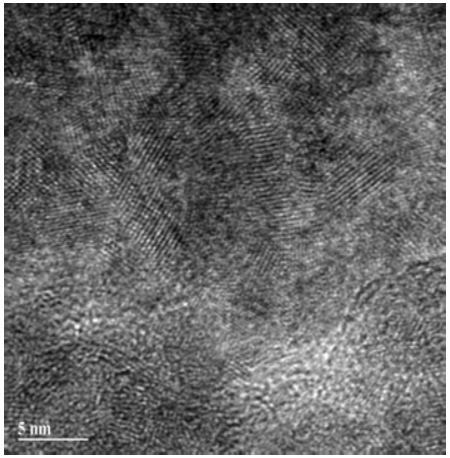
(2) The small size of nanostructures/nano-materials results in huge specific surface .

This play an more important role in chemical field.

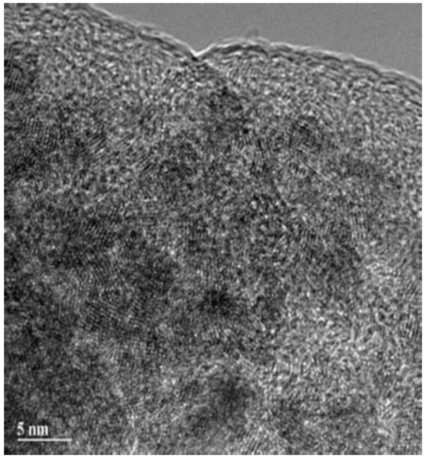
I-3 Nanostructured materials

1. Nanomaterial in nature and history

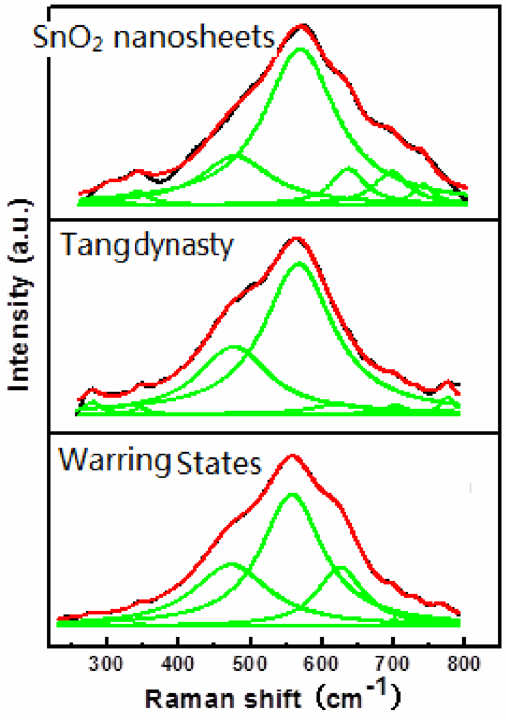
Nano materials already exists in nature and history. For example,
the Chinese ink appeared more than 1000 years ago. In fact, it may be more early, such as, the ancient bronze mirror.



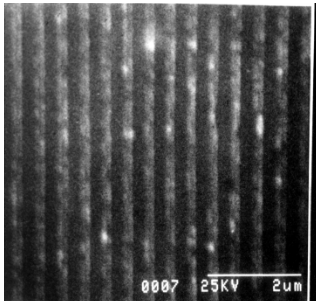
Warring states bronze mirror



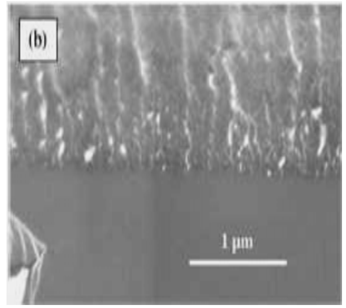
Tang dynasty bronze mirror



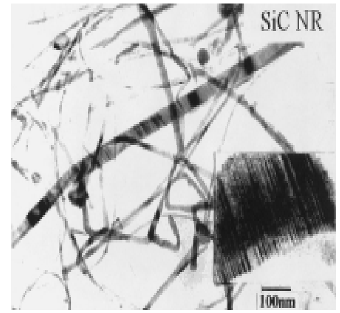
2. Artificial Nanostructured materials



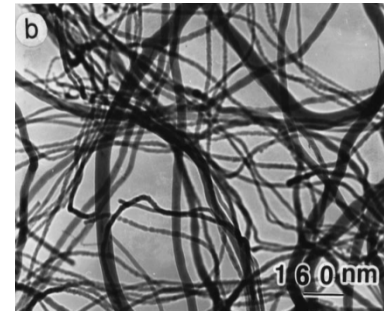
Superlattice



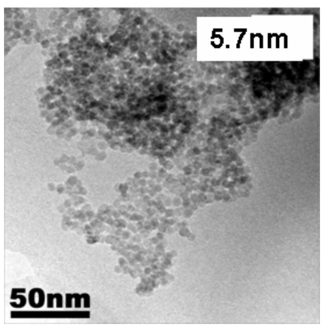
porous silicon



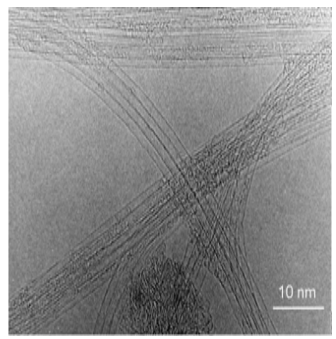
nano rod

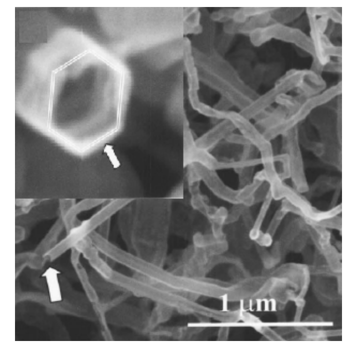


nano wires

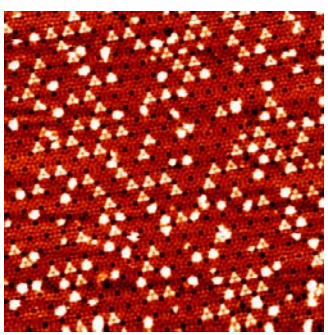


nano particle

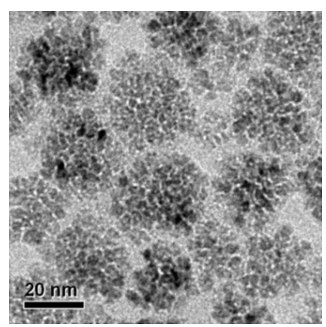




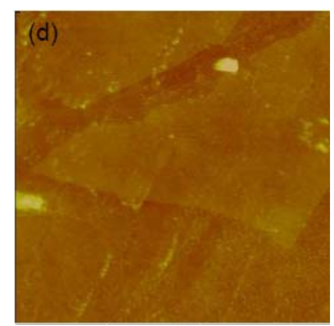
nano-tubes



cluster



nano flowers



graphne

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I. Basic Feature of Raman Spectra and Nanostructures

II. Raman Spectral Feature of Nano-semiconductors

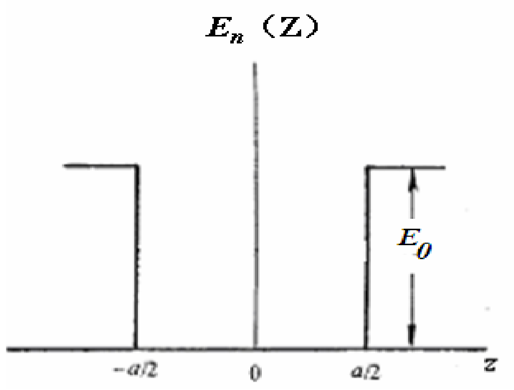
III. Abnormal Raman Spectral Feature Relative to Conventional Raman Spectroscopy.

IV. Abnormal Raman Spectral Feature Relative to Nanostructure Raman Spectroscopy

Ⅱ-1 FSE on basic physical quantity

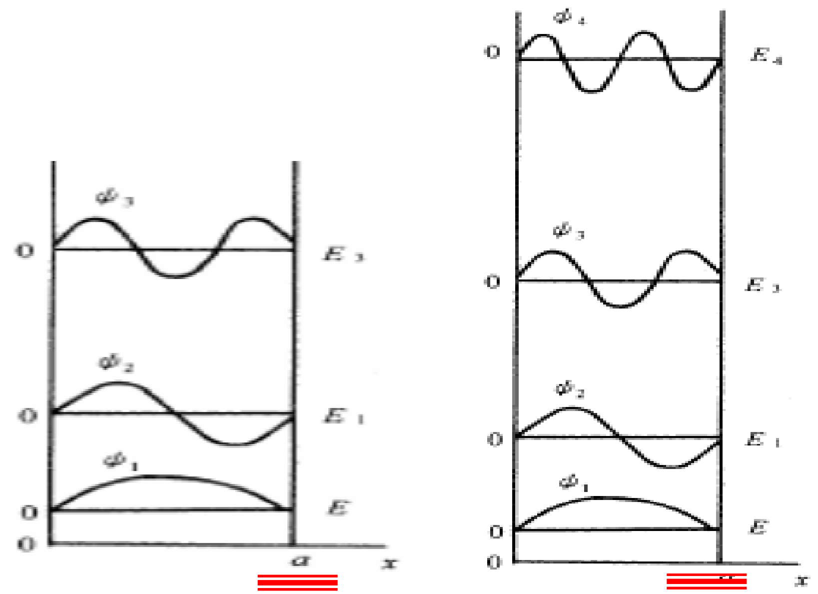
Finite size leads to an infinite and unconfined system becoming a limited and confined system.

(Ⅰ) FSE on Energy-quantum confinement effect (QCE)



$$E_n = \frac{n^2(\pi h)^2}{2m}\frac{1}{a^2} \qquad E_n(k) = E_n + \frac{\hbar^2 k^2}{2m}$$

Energy level and wave function



Energy (Raman frequency) changes with sample sizes *a*

(II) FSE on Symmetry

1. Spatial symmetry - translation symmetry

In Bulk (infinite) semiconductors, there must have the translation symmetry

↓

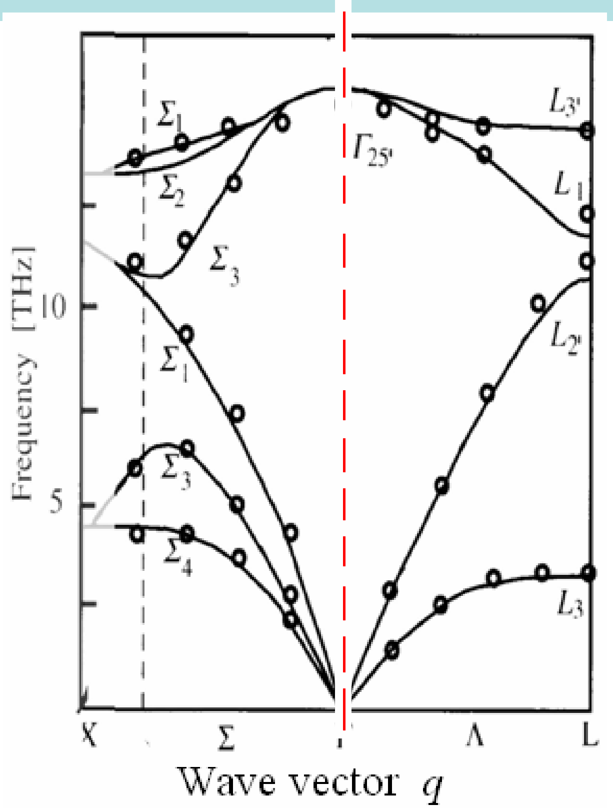
Long-range order ~ crystalline

↓

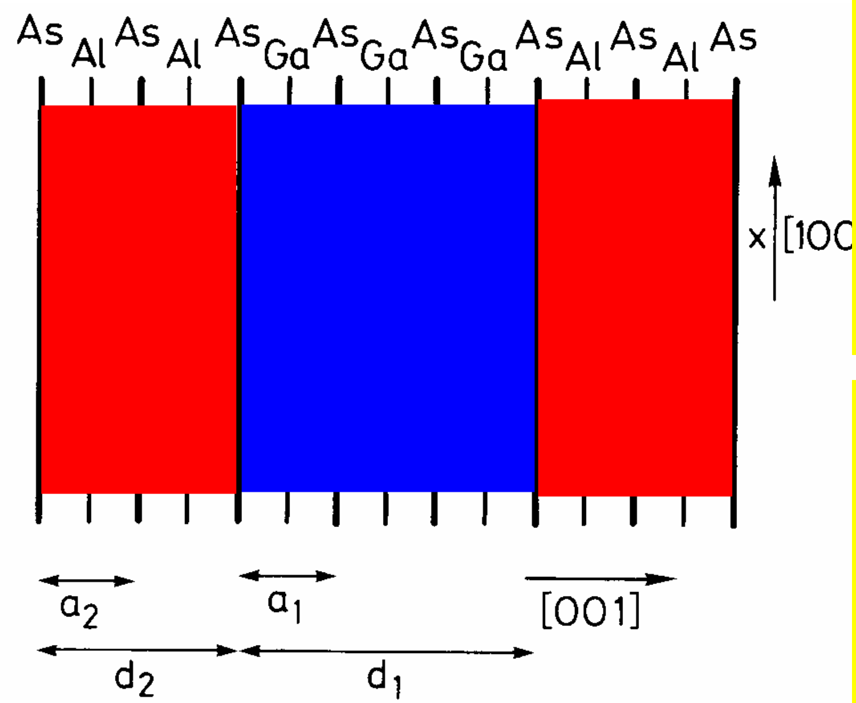
Momentum *hq* (wavevector *q*) conservation

↓

For visible Raman scattering means wavevector selection rule $q = 0$.



2. Crystallographic symmetry



● The symmetry of GaAs/AlAs SLs is changed

from

D_{4d} of GaAs and AlAs

to

T_d of GaAs and AlA

● Correspondently, the period (~lattice constant) is

$$L = d_1 + d_2 = (n_1 + n_2)a$$

a - Lattice constant of GaAs and AlAs;

n_1 and n_2-single layer number of GaAs and AlAs in SLs.

(III) FSE on Momentum

1. Uncertainty relation

$$\Delta \boldsymbol{k} \Delta \boldsymbol{r} \leq \hbar$$

$$\Delta k_i \Delta r_i \leq \hbar \qquad i=x,y,z$$

When the size $\boldsymbol{r}$ is very small, the uncertainty of the momentum will be very big.

The momentum of phonons appears diffusion.

Since momentum diffusion

↓

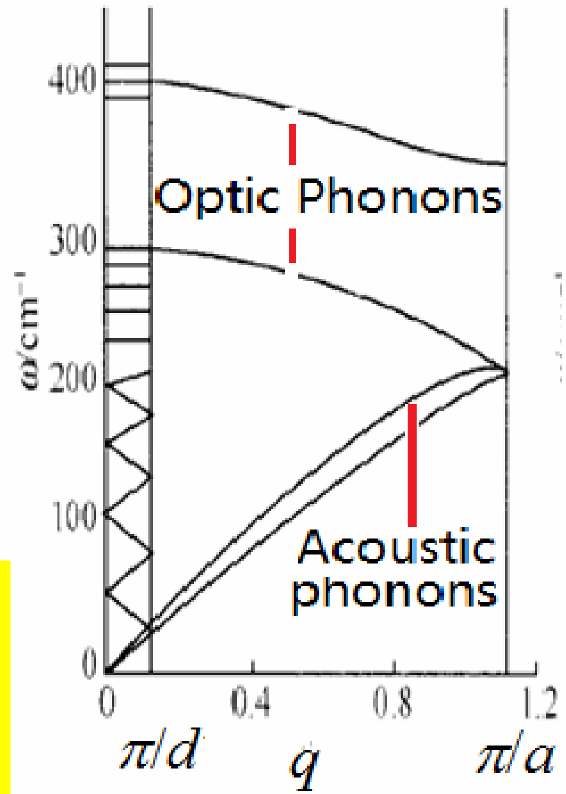
The phonons of wavevectors $\Delta \boldsymbol{q}$, rather than $\boldsymbol{q} = 0$ are possible to join Raman scattering scattering

II-2 FSE on Raman Features

It can be described by the models setup on the change of physical quantity mentioned.

(I) Layered nanostructure materials-Superlattices (SLs)

- The big period $d = na$ of SLs has the large B-zoon of π/a changing as a small one of π/d.
- The bulk dispersion curve folded into a small zoon. Phonon energy is spllitted into many sub-energy-levels in SLs.



Raman features of SLs

(1) Active optic mode in bulks "split" into many sub-modes.

(2) Forbidden acoustic become active.

(II) Non-layered nanostructure materials

- Nanomaterials (NMs)

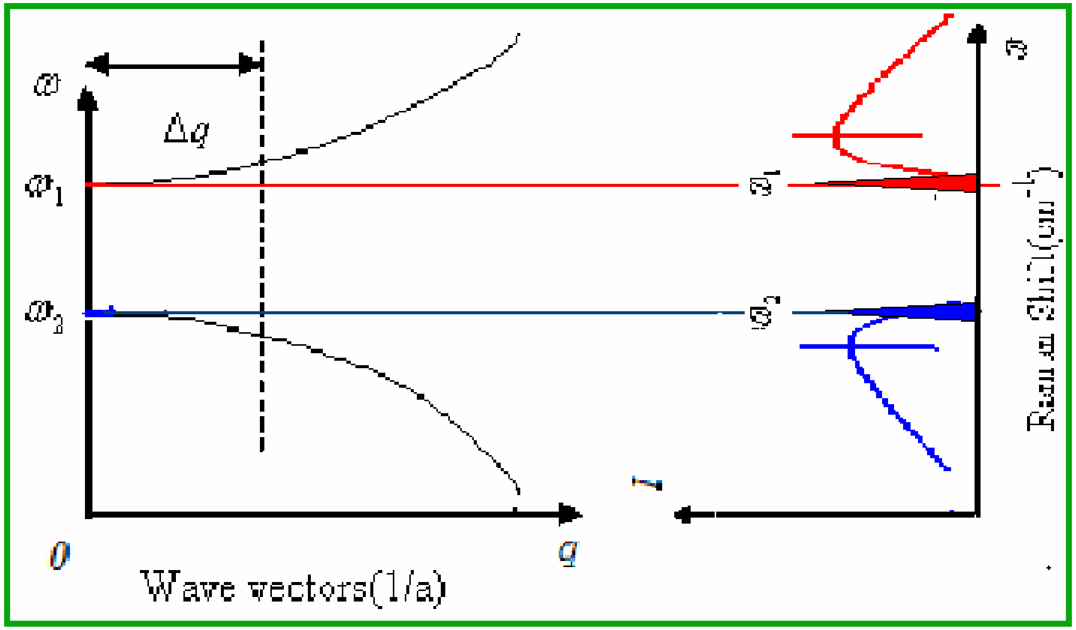
Microcrystal model (MCM)

Based on FSE on momentum and translation symmetry

$q \neq 0$ and $\Delta q \neq 0$

$$I(\omega) = \int \frac{d^3 q C(0,q)^2}{(\omega - \omega(q))^2 + (\frac{\Gamma_0}{2})^2}$$

Raman feature of NMs predicated by MCM



Frequency and line shape of Raman spectra related with sizes!

(III) Prediction for the Raman features of nano-materials based on above models

Appearing of new Raman modes

(1) Active model in bulks "split" into many sub-modes such as optical mode in superlattices

(2) Forbidden modes in bulks (e.g., acoustic modes) become active modes 。

(3) Induce new modes, e.g, the interface and surface modes.

Appearing new characteristic of active modes in bulks

(4) Frequency shift ；

(5) Linewidth broaden

(6) Symmetrical Lineshape may become into unsymmetrical ones.

II-3 Observed Raman Spectra

- Examination of above predictions of Raman features

(I) Superlattices (SLs)

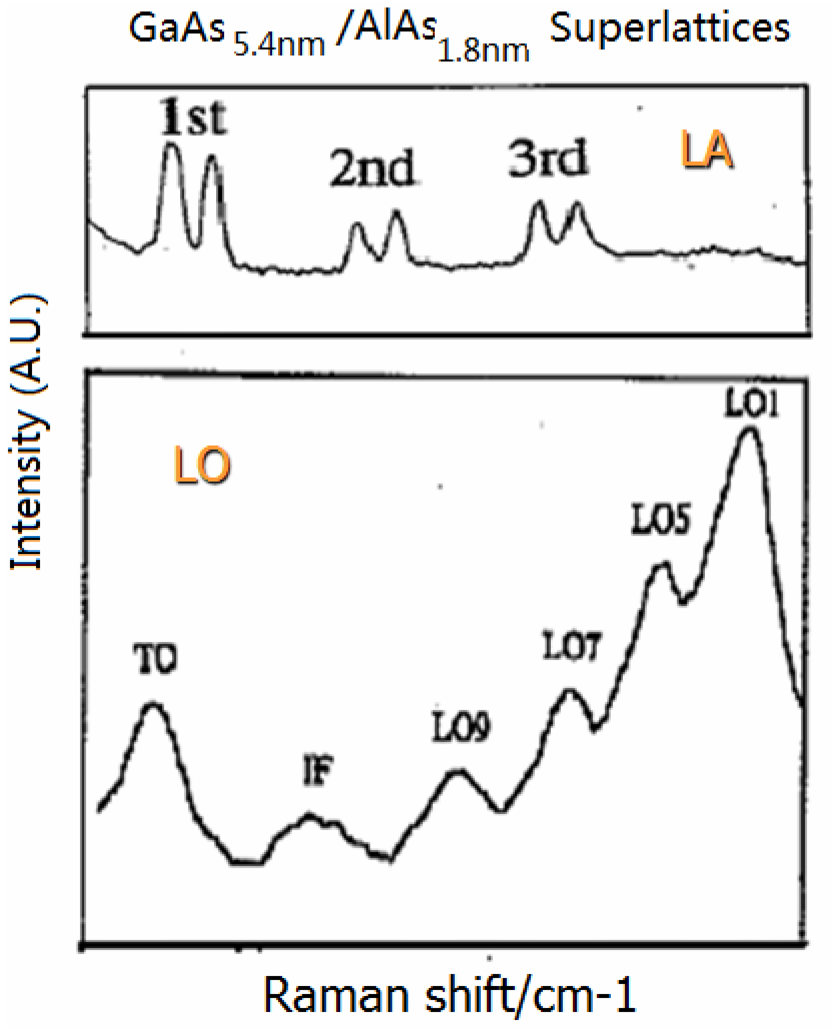
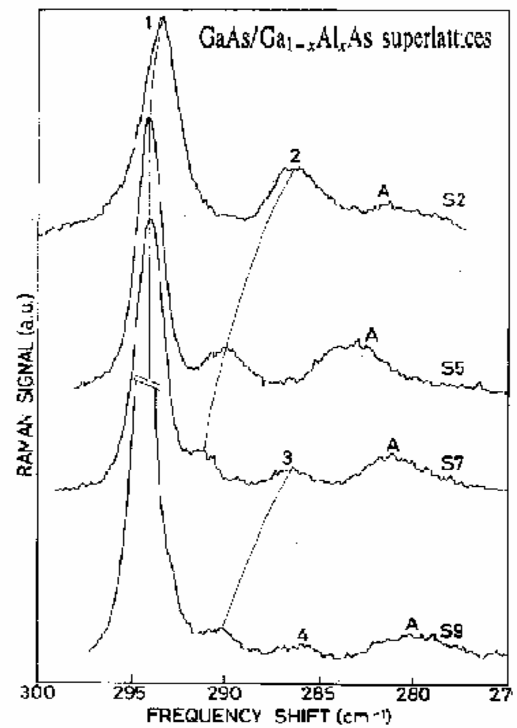


TABLE I. Sample parameters as defined in the text. For samples S6 and S8 the parameters have been estimated from the growth conditions.

	d (Å)	$\bar{x}$	n_1	n_2
S2	29.2	0.123	6	4
S5	51	0.147	9	9
S7	54.4	0.141	12	7
S9	81.4	0.145	17	12

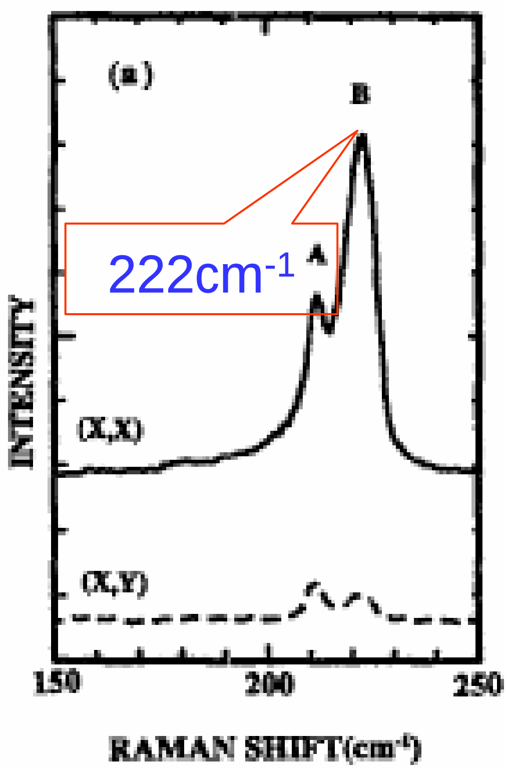


- B. Jusserand et al, PRB30(84)06245

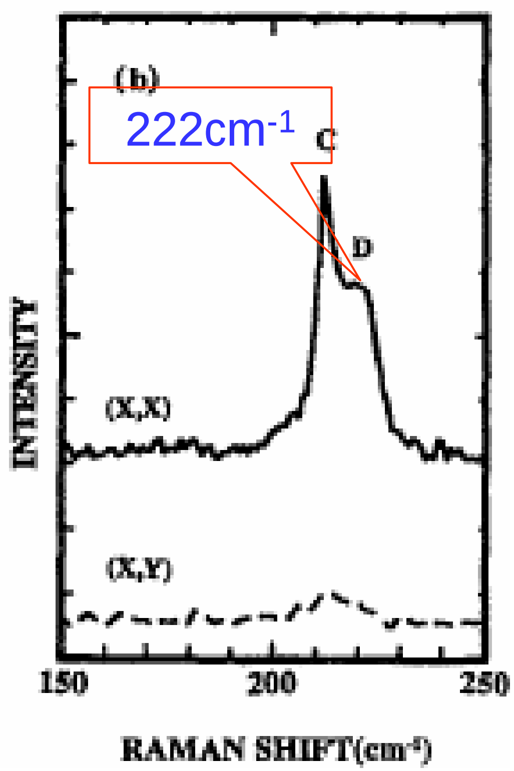
超晶格**界面**键的振动模

(CdSe) /(ZnTe)的 Se-Zn键

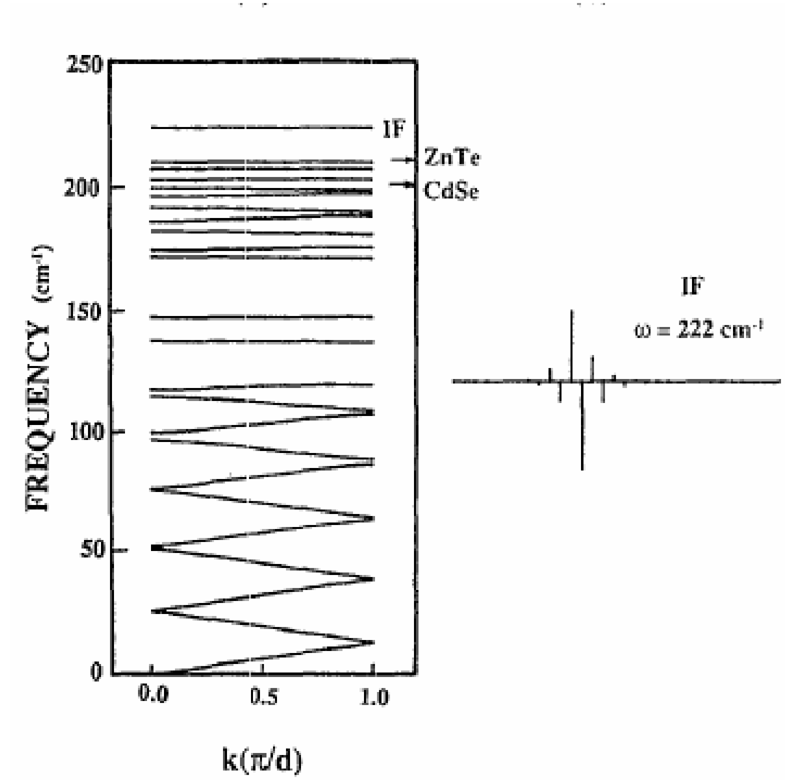
理论比较/cm^{-1}	
实验	222
Fesolino	211
我们计算	222



$(CdSe)_4/(ZnTe)_8$



$(CdSe)_8/(ZnTe)_{12}$

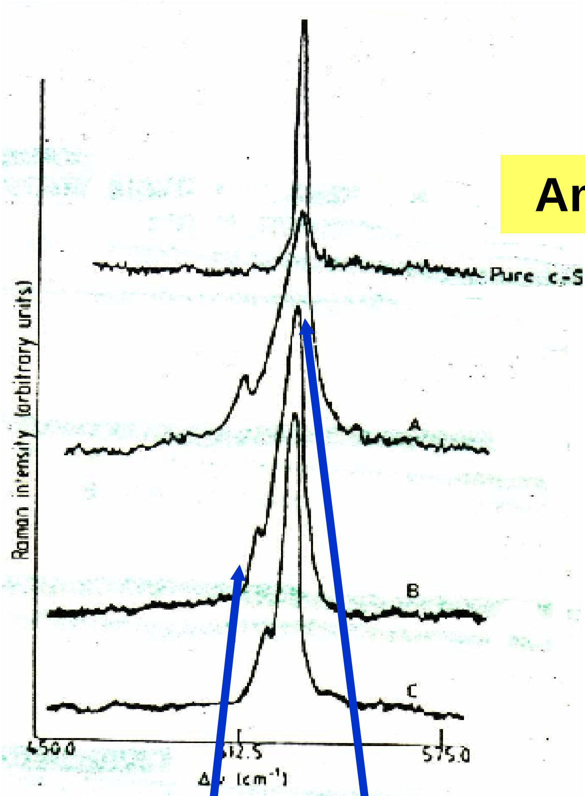


(II) Nanomaterials (NMs)

1. Porous Silicon (PS) - The first studied NMs widely

Early works: Consisted of two Bulk Raman spectra

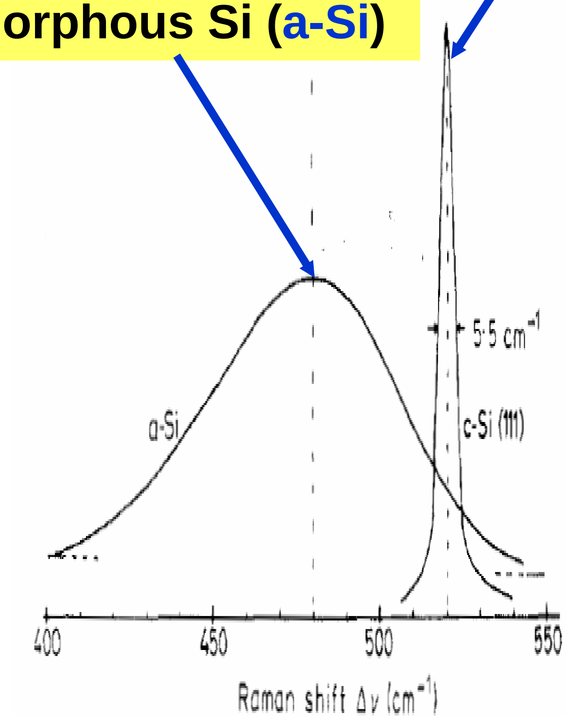
??: Not match the prediction based FSE!

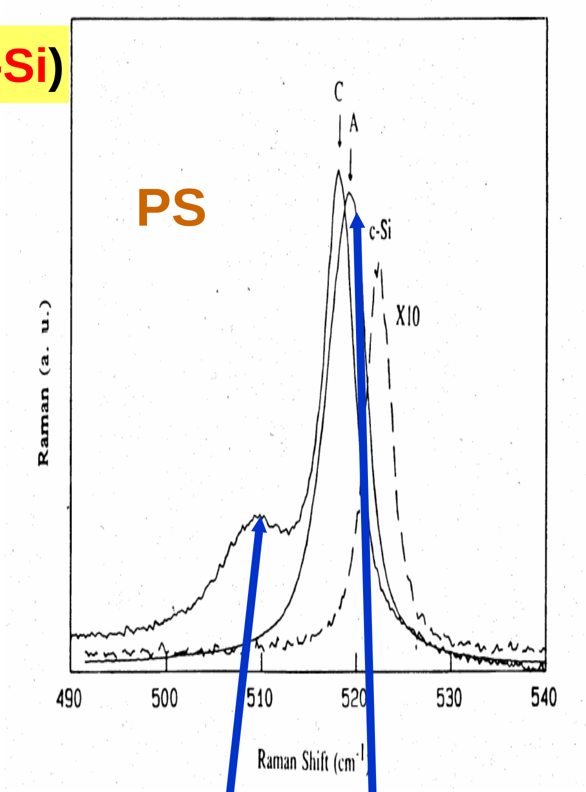


a-Si / c-Si

Amorphous Si (a-Si)

Crystalline Si (c-Si)





Split TO / LO modes

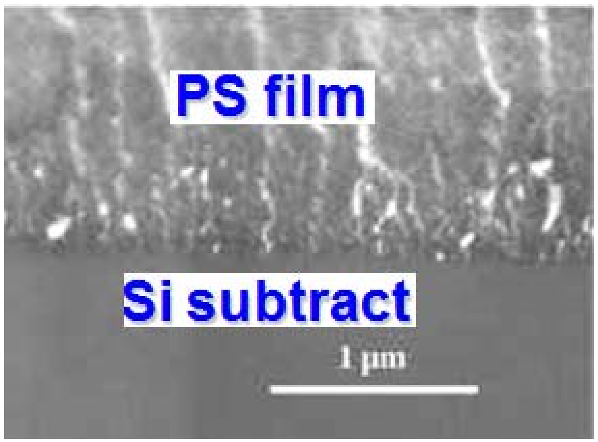
-Goods,et al, Semi. Sci.Tech.3(1988)483

-T. Tsu,etal APL,60(1992)112.

Aanalyses and measurement for PS Raman spectra

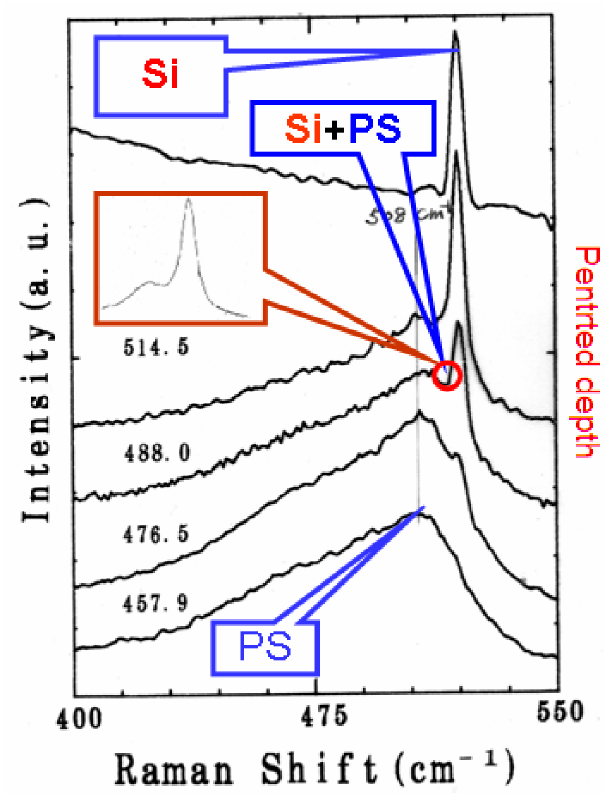
—S.L.Zhang, J. Appl Phys, 69(1995)3399; 62(1993)642

PS Structure

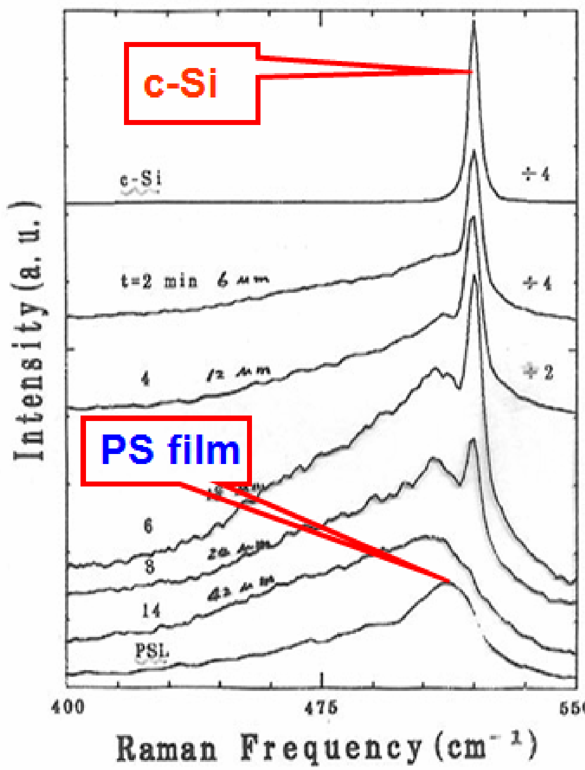


Mix two spectra of PS and Si substrate?

Chang exciting light wavelength



Chang PS film thickness

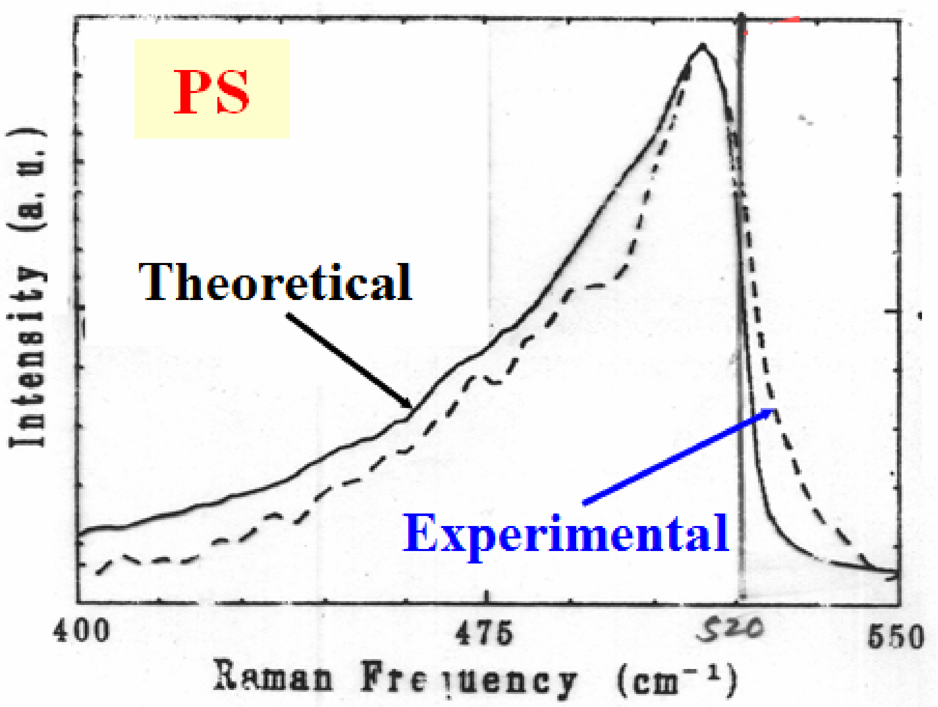


Theoretical fitting of PS Raman spectra

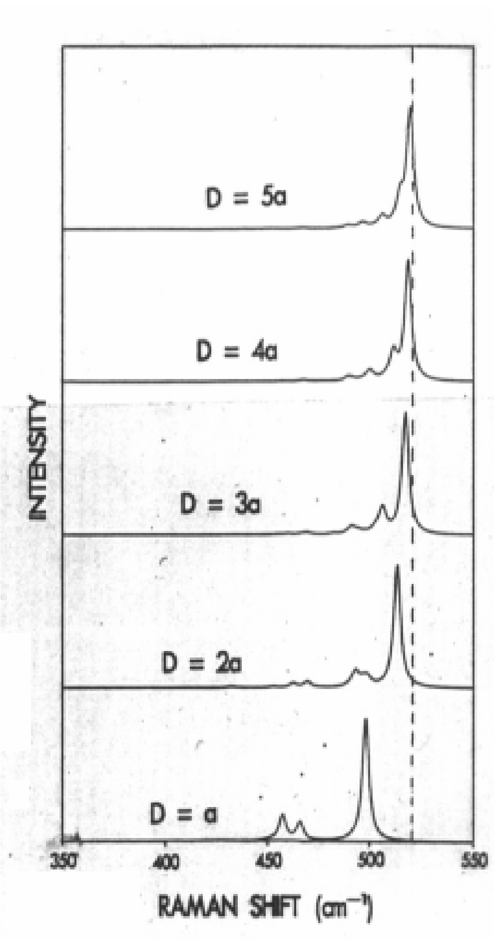
—J. Appl Phys, 69(1995)3399; 62(1993)642

(1) MCM

$$I(\omega) = \int \frac{d^3 q C(0,q)^2}{(\omega - \omega(q))^2 + (\frac{\Gamma_0}{2})^2}$$

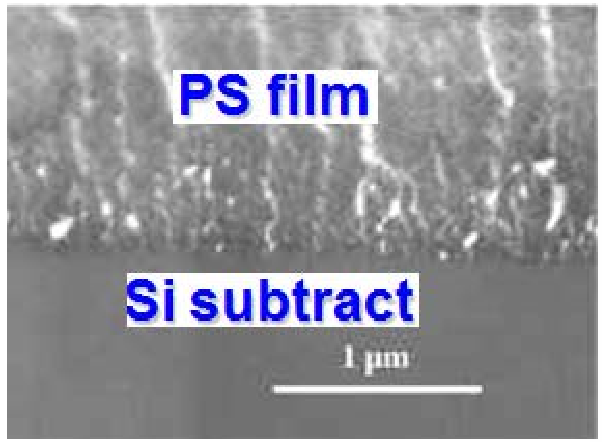


(2) Bond polarizability theory

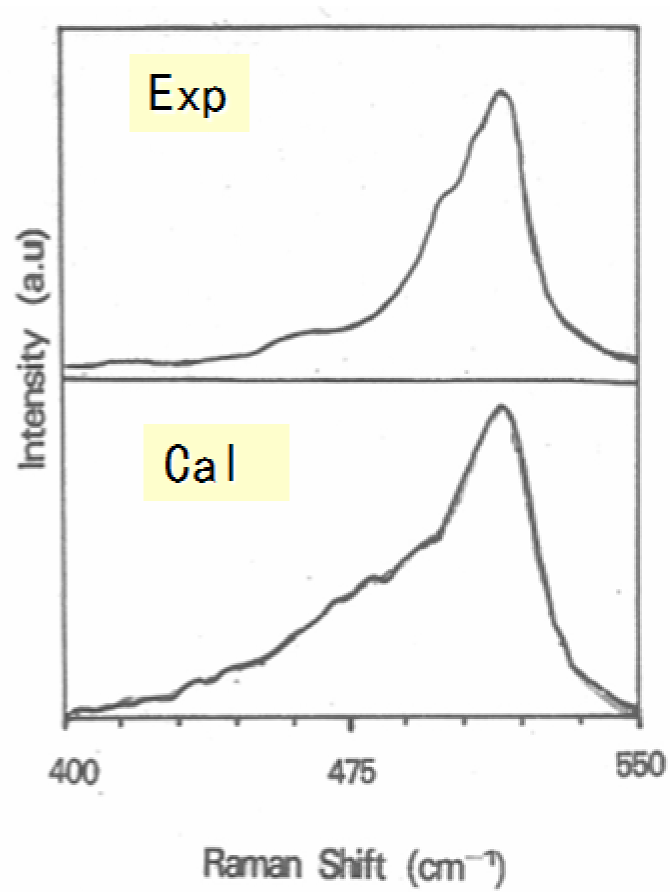


TO – LO split

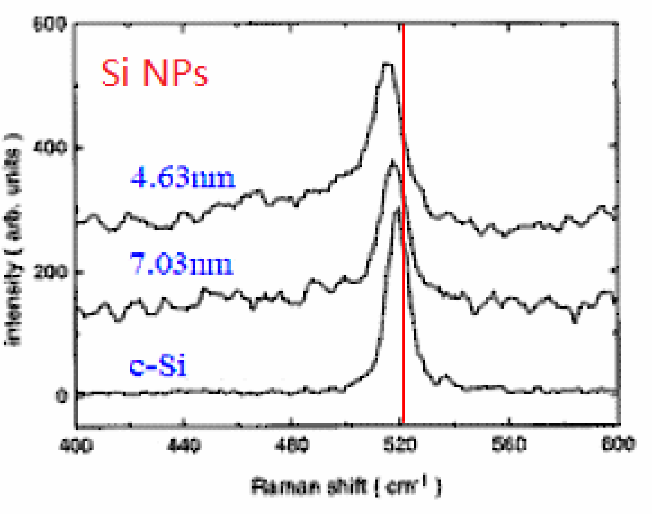
Size-distributed



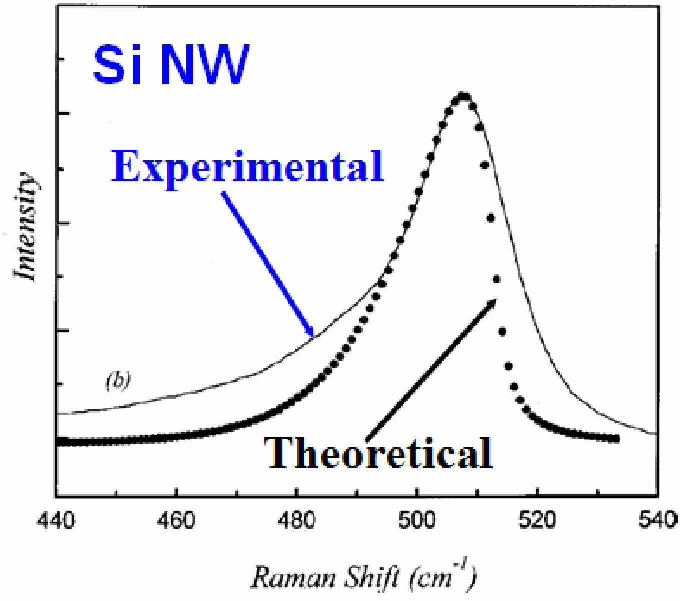
Considered size-distribution

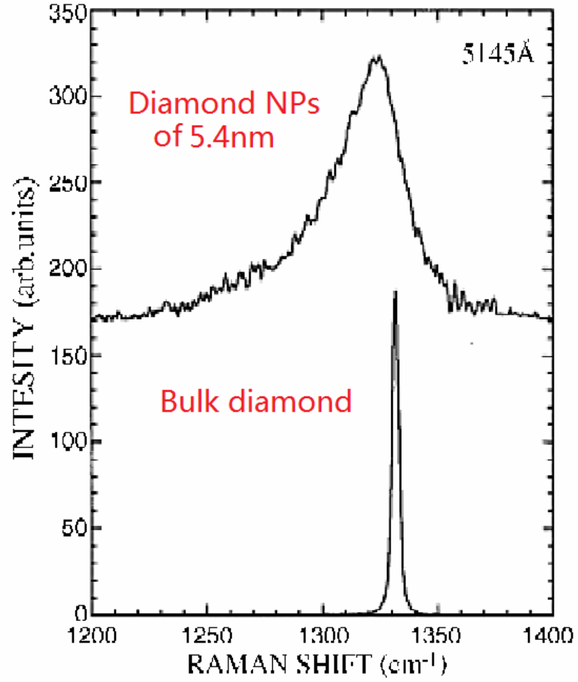


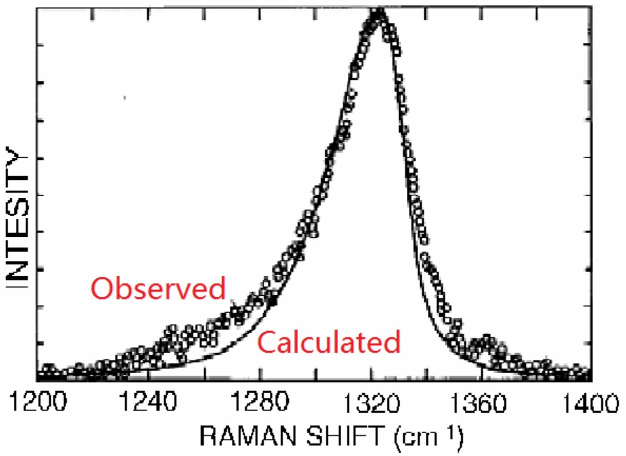
2. Si and diamond NMs



-Ehbrecht et al. PRB,56(1997)6958







- M. Yoshikawa, et al., APL,67, 694(1995)

Brief summary

In past 30 years
Above predication for Raman features
of nanostructured materials
was confirmed.

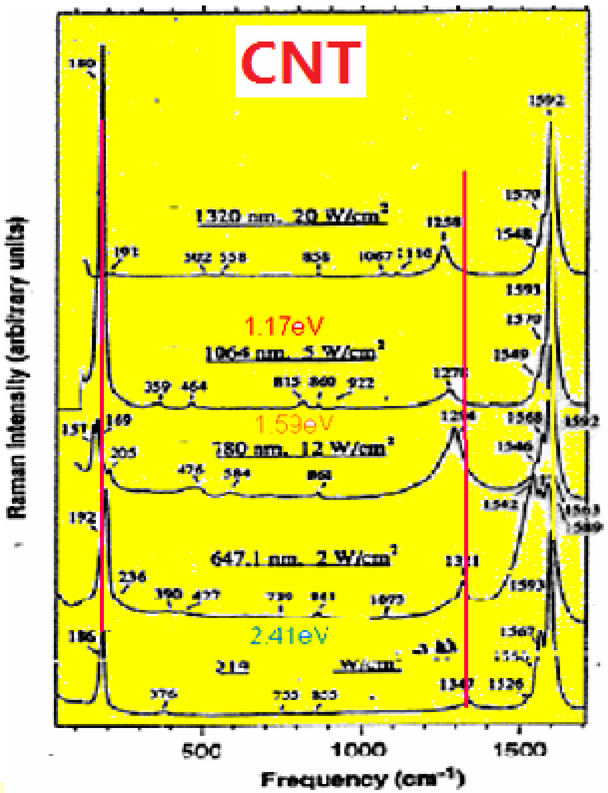
However, many novel phenomena
not fitting above predication
were also observed

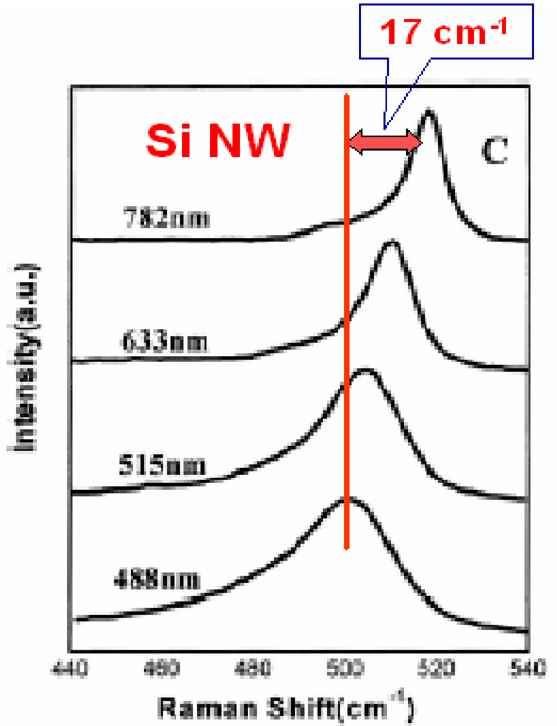
What’s those ? See next chapters !

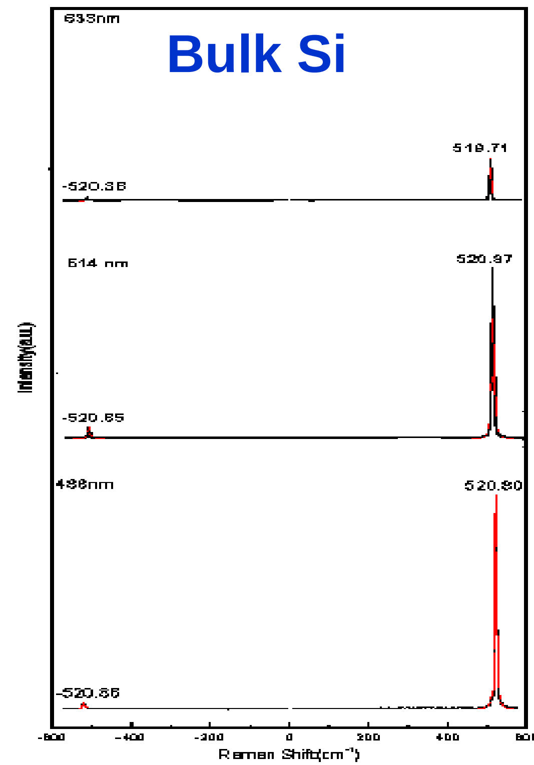
CONTENTS

III-1 Raman Frequency Dependent of Excited Wavelength-Resonant size selection effect (RSSE)

(I) Experimental results







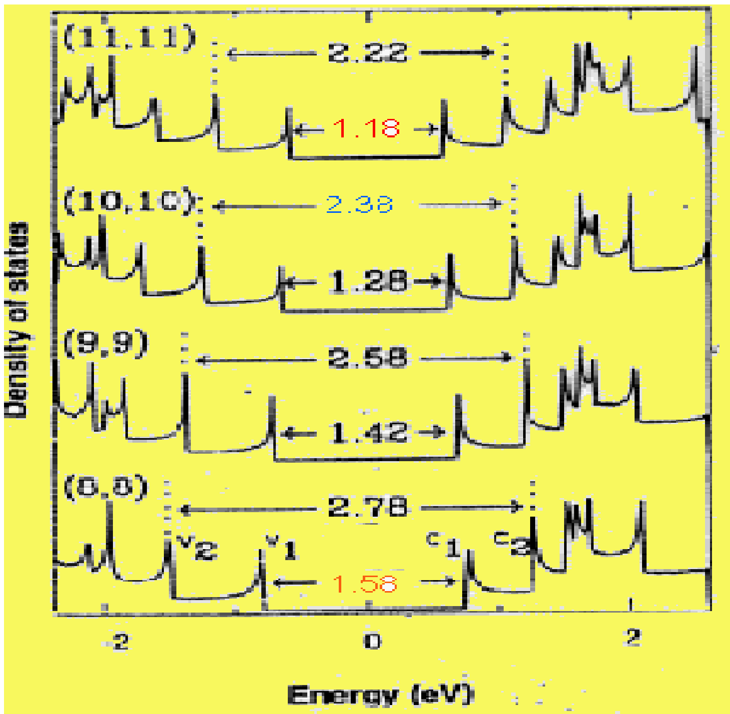
-M. Rao, et al, Science, 275, 187(1997)

Against one of universal features in traditional Raman spectroscopy: frequency independent of incident wavelength, also energy conservation law.

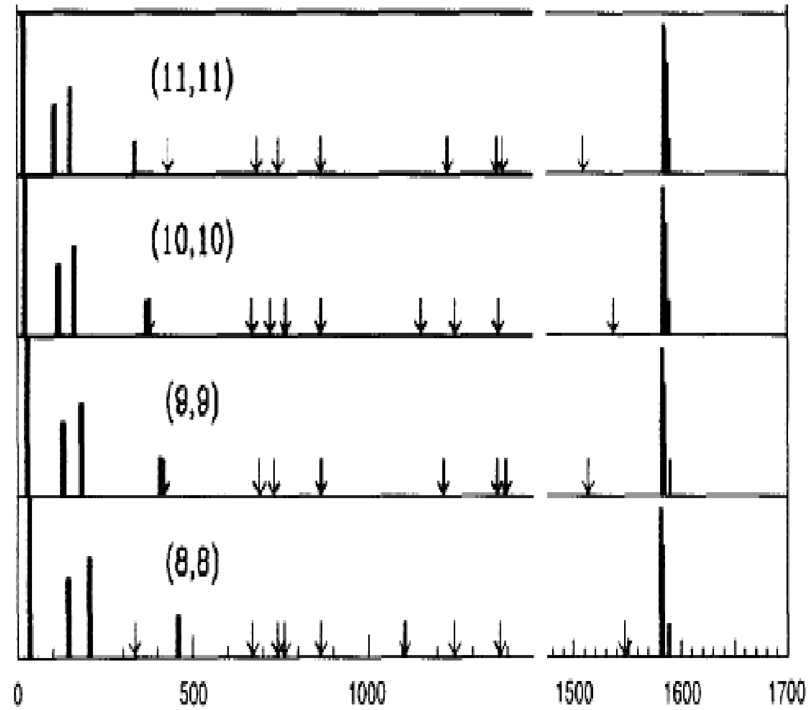
(II) Origin and nature

- Theoretical analyses - M. Rao, et al, Science, 275, 187(1997)

Calculated DOS of electron



Calculated Raman frequency



It is due to

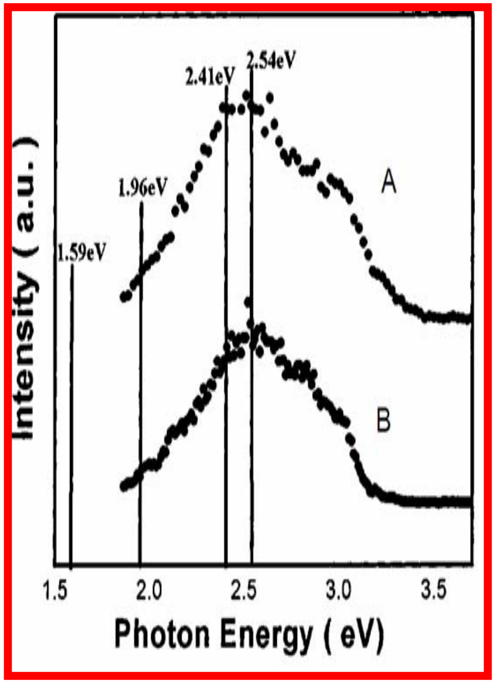
1. Resonant Raman scattering.
2. Size-distributed NMs.

Called as resonant size selection effect (RSSE).

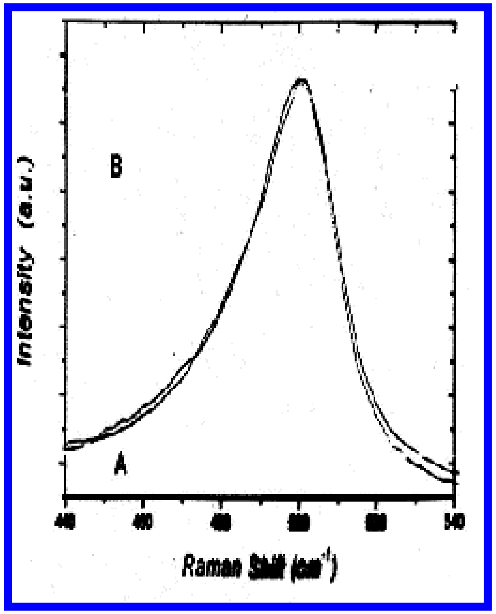
Experiment Confirmation of RSSE.

-Zhang at al, APL, 81, 4446(2002).

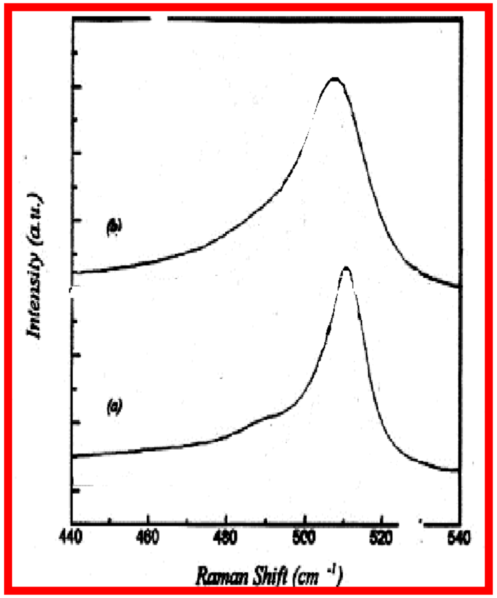
Different size-distributed samples	Resonance with same excited λ	Non- resonance with same excited λ



2.54eV



1.59eV



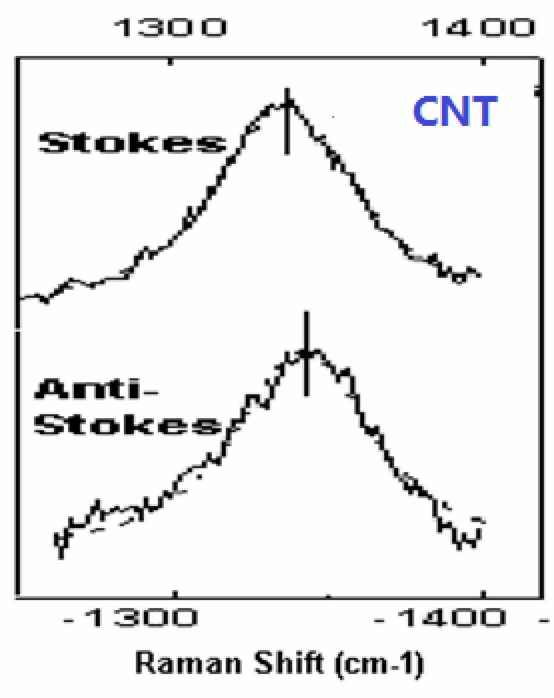
RSSE is still the FSE behavior, No violation for:

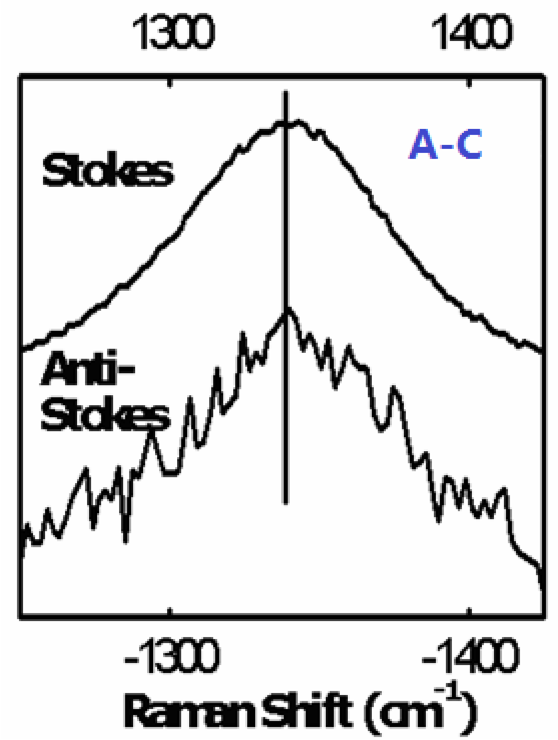
- FSE on frequency;
- Energy conservation law.

III-2 Unequal Absolute Raman Frequency of Anti-Stokes and Stokes Peaks

-Phys Rev B, 66(2002)05431

(I) Experimental results





In CNTs, found $\Delta = |\omega_{AS}| - |\omega_{S}| \neq 0$

Against to universal feature two.

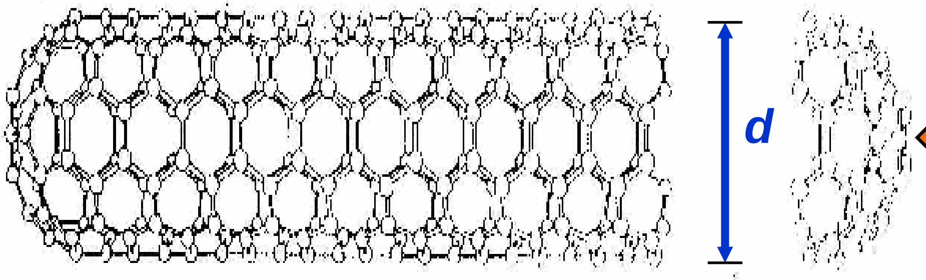
(II) Origin and nature of $\Delta \neq 0$

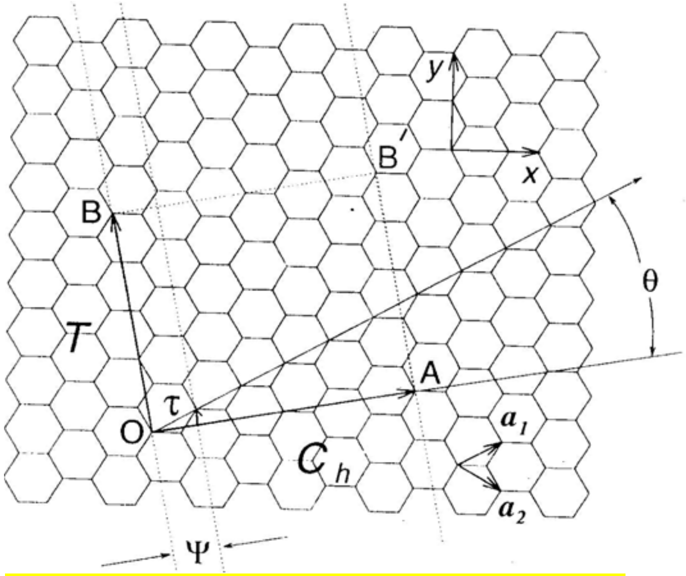
Δ values of CNTs and perfect graphite - HOPG

Sample	MW-CNT	SW-CNT	HOPG	$HOPG_{Au}$
$\lvert\omega_{AS}\rvert - \lvert\omega_{S}\rvert$	+7	+7	/	-7.7
Δ	$\neq 0$	$\neq 0$	$= 0$	$\neq 0$

- $\Delta \neq 0$ **Related with tubular structures !**
- $\Delta \neq 0$ **Related with defected materials !**

Inspect CNT structure:





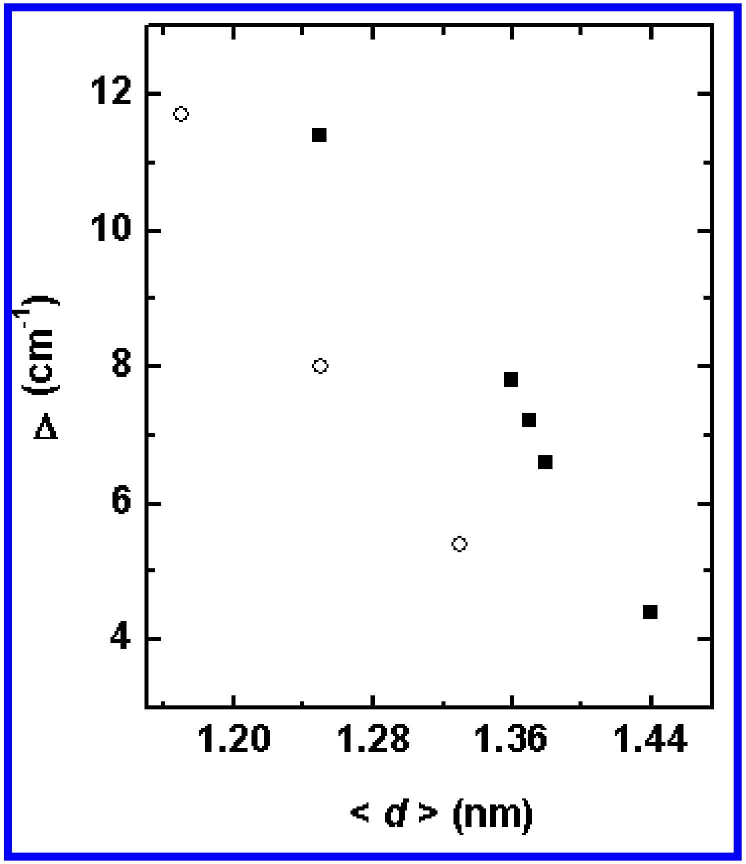
Graphite tube

Graphite sheet- HOPG

1. **CNTs is a defect structure; Defects ~ *d* .**
2. **$\Delta \neq 0$ may from tubular structure itself!**

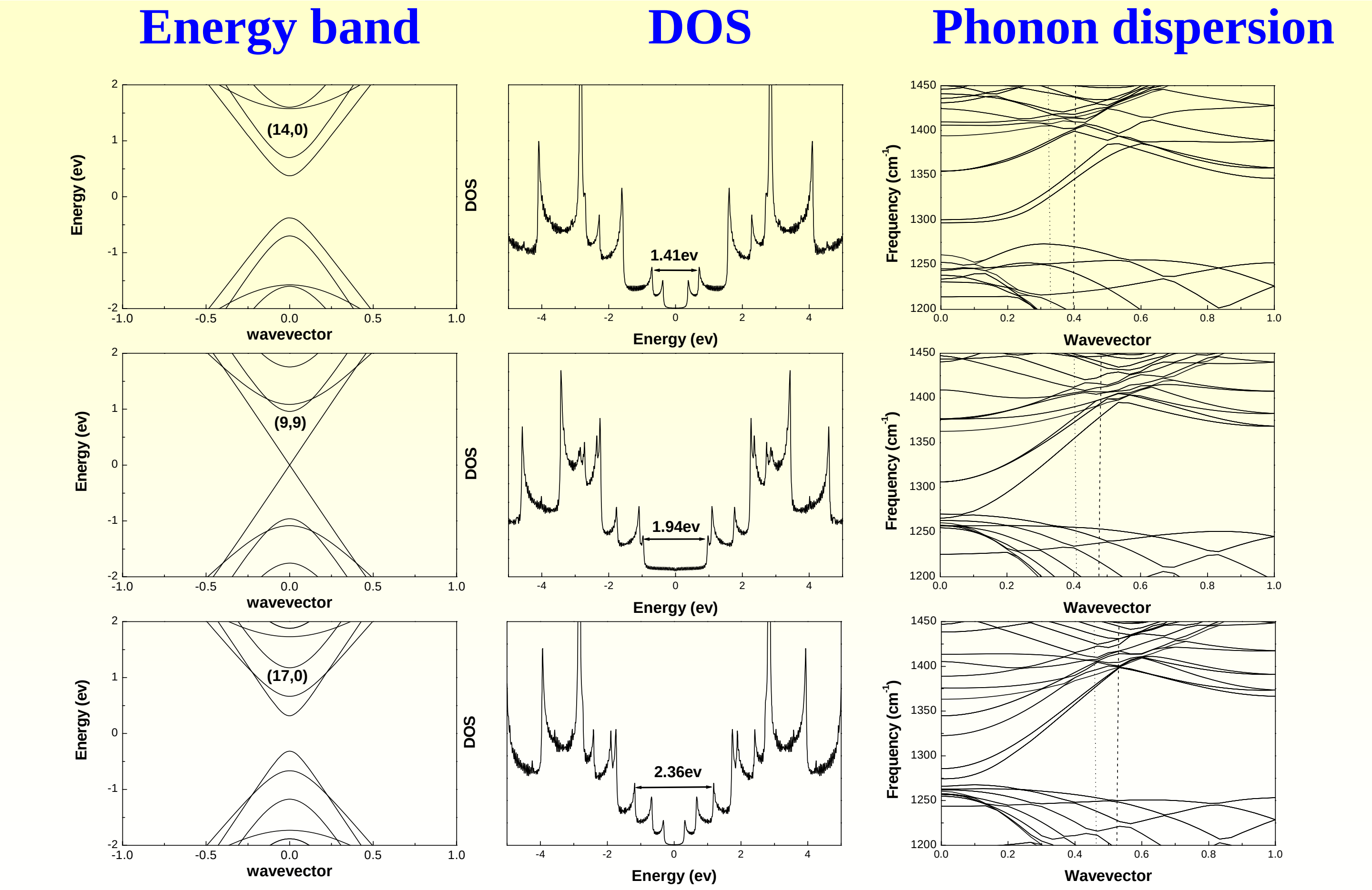
Expectation:
Larger the <d> , Smaller the Δ

- **Experimental confirmation**



Confirmed experimentally

● Theoretical calculation



Found

Double resonance can be happened in CNTs

Calculate Δ by double resonance

$$q = (E_1 - \mathbf{h}\omega_{ph}) / \nu_1 \quad or \quad (E_1 - \mathbf{h}\omega_{ph}) / \nu_2 \qquad (1)$$

$$\omega_{ph}(q) = f(q) \qquad (2)$$

Comparison between observation and calculation

Tube		ω_S (cm^{-1})	ω_{AS} (cm^{-1})	Error(%)	Δ (cm^{-1})
(17,0)	Cal.	1388	-1349	4	+6
	Obs	*1337*	*-1342*		*+5*
(9, 9)	Cal	1399	-1408	6	+9
	Obs	*1314*	*-1322*		*+8*

Confirmed theoretically

Brief summary

- The RSSE is an embody of FSE, i.e.,:

$$RSSE \approx FSE$$

- The $|\omega_{AS}| - |\omega_S| \neq 0$ explores a important nature of nanostructures.

- Above two 'abnormal' are originated from the defect property of sample: intrinsic and artificial defects, respectively.
- Therefore It is should be expected from bulk/traditional Raman spectroscopy and the principle of Raman scattering and two basic laws are still hold in nanostructures.

CONTENTS

IV-1 Abnormal Feature of Raman Frequency

APPLIED PHYSICS LETTERS VOLUME 81, NUMBER 23 2 DECEMBER 2002

Variation of Raman feature on excitation wavelength in silicon nanowires

Shu-Lin Zhang,[a)] Wei Ding, Yan Yan, Jiang Qu, Bibo Li, Le-yu Li, Kwok To Yue,

e.g., SiC nanorods,[9] consisting of smaller grains, we expect that a similar Raman scattering should be present in such kinds of systems.

It is reasonable, but not observed!

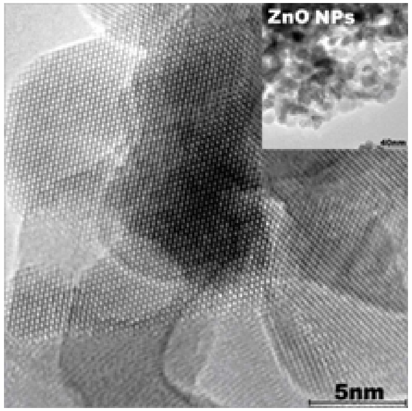
A. Frequency Feature

A-1. No RSSE

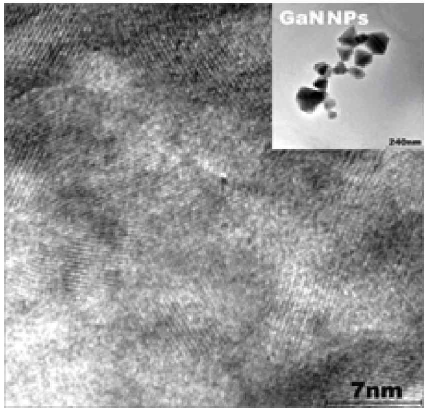
(I) Sample

HRTEM

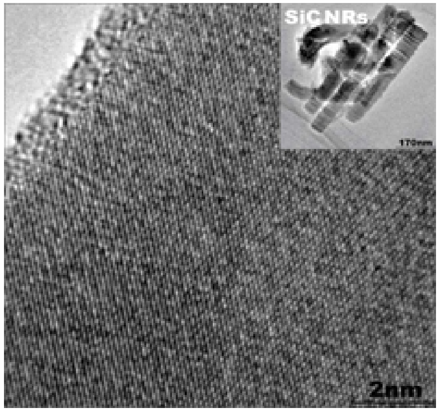
ZnO NPs



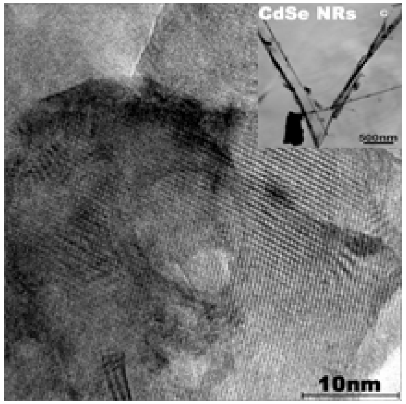
GaN NPs



SiC NRs



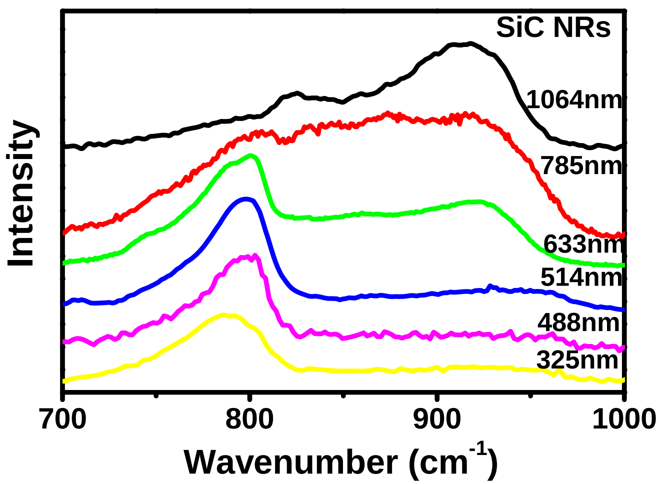
CdSe NRs

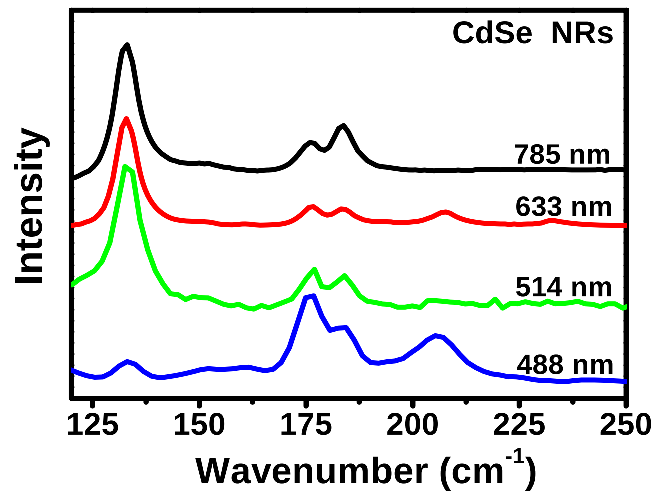


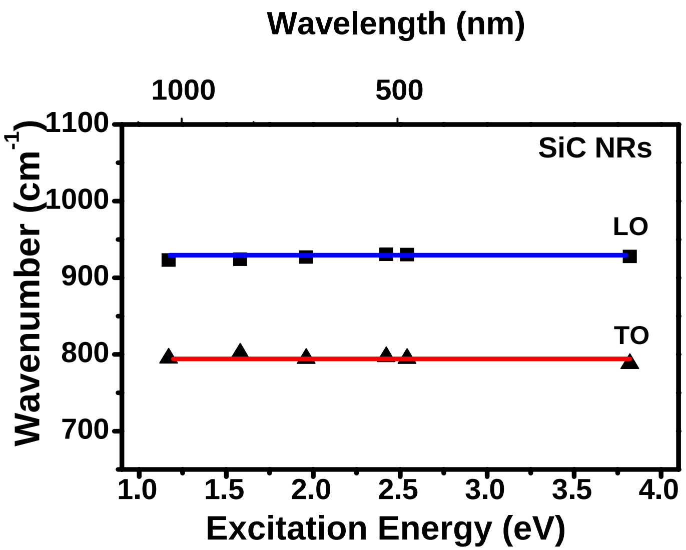
The samples are consisted of
a collection of crystalline grain with different sizes

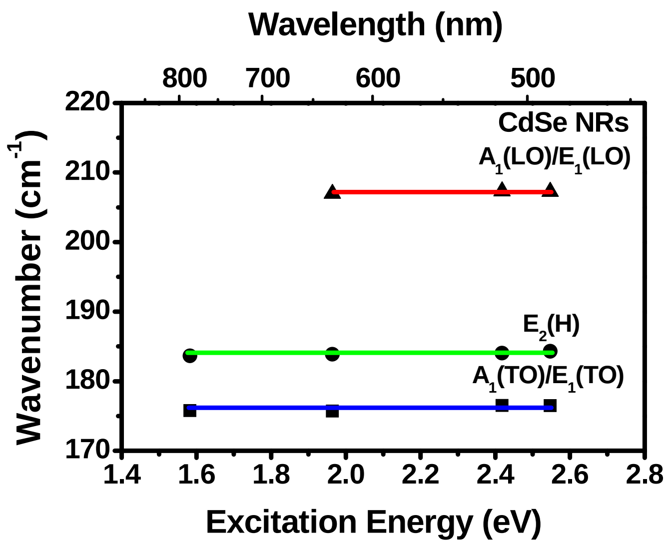
Sample	ZnO NPs	GaN NPs	SiC NRs	CdSe NRs
L_{Averge}	7nm	4nm	10nm	4nm

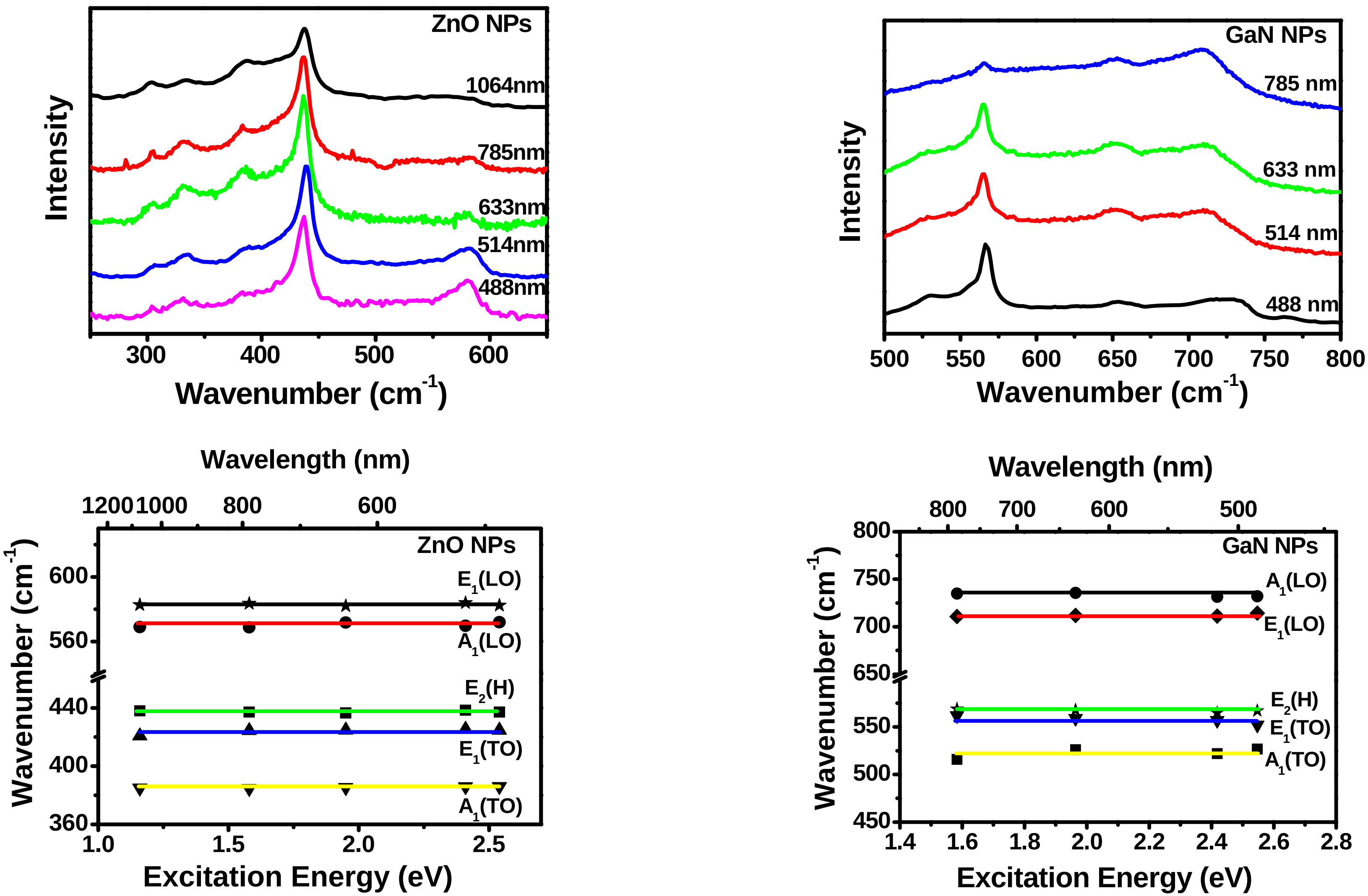
(II) Observed result











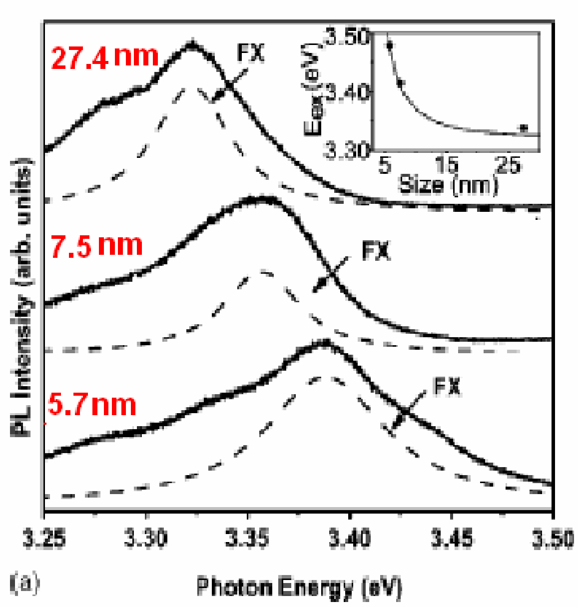
RSSE is not found!

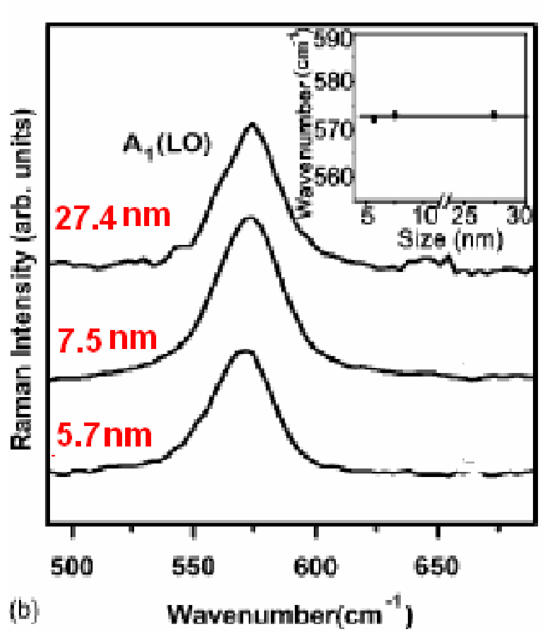
(III) Origin and nature

Suggested Origin 1 : Sample sizes not too small to induce FSE

Test : by PL /Raman spectra for same group ZnO NPs

- Z. D. Fu, et al, Appl Phys Lett., **90**, 263113(2007).



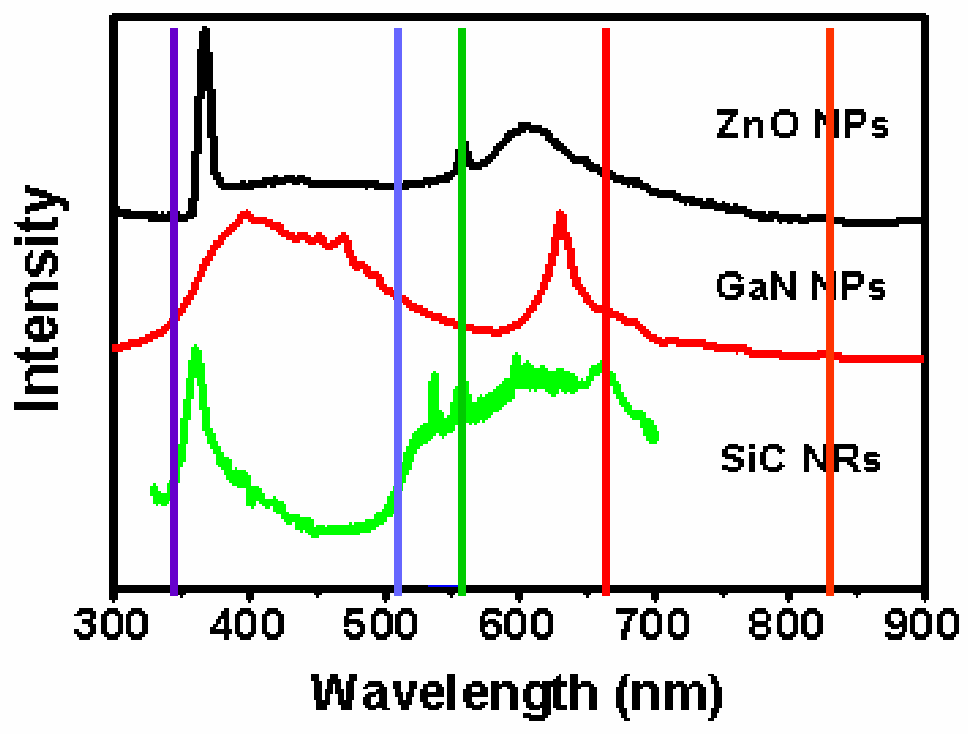


Size (nm)		5.7	7.5	27.4
FX energy (eV)	EXP	3.388	3.355	3.313
	THEO	3.389	3.357	3.319

FSE? PL: Yes! Raman: No!

Suggested Origin 2 : **Not in resonance**

-S.L.Zhang et al, APL, **89**, 063112(2006):



Electron transition energy cover a broad wavelength region.

is

resonant Raman spectra

Meet conditions: 1. Size-distributed NMs;

2. Resonant Raman scattering.

Should expect the RSSE. But no!

Suggested Origin 3 : **Resonance with impurities/defects**

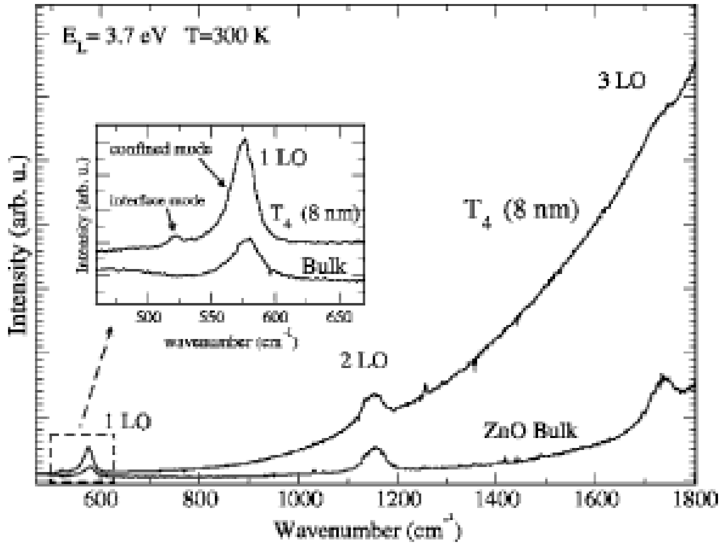
As the condition of such kind of resonance:
The energy of exciting light must be below *Eg*.

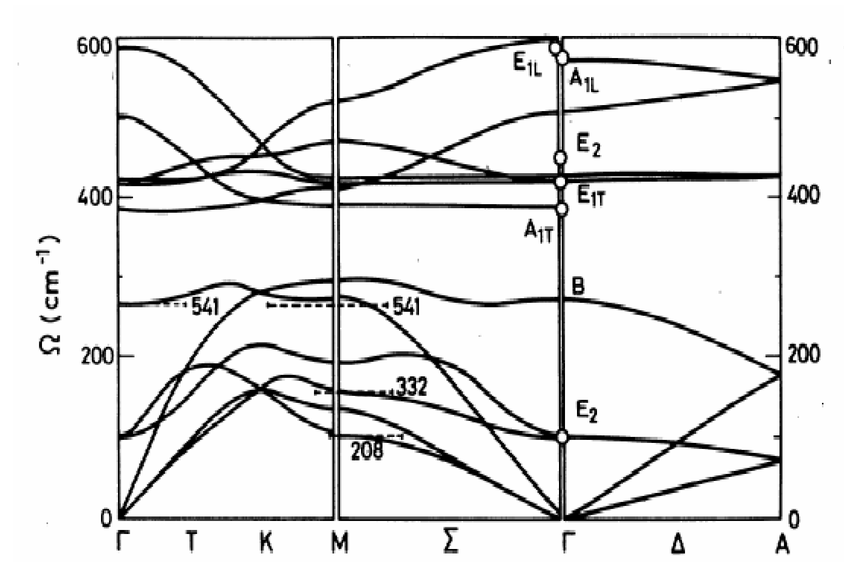
Check:

Sample	Eg (eV)	E of laser (nm/eV)					
		1054 /1.18	785 /1.58	633 /1.96	514 /2.41	488 /2.54	325 /3.82
ZnO	3.2	√	√	√	√	√	×
GaN	3.44	√	√	√	√	√	×
CdSe	1.8	√	√	×	×	×	×
SiC	2.4	√	√	√	×	×	×

×: **High than Eg. Not all are in gap!**

Suggested origin 4: **No much or not ispersive**





-F. Demangeot *et al.*, Appl. Phys. Lett. 88 (2006)071921.

size. This seems however understandable looking at the optical phonon dispersion curves which are very flat near the Brillouin zone center. However, further work needs to be

See the deviated values

at 1/4 away from the center of Brillouin zone

Phonon		ZnO		GaN	CdSe	3C-SiC
E_{1L}	LO	8.7	/	0	1.3	33.3
A_{1T}		1.3	/			
A_{1L}		/	1.3	2.4	1.3	
E_2(H)		/	0	1.2	0.3	
E_{1T}		/	0			
E_2(L)	TO	/	2.5	2.4	0.3	8.3
		$\Gamma-\Sigma$	$\Gamma-A$			

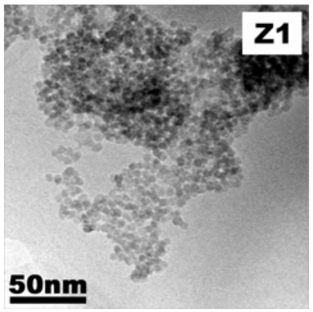
Red numbers: Much dispersive values.

Not all are little dispersive

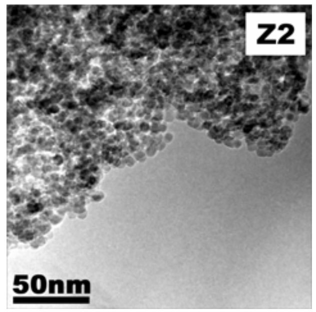
A-2. No FSE

- Appl Phys Lett, **89**, 243108 (2006,

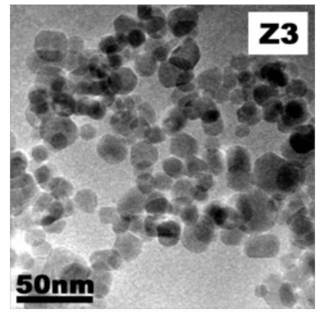
(I) Sample: Nearly Uniformed **ZnO NPs** samples



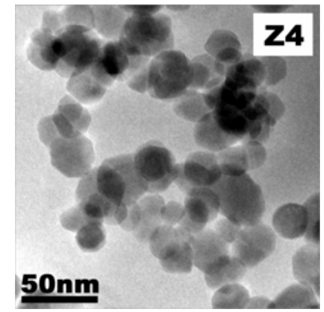
5.7±0.6nm



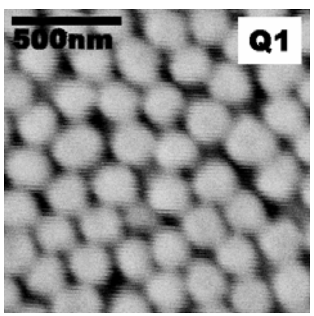
7.5±0.9nm



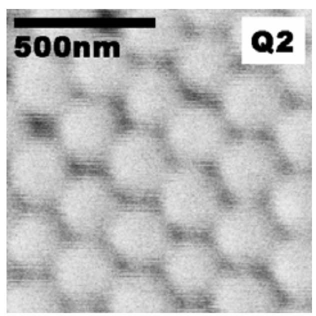
18.2±1.7nm



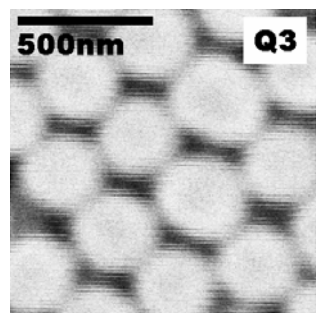
27.4±1.8nm



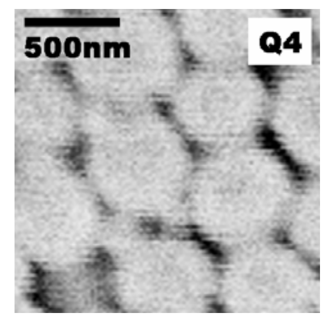
170±10 nm



250±10nm



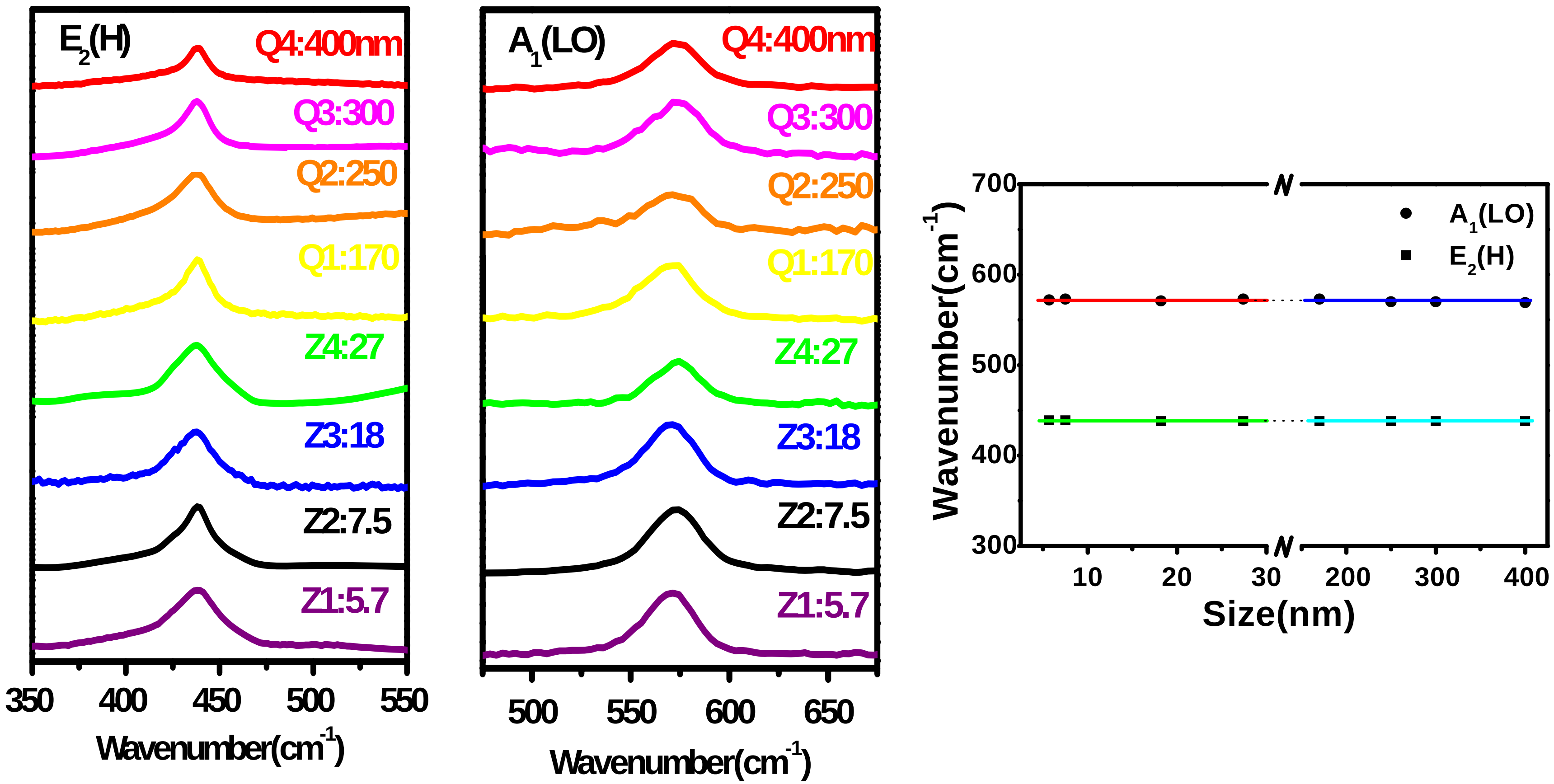
300±9nm



400±12nm

Size deviation ⩽ 10% ~ Nearly Uniformed!

(II) Single-phonon Raman spectra of E_2(H) and A_1(LO) modes

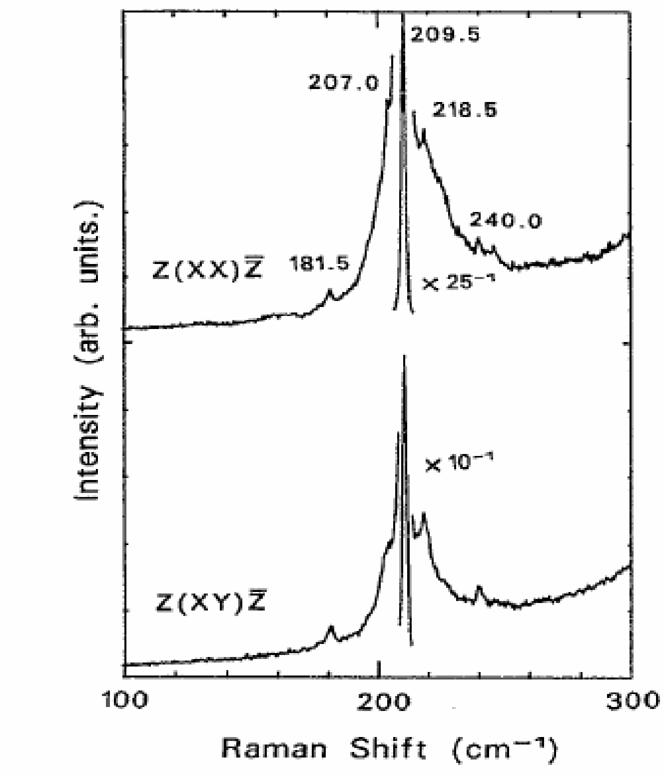


The Raman frequency not change with sample sizes

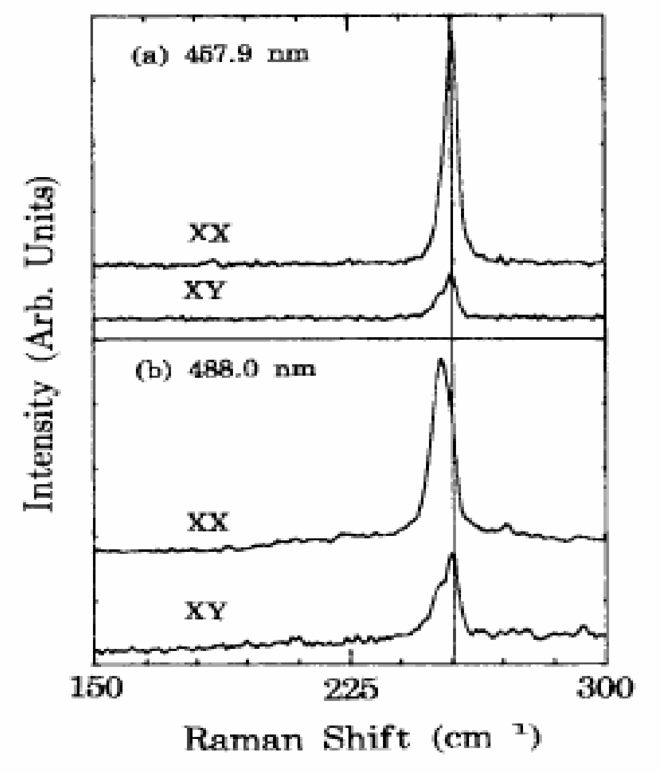
B. Selection Rule

B-1 LO modes

- (CdTe)2(ZnTe)4/ZnTe MQWs
  – PRB,47 (1993)12937



- $[(CdSe)_1(ZnSe)_3]_1/(ZnSe)_{130}$ MQWs
  -Phys Lett A, 186(1994)433

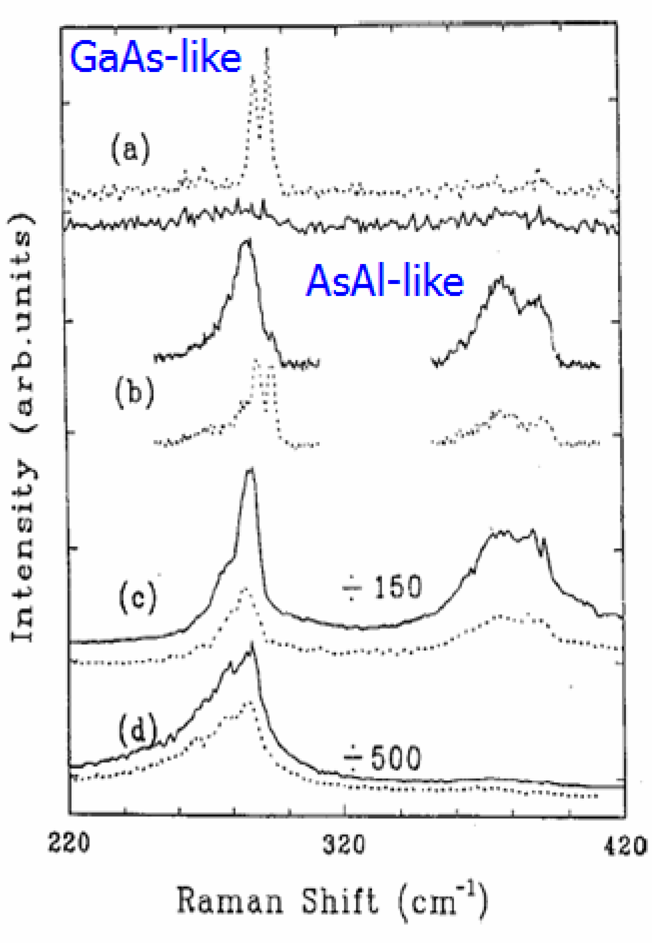


Selection rule of LO		
Experimental	XY	XX
Theoretical	XY	/

B-2 Interface (IF) Modes of $(GaAs)_4/(AsAl)_2$ SLs

(I) Experimental results

-JAP. 76(2000)2053



	GaAs-like				AlAs-like			
	Low F		High F		Low F		High F	
	XY	XX	XY	XX	XY	XX	XY	XX
Theo$_{Huang}$	O			O		O	O	
Exp	O	O	O	O	O	O	O	O

The result is not matching the selection rule by Huang and Zhu.

The model is incorrect?

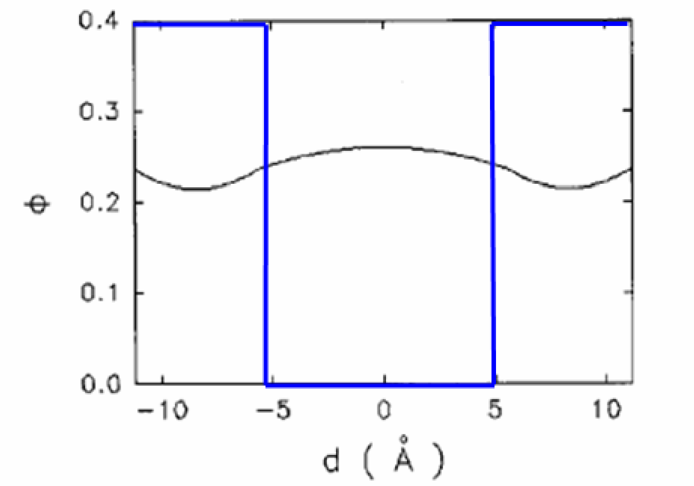
(II) Origin

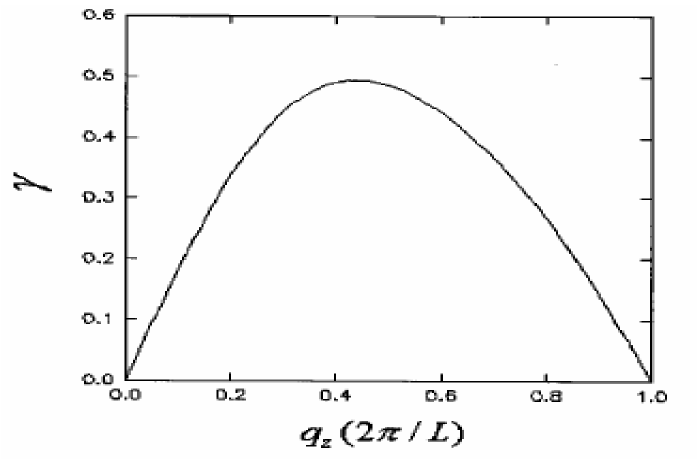
Huang-Zhu model has two precondition:

1. Electronic wave-function Φ is confined in QWs.
2. Parity γ is definite.

The origin may be the sample not match the preconditions.

Calculated Φ and γ of the sample





- Electron is not confined and retransmitted (bulk-like);
- Parity is not definite.

The suggested origin is conformed and also give the correctness of H-Z model a new conformation.

C. Spectral ensemble Features

C-1 Single Phonon

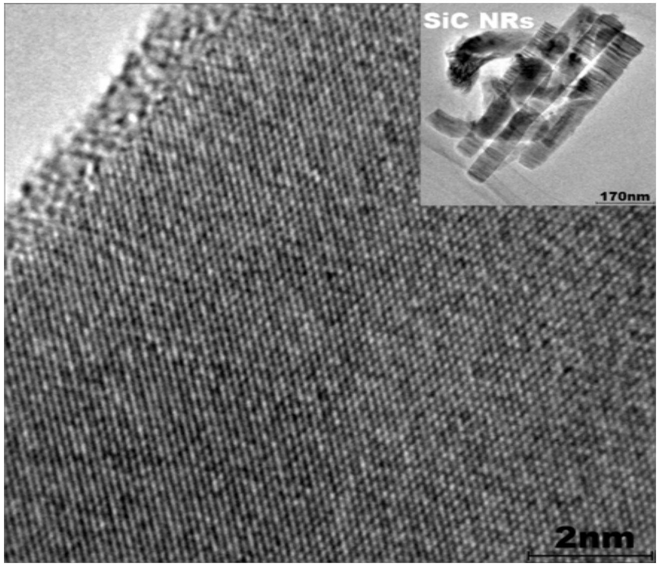
- Solid State Commu. 111(1999) 47.

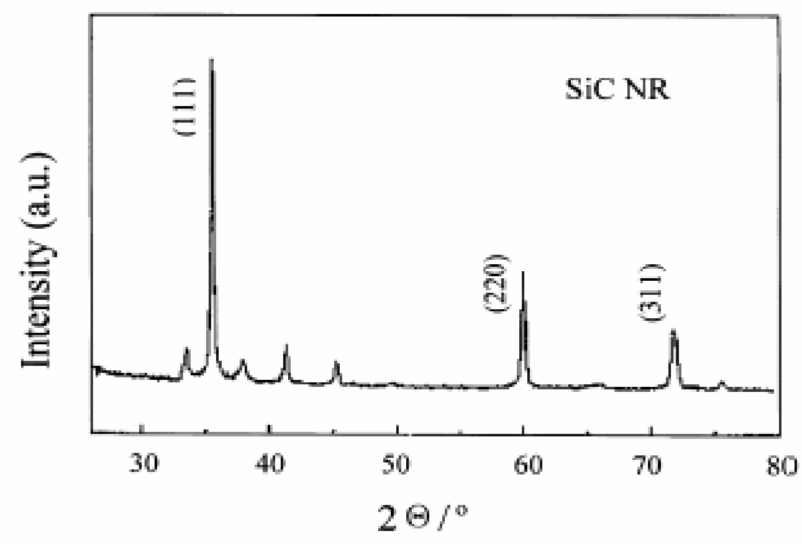
(I) Sample

Crystalline SiC Nano-roads (NRs)

Morphology /TEM

Structure/X-ray diffraction



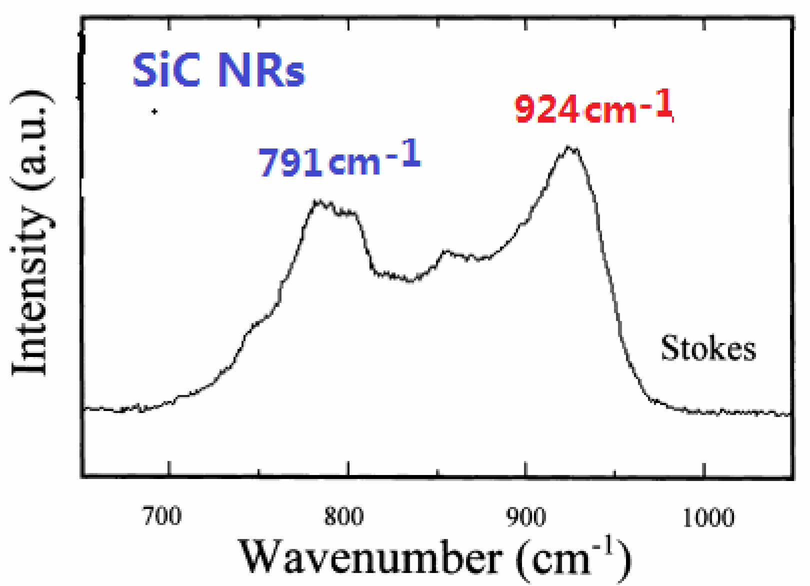


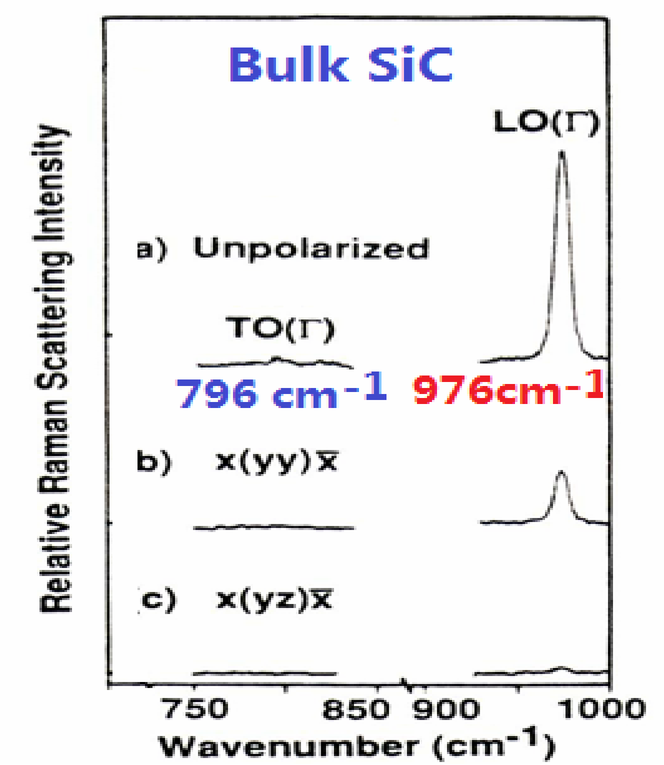
Diameters range from 3-30 nm

Zincblende nano-crystal (β-SiC).

(II) Raman spectrum

1. Observed result





— Z. C. Feng et al, JAP, 64(1988)3176.

Should be identified !

2. Identification by theoretical result

In nano-semiconductors, crystalline and amorphous Raman spectra can be fitted, respectively, by

Micro-crystal model (MCM)

$$I(\omega) = \int \frac{d^3 q C(0,q)^2}{(\omega - \omega(q))^2 + (\frac{\Gamma_0}{2})^2}$$

Amorphous-crystal model (ACM)

$$\boldsymbol{I_{\alpha\beta,\gamma\delta}(\omega) = \Sigma_b C_{b\ \alpha\beta,\gamma\delta} [(1+n(\omega))/\omega] D_b(\omega)}$$

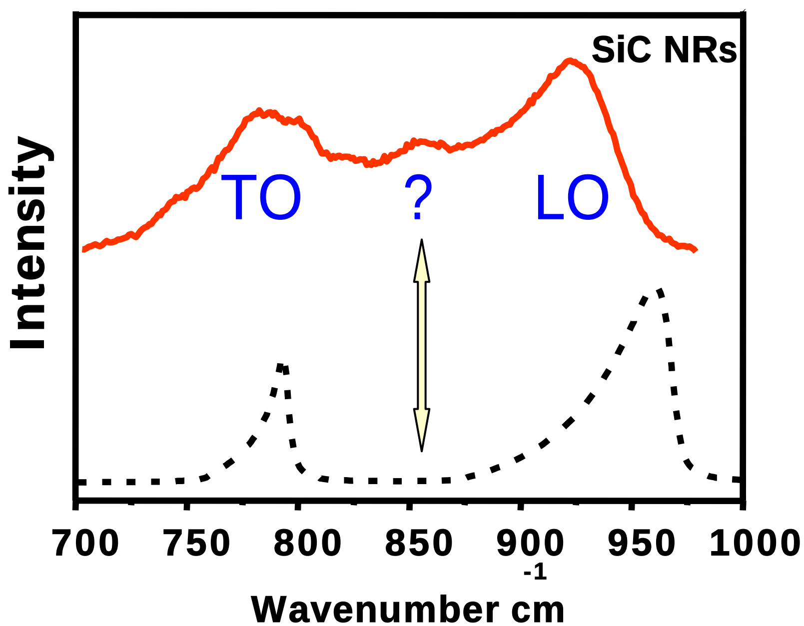
MCM and ACM fitted spectra are recognized as crystalline and amorphous, respectively.

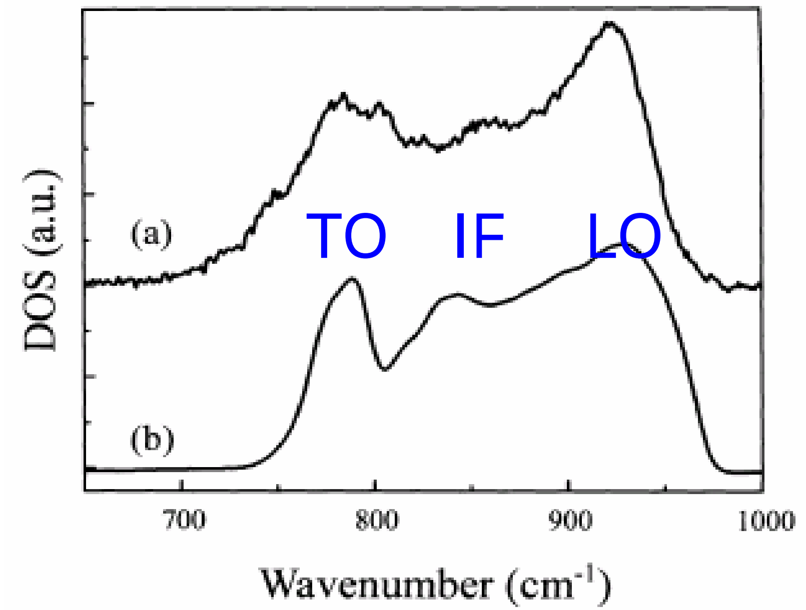
MCM

$$I(\omega) = \int \frac{d^3 q C(0,q)^2}{(\omega - \omega(q))^2 + (\frac{\Gamma_0}{2})^2}$$

ACM

$$I_{\alpha\beta,,\gamma\delta}(\omega) = \Sigma_b C_b^{\alpha\beta,,\gamma\delta}[(1+n(\omega))/\omega]\underline{D_b(\omega)}$$





Can't fit by MCM:

LO mode: $\omega_{Cal} - \omega_{Exp} = 31$ cm^{-1};
No Peak at middle in calculated one.

Good fitting By ACM:
Raman spectrum of SiC
crystalline NRs
possesses
amorphous feature

C-2 multiple phonons

-Phys. Rev.，B52，1477(1995).

Features of MP in traditional Raman spectroscopy:

- Frequency

$$\omega_k = k\omega_1 \sim \omega_k / k = \omega_1$$

- Linewidth

$$\Delta\omega_k = k\Delta\omega_1 \sim \Delta\omega_k / k = \Delta\omega_1$$

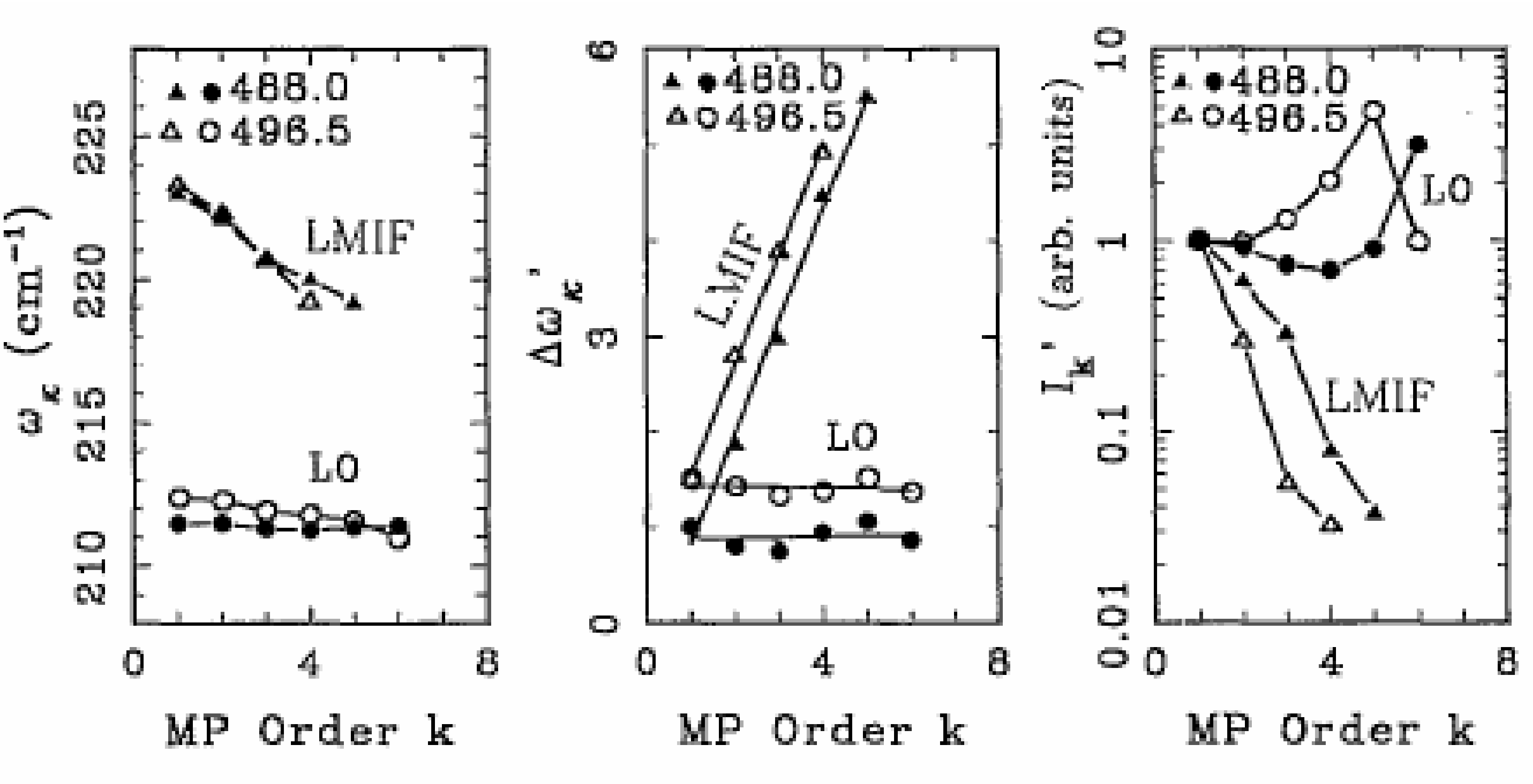
- Intensity

$$I_k < I_{k-1}$$

A. Superlattices

1. Sample: $(CdSe)_4/(ZnTe)_4$ SLs

2. Observed results of micro-IF MP modes



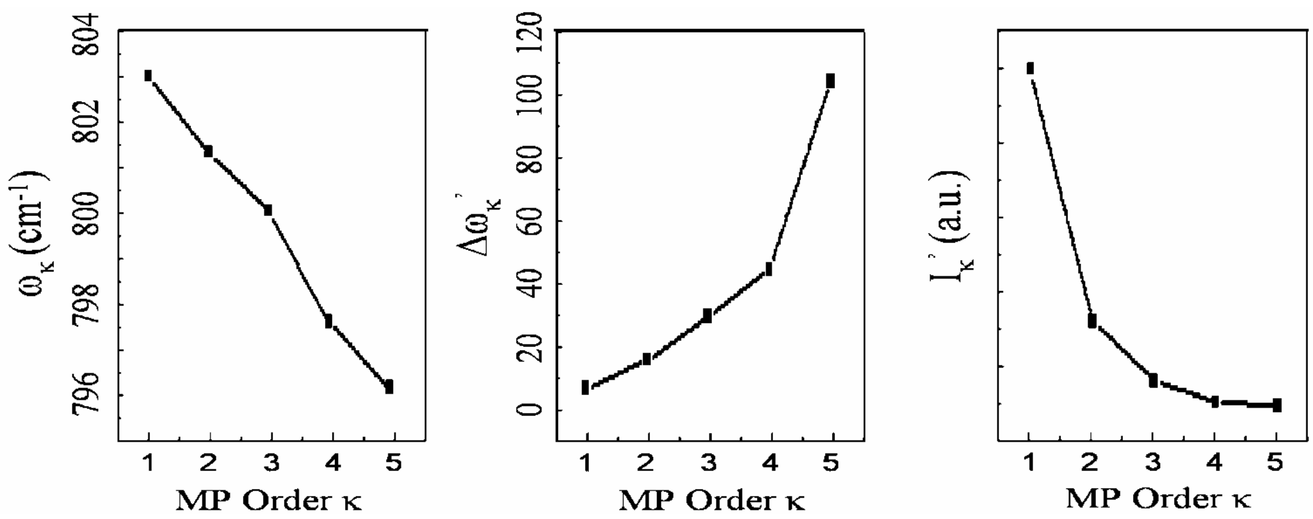
2. Interpretation

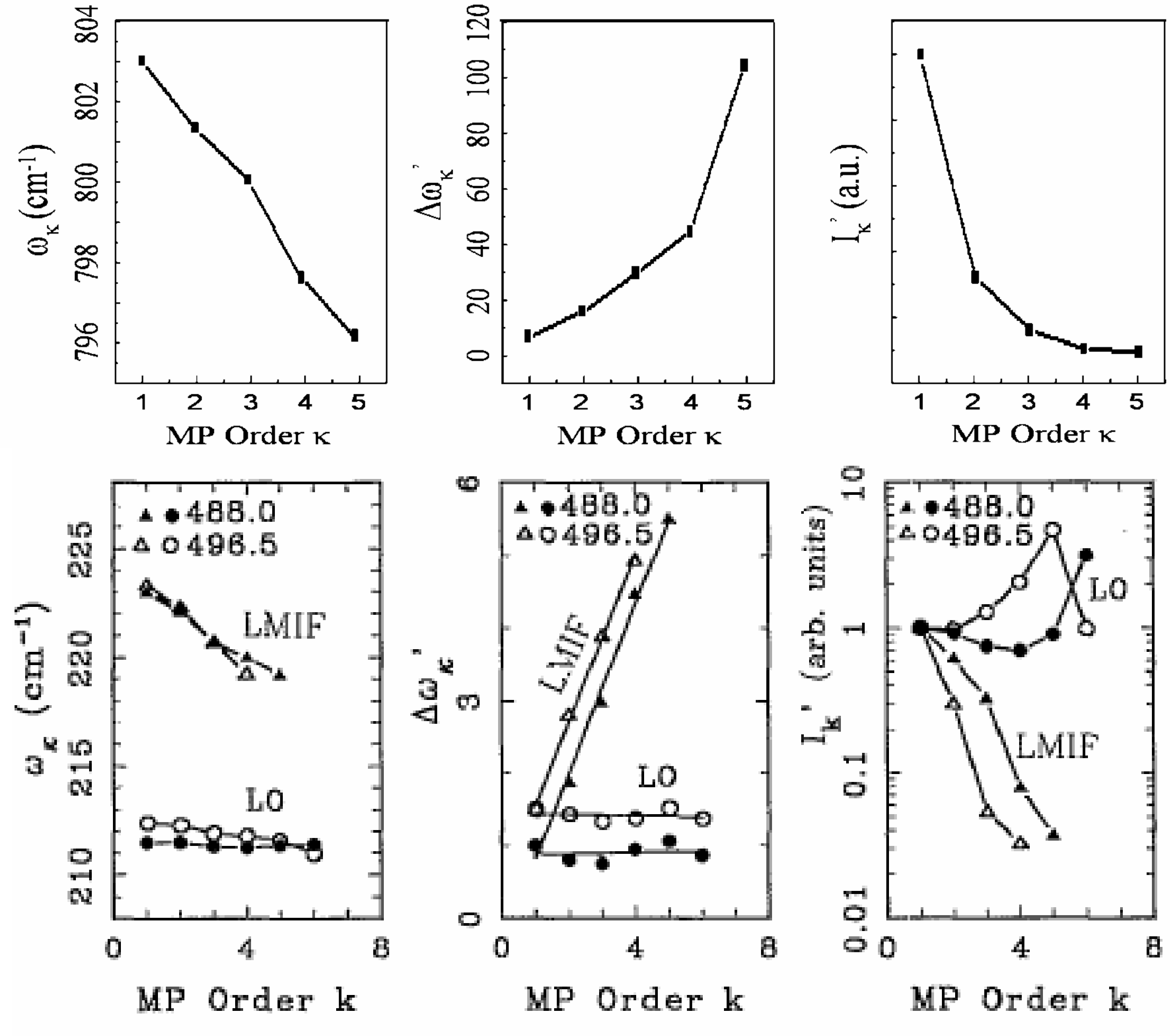
We note a paper:

PHYSICAL REVIEW B VOLUME 15, NUMBER 2 15 JANUARY 1977

Multiple-order Raman scattering in MnO_4^{2-}-doped CsI

T. P. Martin and S. Onari†
Max-Planck-Institut für Festkörperforschung, Stuttgart, Federal Republic of Germany



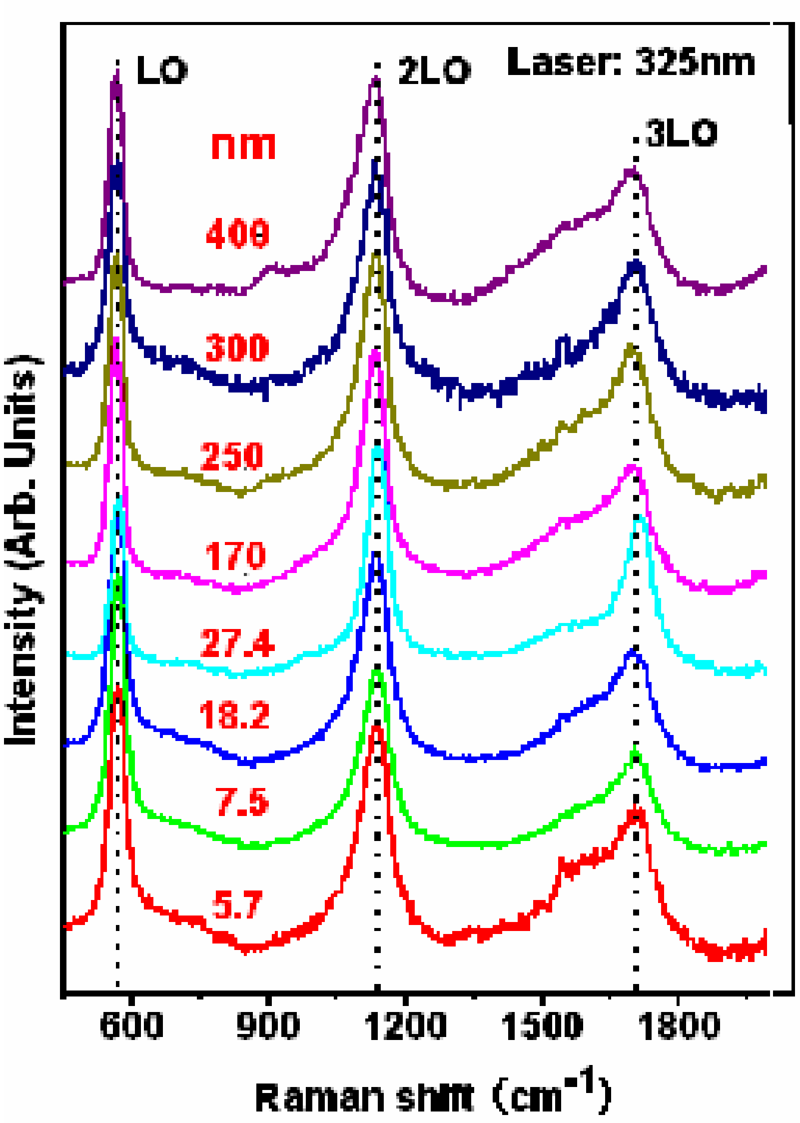


❑ **Interface in SLs is a defect-like;**

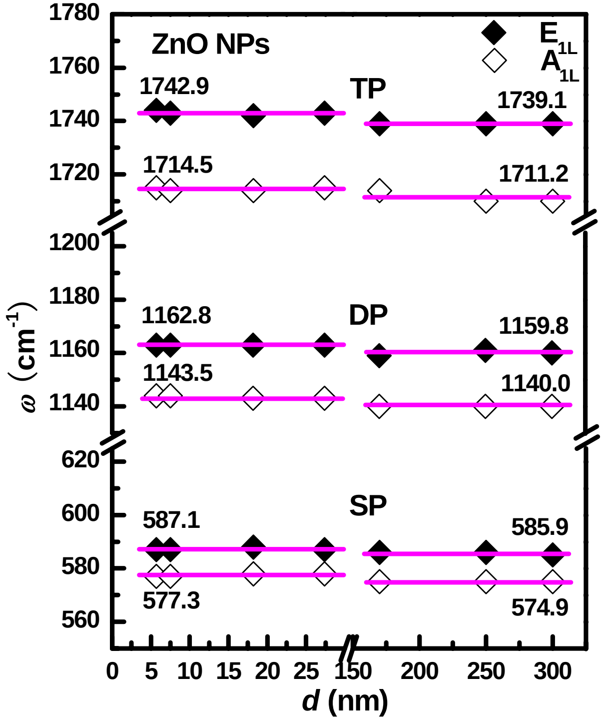
❑ **SLs is a defect-likestructure**

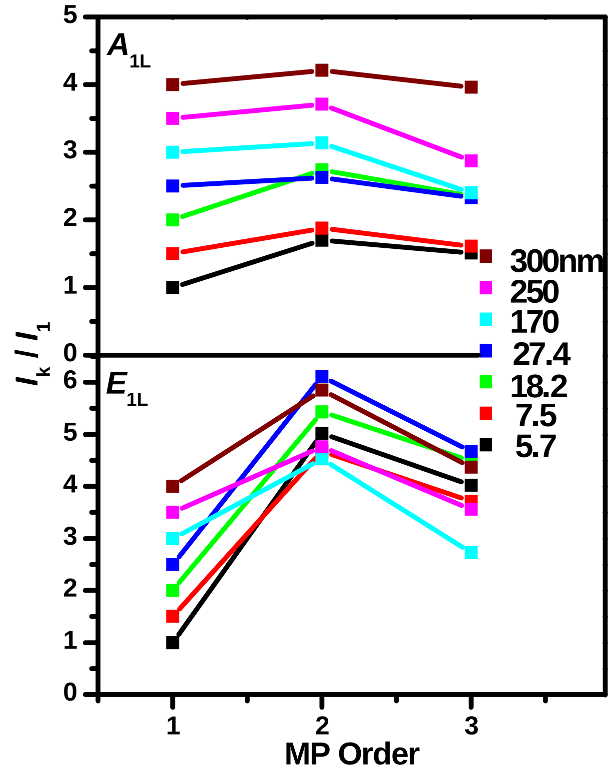
B. Nano-matrerials

1. MP Raman spectra of ZnO NPs



Dependence of MP Raman frequency and intensity on sample sizes





Observed

$\omega_k = k\omega_1$

$I_3 < I_2 > I_1$

The predication of MP Raman features:

- The Raman frequency of higher order *k* phonons, ω_k, should be integral times of the frequency of first order phonon ω_1:

$$\omega_k = k\omega_1.$$

- The Fröhlich coupling constant in nano-crystals is smaller than one for nano-crystals and the intensity of MP relation should be expected

$$I_{R,1} < I_{R,2} > I_{R,3}$$

However, they violate the traditional view of MP Raman spectra:

$$\omega_k \neq k\omega_1$$

$$I_{R,1} > I_{R,2} > I_{R,3}$$

Brief summary

- In the features of frequency, selection rule and ensemble spectra, we have found some abnormal features that violates the features and understanding of present nanostructure Raman spectroscopy.

- In the interpretation of above abnormal phenomena, abnormal frequency and amorphous features still not get a reasonable interpretation, although the others has found to be ascribed the defect-like and super-thin structures of samples.

In the next part we will concentrate to discuss their origin and nature

IV-4 The origin of above novel features

Note:

- No RRSE and NFSE mentioned above is limited in ZnO NPs.
- The suggestions are all based on the Raman spectroscopy of present nanostructures and theory.

To obtain a reasonable origin and nature, it is needed having;

- A much more experimental facts to obtained regular pattern of NRSSE and NFSE.
- Giving up traditional idea to found interpretaion.

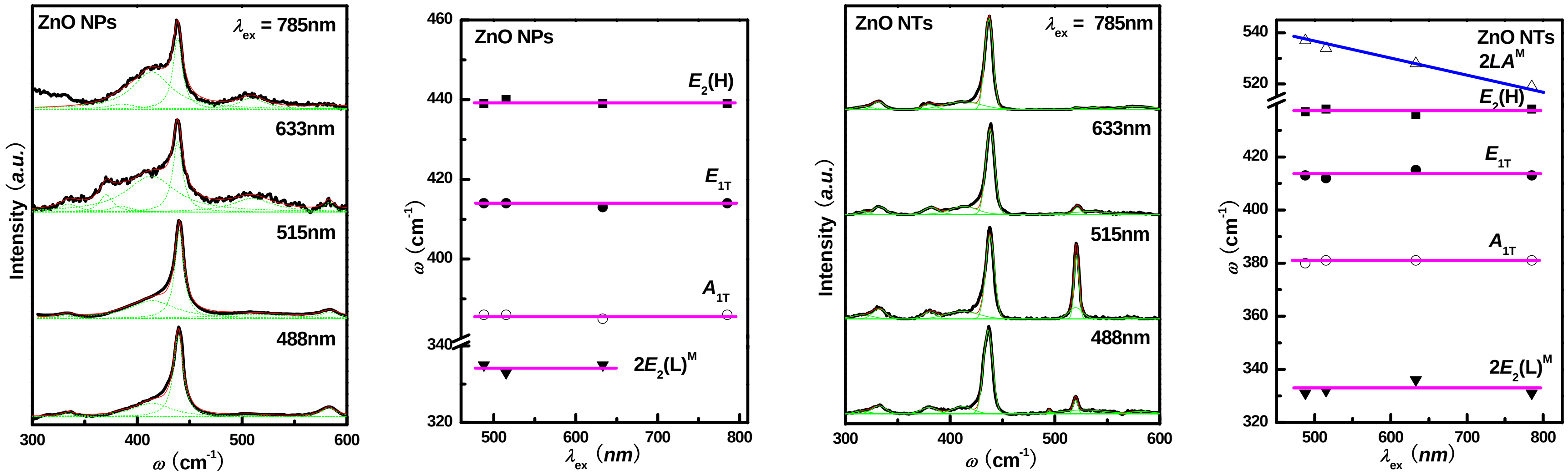
(I) Regular paten of RSSE and FSE

1. Observed results

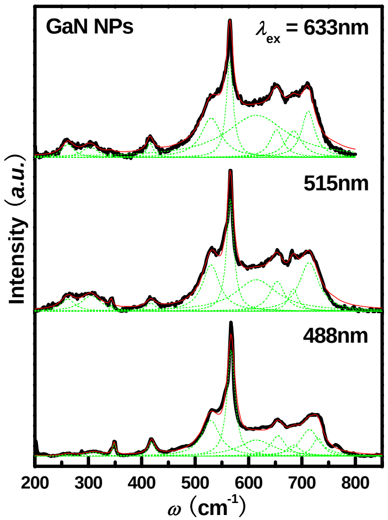
(1) Optical Phonons

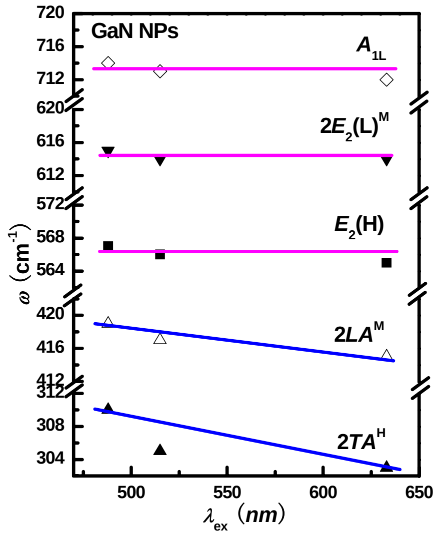
RSSE

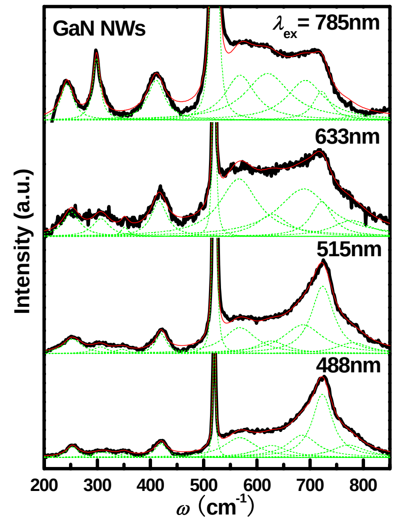
● ZnO nanoparticls and tubes

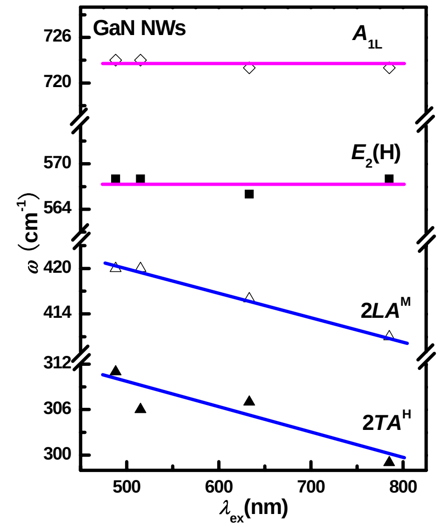


● GaN nanoparticles and wires

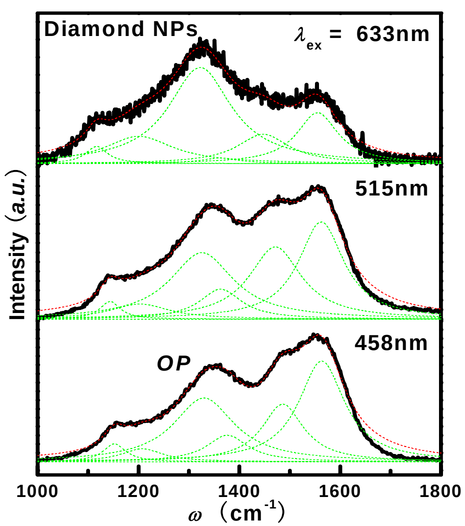


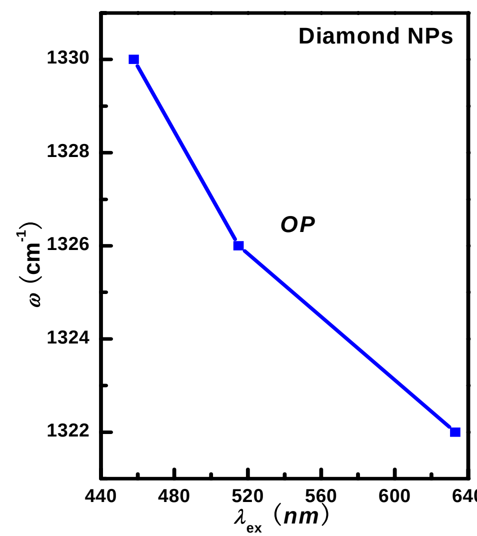






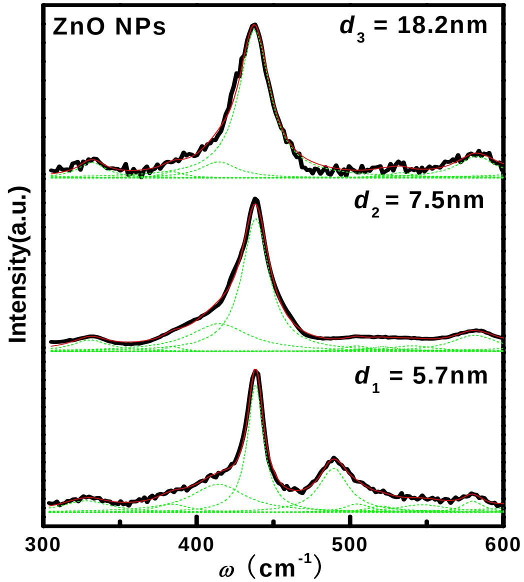
● Diamond nano-paticles

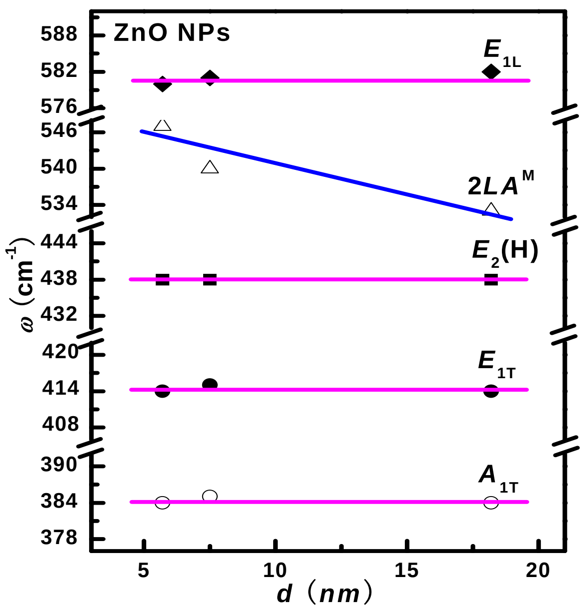




FSE

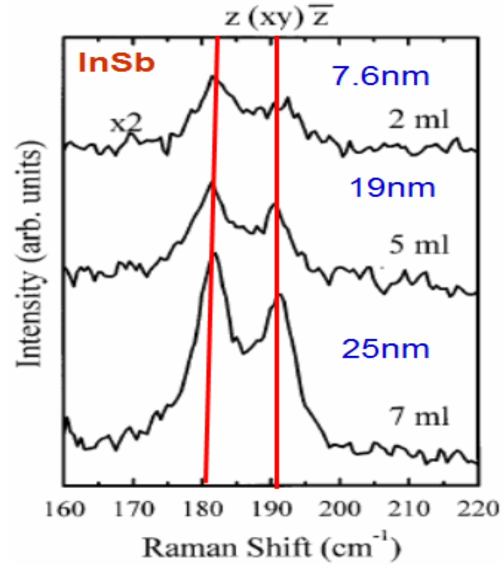
ZnO NPs

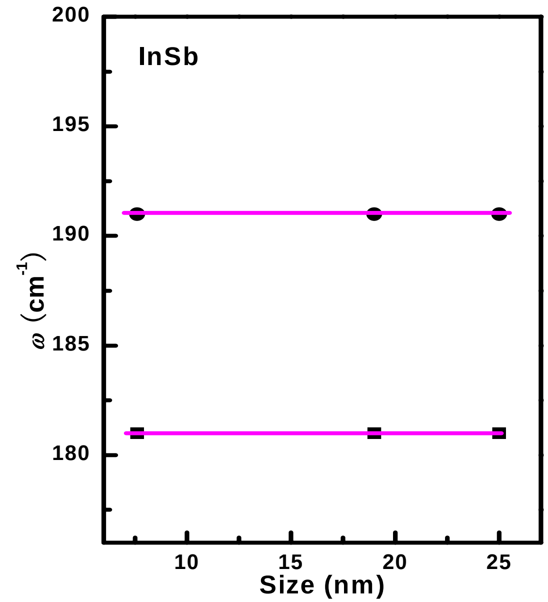




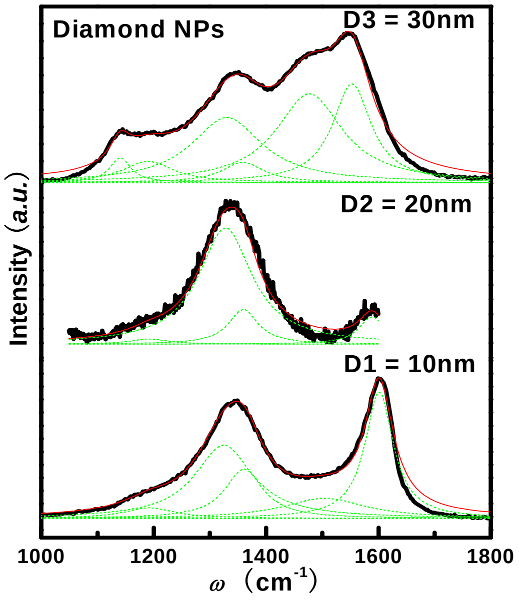
InSb NPs

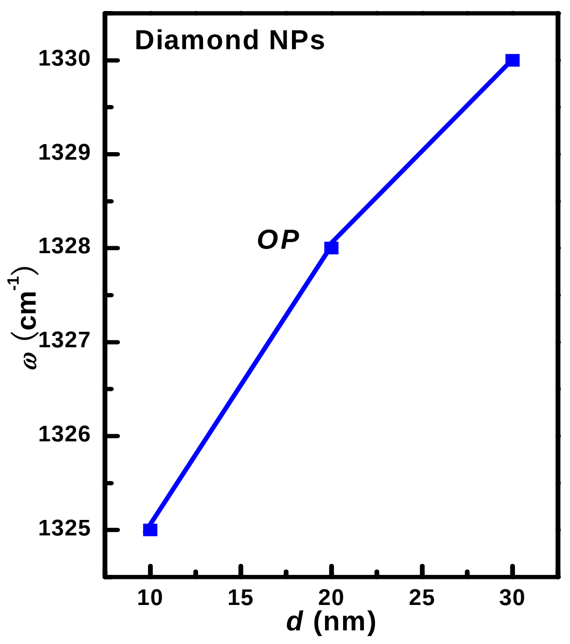
-Armelles, 81(1997)6339





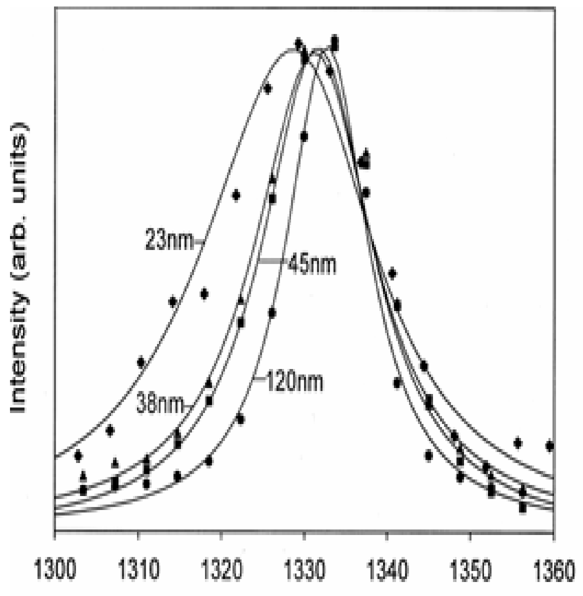
Diamond NPs

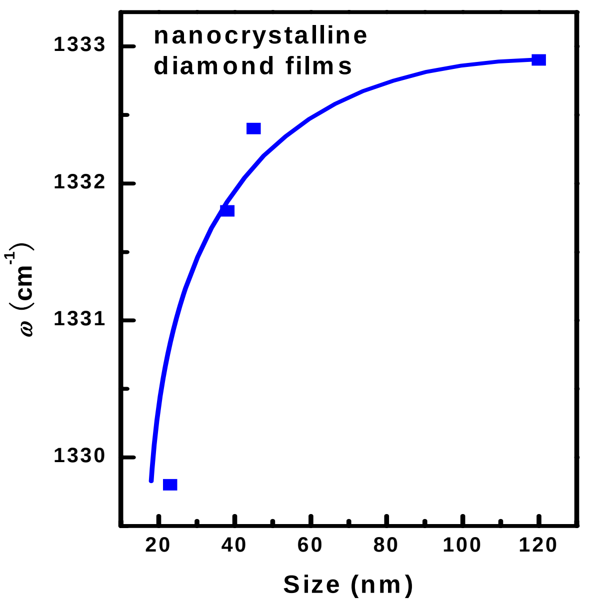




Diamond NCs

-Z. Sun et al. DRM, 9(2000)1979





(2) Acoustics phonon

- CdSe NRs
  -H. Lange, et al, Nano Lett., 8(08)4614

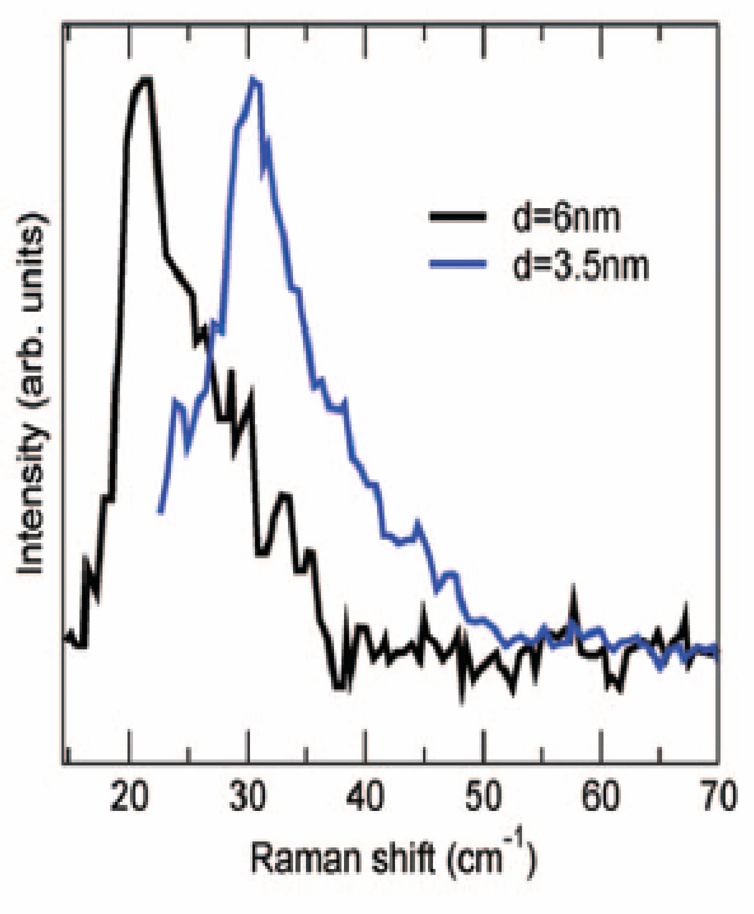
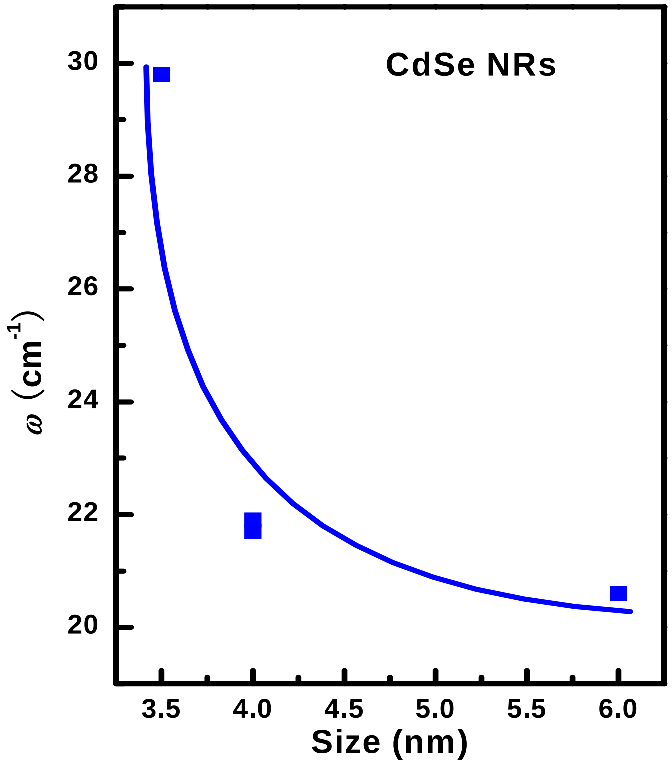


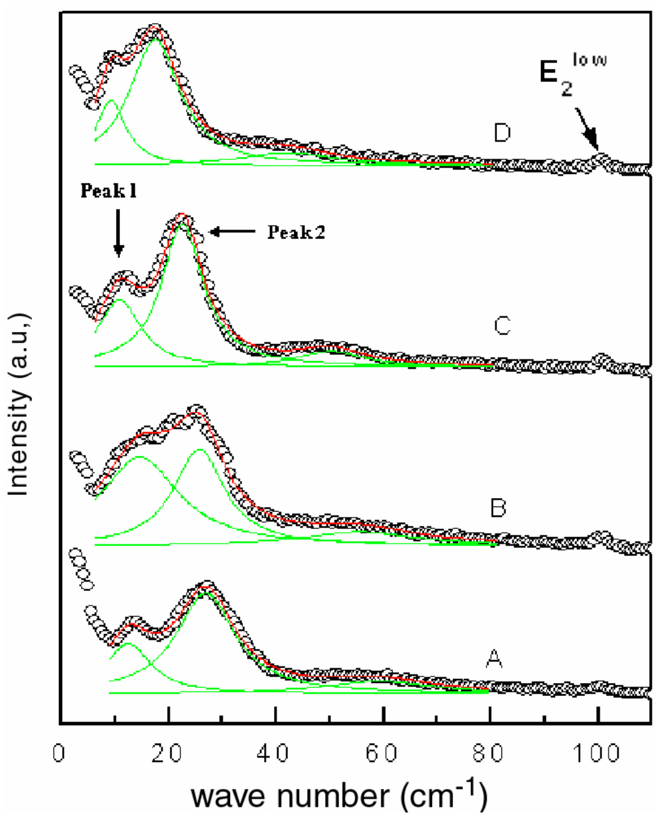
Table 1. Radial Breathing Mode Frequency of CdSe Nanorods

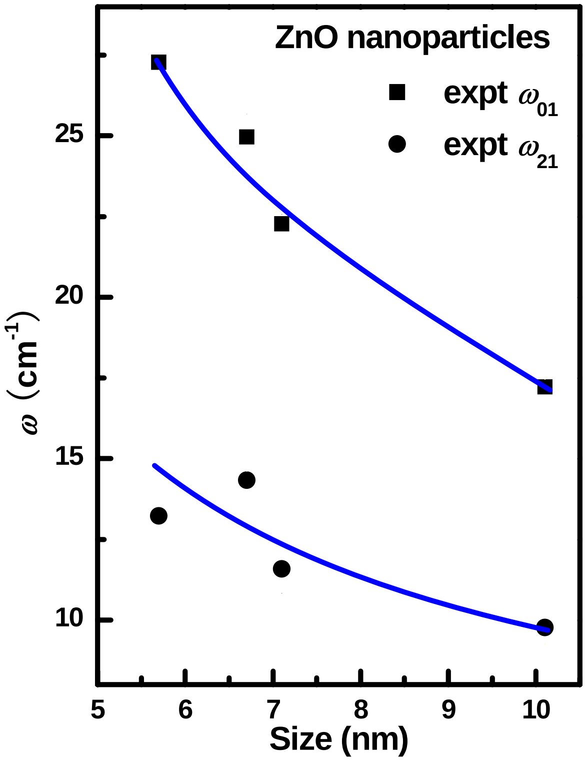
sample dimensions	ω_{RBM}, cm^{-1}
3.5 nm × 20 nm	29.8
4 nm × 25 nm	21.9
4 nm × 30 nm	21.7
6 nm × 35 nm	20.6



● ZnO nanoparticles

- Harish Kumar Yadav, PRL. **97**, 085502 (2006).

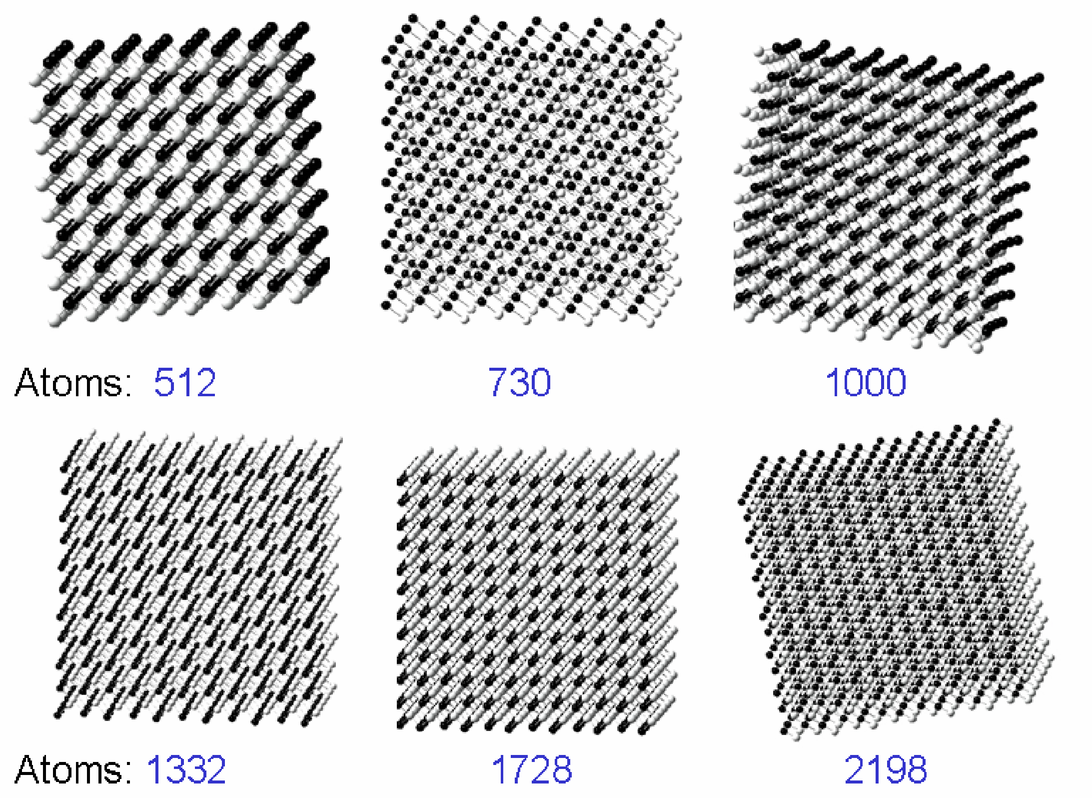




(II) Calculated regular paten

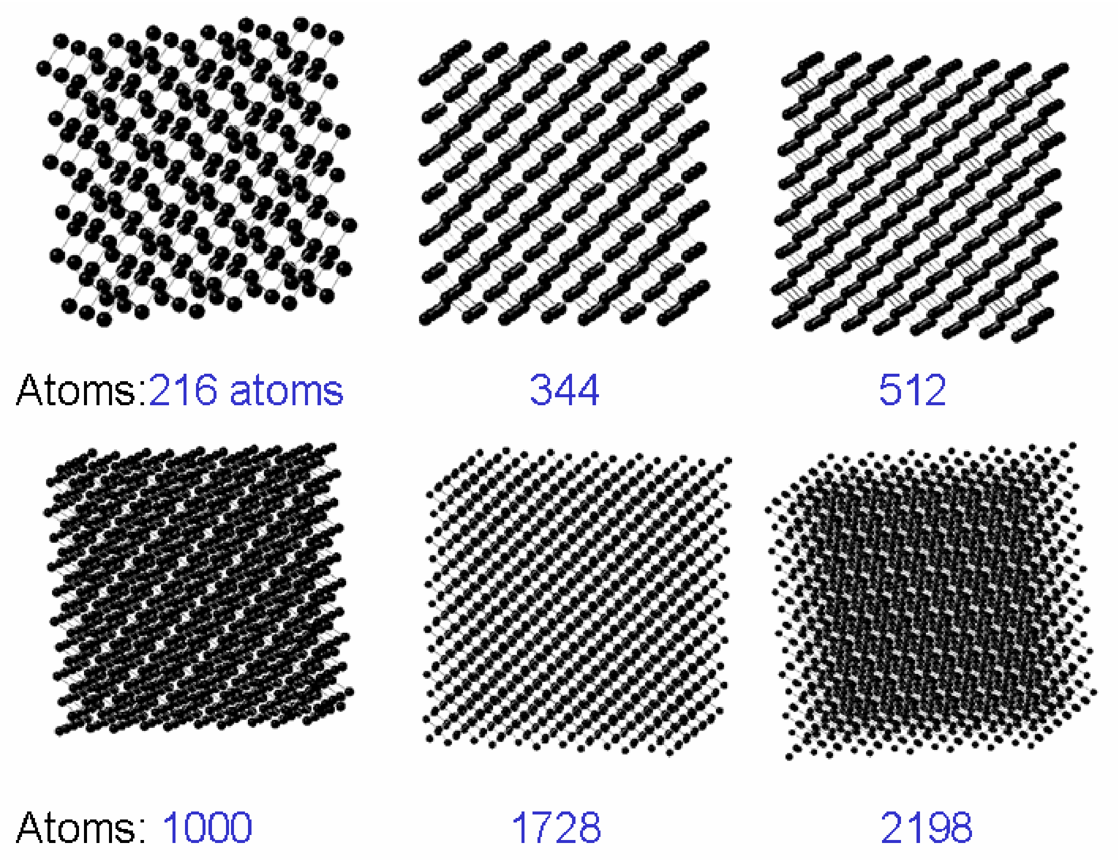
● Atomic structure in cluster model

ZnO/InSb



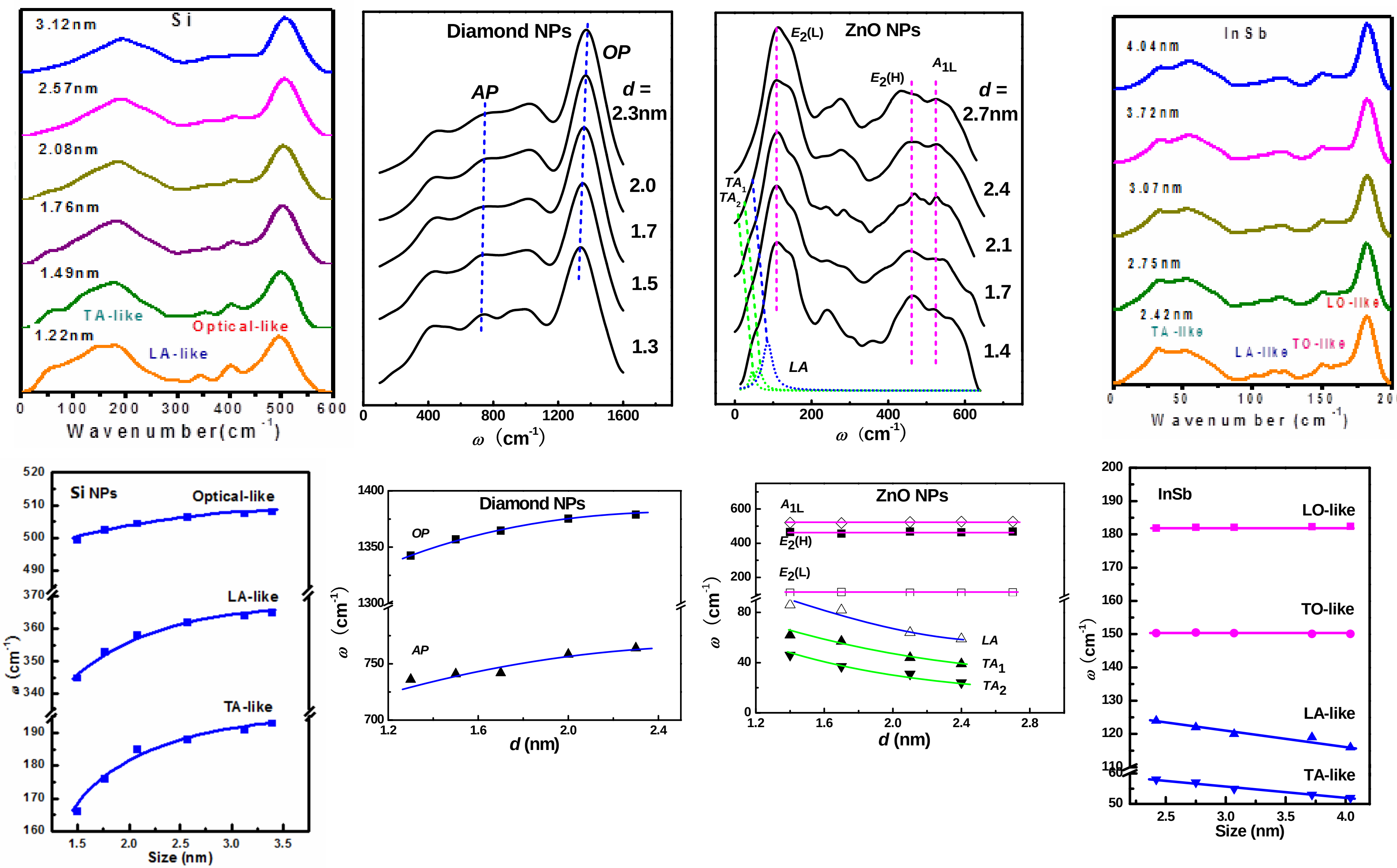
Atom Number	Sizes (nm)	
	ZnO	InSb
512	**2.12**	**2.42**
730	**2.40**	**2.75**
1000	**2.69**	**3.07**
1332	**2.97**	**3.39**
1728	**3.25**	**3.72**
2198	**3.53**	**4.04**

Si / diamond

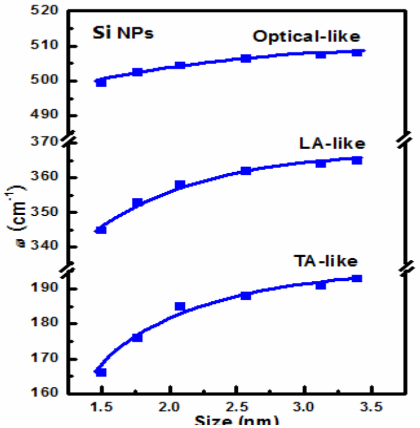


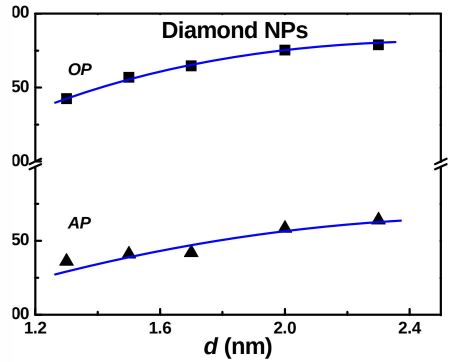
Atom number	Sizes (nm)	
	Si	diamond
216	**1.49**	**0.98**
344	**1.76**	**1.16**
512	**2.08**	**1.34**
1000	**2.57**	**1.69**
1728	**3.12**	**2.05**
2198	**3.39**	**2.23**

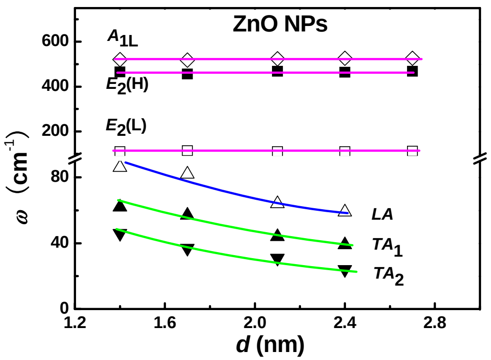
Calculated spectra and frequency dependence on sizes

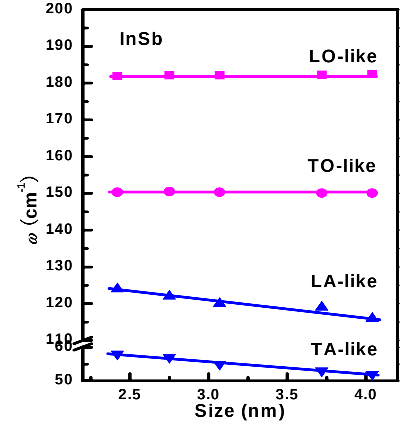


Calculated results

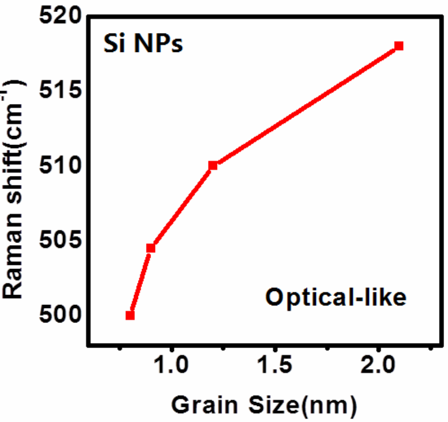


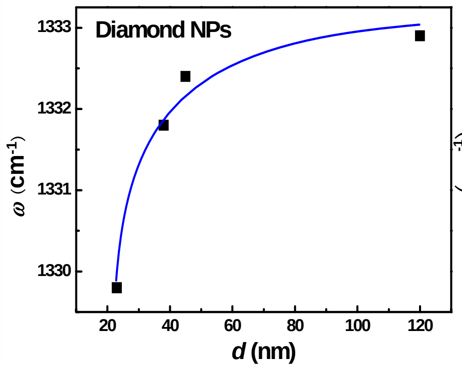


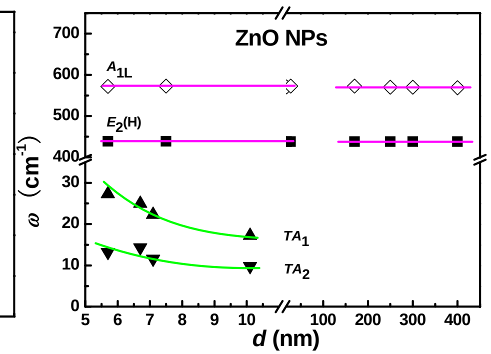


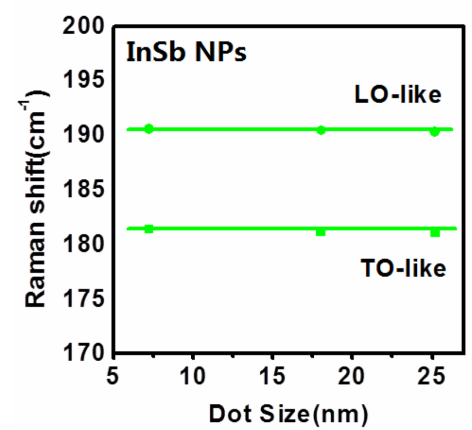


Observed results







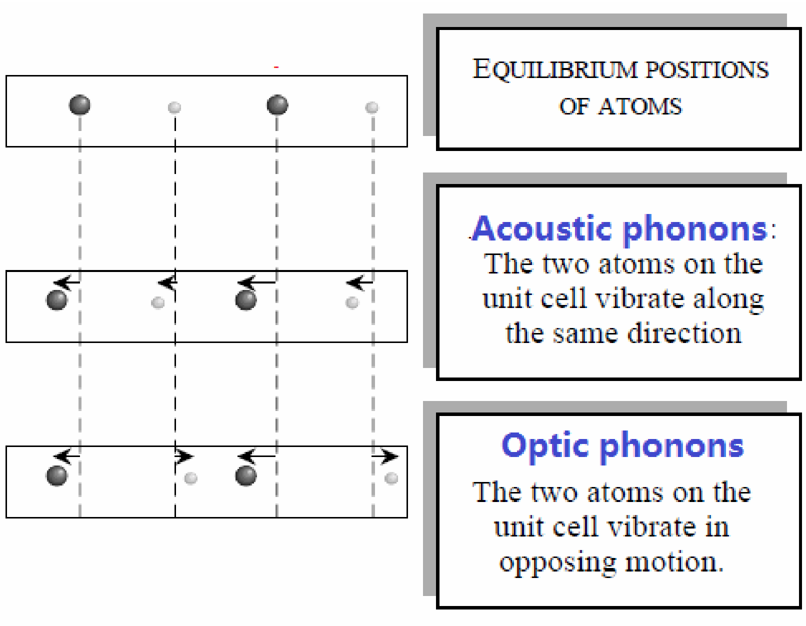


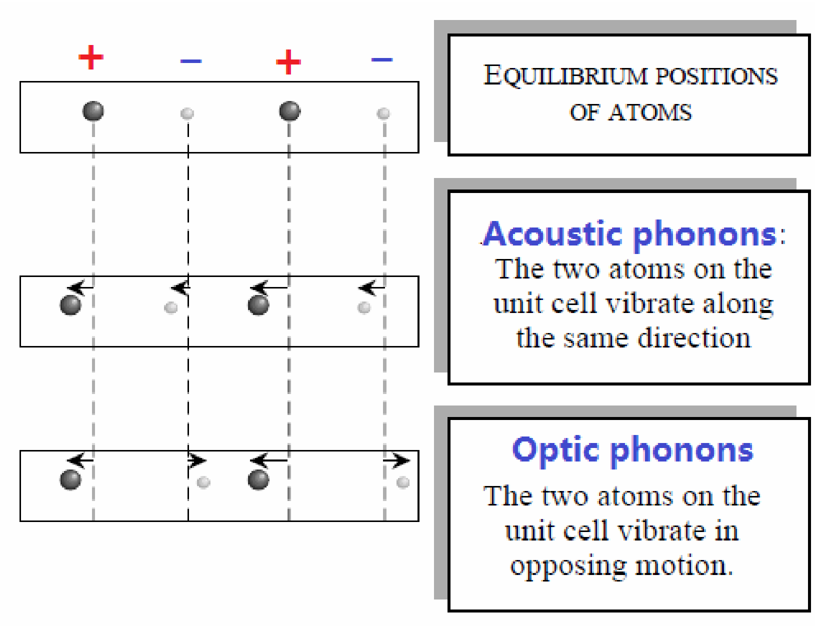
Calculated results Match observed results, Both show:

● The optic phonons of polar nano-semiconductors:
No FSE.

● The optic phonons of non-polar nano-semiconductors and all of acoustic phonons of nano-semiconductors:
Do FSE.

Non-polar semiconductors | Polar semiconductors





1. non-polar semiconductors — electric neutrality
   polar semiconductors — ionicity
2. Acoustic phonons — Deformation (no charge) interaction
   Optical phonons — Coulomb (Fröhlich) interaction added

In the calculation:
Do and Not to take account of the **charge** for polar and non-polar samples, respectively.
Charges paly a key role!

Existence of Positive and negative charges

⬇

- **In matters, have a long range Coulomb potential**
- **In phonon systems, appear a long range electron-phonon (Fröhlich) interaction**

The No FSE may be originated from Fröhlich interaction.

It should be confirmed!

The predication of MP Raman features:

- The Raman frequency of higher order *k* phonons, ω_k, should be integral times of the frequency of first order phonon ω_1:

$$\omega_k = k\omega_1.$$

- The Fröhlich coupling constant in nano-crystals is smaller than one for nano-crystals and the intensity of MP relation should be expected

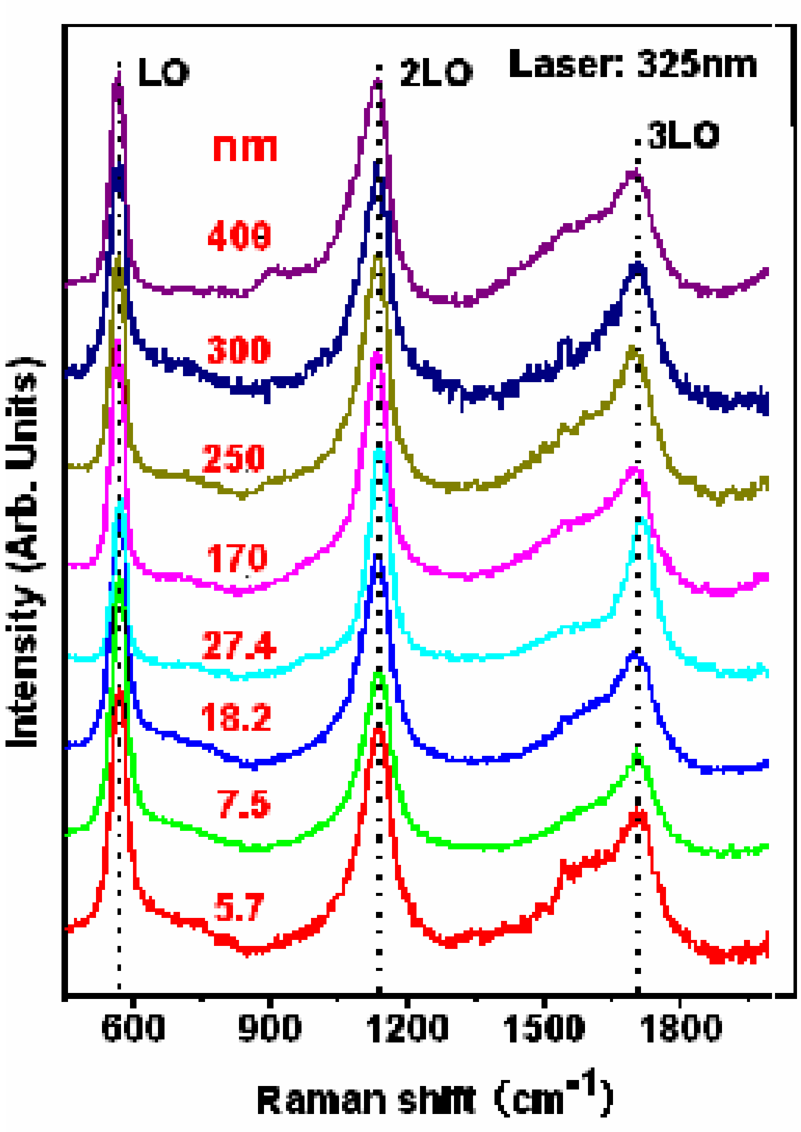
$$I_{R,1} < I_{R,2} > I_{R,3}$$

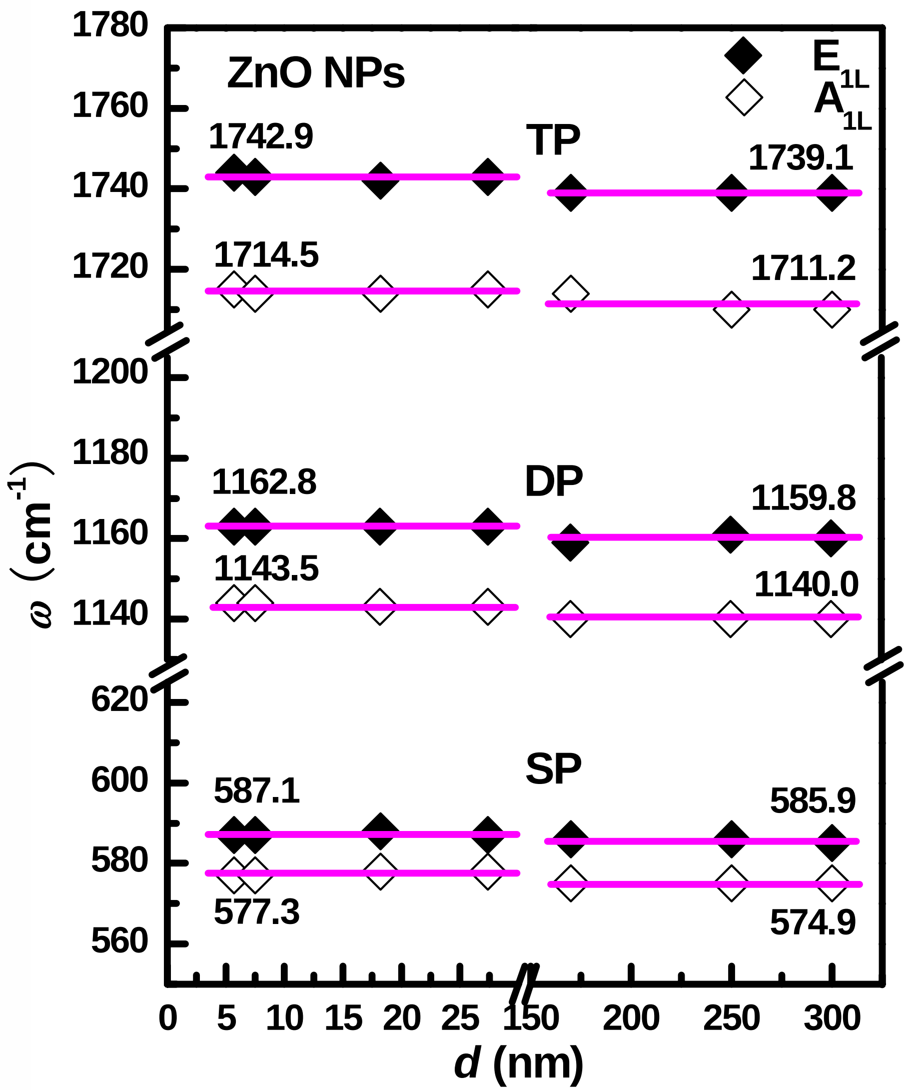
However, they violate the traditional view of MP Raman spectra:

$$\omega_k \neq k\omega_1$$

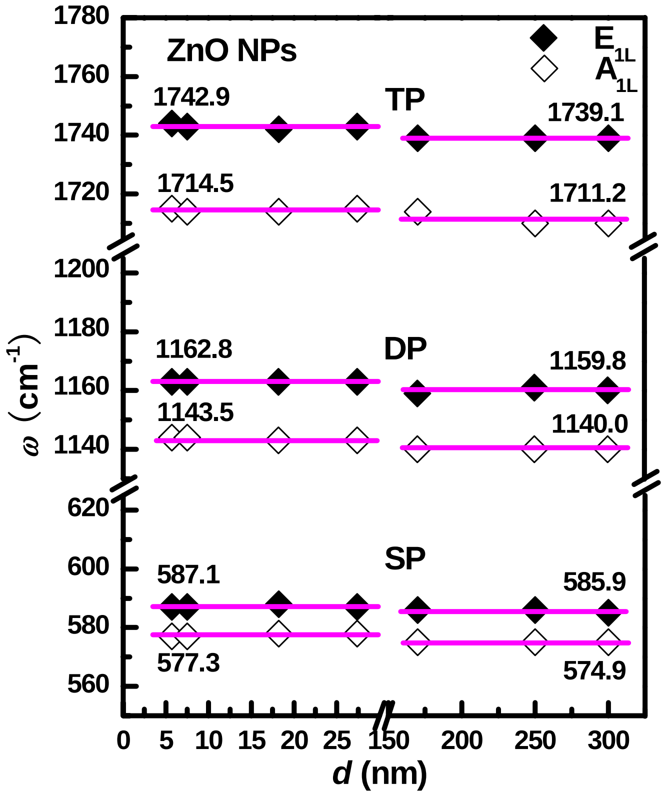
$$I_{R,1} > I_{R,2} > I_{R,3}$$

2. Confirmation by MP Raman spectra of ZnO NPs





Feature 1: Dependence of MP Raman frequency ω_{Obs} Of A_{1L} and E_{1L} mode on sample sizes



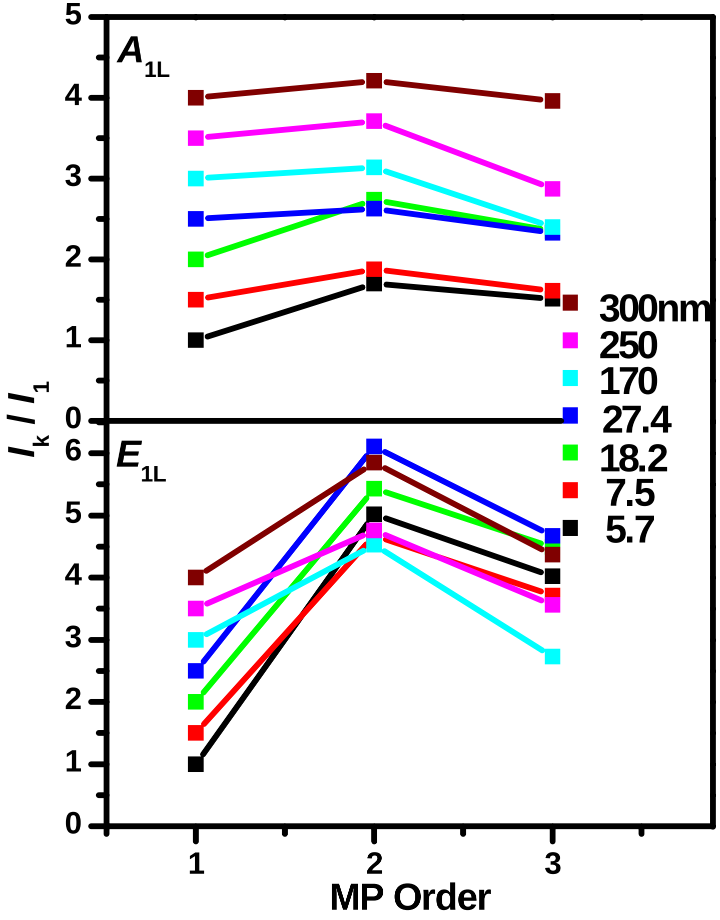
Observed

$$\omega_k = k\omega_1.$$

Confirm the role of Fröhlich interaction

Dependence of relative intensity I_k / I_1 of A_{1L} and E_{1L} mode on MP order k.

$I_3 < I_2 > I_1$



Confirm again the role of Fröhlich interaction

(II) Confirmation of suggested origin

1. Fröhlich interaction H_F and predication for Raman spectra

H_F with phonon wavevector q and the sample volume V can be expressed as approximately[21]

$$H_F \sim q^{-1} V^{-1/2}$$

- At $q \approx 0$ of the Brillouin zoon, Fröhlich interaction plays a key role.
- Since the V of nano-semiconductors is very small, H_F will be critical.

For frequency of single and multiple phonon:
the scattering of OPs in polar nano-semiconductors occur at $q \approx 0$ only

No FSE!

For intensity of multiple phonon: The abnormal has been interpreted successfully in terms of Fröhlich interaction by Rodríguez-Suárez, et al.

-Multiphonon resonant Raman scattering in nanocrystals, *Phys. Rev. B* **62**, 11006-11016 (2000).]

IV-5 Nature of above novel features

Active range of Fröhlich interaction is

10 times of lattice constants ~ 50 nm.

↓

In optic phonon system polar NC-semiconductor:

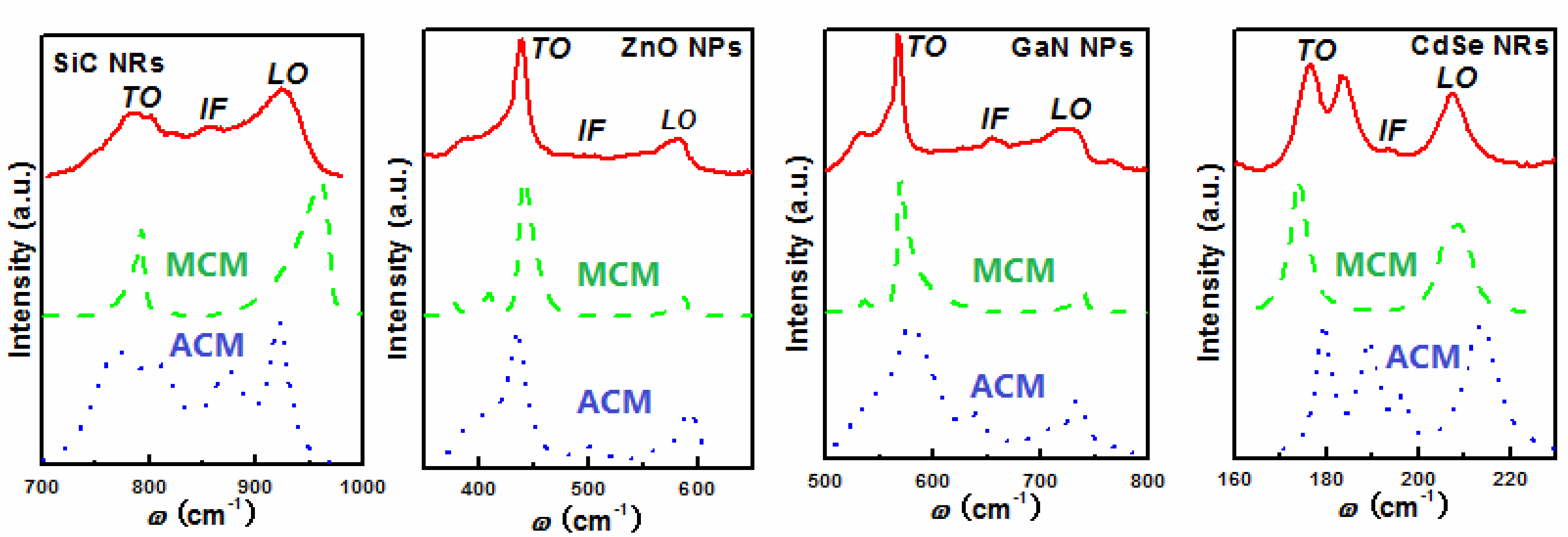
No long-range order

No long-range *order*

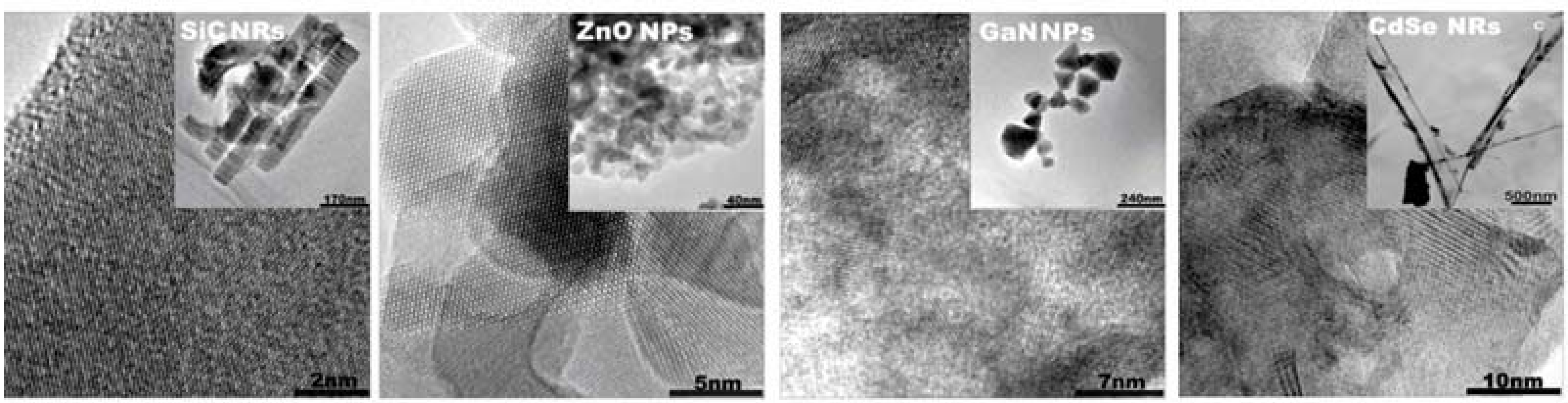
↓

- **Translation symmetry breaking!**
- **Raman spectra must be amorphous!**

Raman spectra are amorphous



Samples are crystalline



Origin and nature are confirmed !

Summery-New Physics

A. On Structure

A perfect nanostructure can be the defect one intrinsically.

- CNTs: $\Delta = |\omega_{AS}| - |\omega_S| \neq 0$
- SLs: In (CdSe)4/(ZnTe)4 SLs, abnormal dependence of micro-IF MP Raman spectra with MP order.

B. On FSE

- For same size of NPs, different elementary excitations have FSE or no FSE. Such as, in ZnO NPs,

  Electron and phonon; Optic and acoustic phonons.

  In fact, it is the issue related with characteristic lengths.

- For different barrier size of SLs have FSE or no FSE. Such as, Abnormal selection rule of IF Mode of $(GaAs)_4/(AsAl)_2$ SLs.

C. On Spectral Ensemble Feature

For optic phonons of polar nano-semiconductors.

The Raman spectrum of crystals appears amorphous feature!

D. On Symmetry

In crystalline nanostructure

Some sub-system can be translation symmetry.

Such as optical phonon system of polar nano semiconductors.

E. On Fröhlich Interaction.

In nano-structure

Fröhlich interaction plays a distinct and crucial role.

which has been verified to be the origin of abnormal phenomena appeared in OPs of polar nano-semiconductors.

Acknowledge:

National Basic Research Program of China (973 Program) under grants No. 2009CB929403;

NSF of China under grants Nos. 10774006 and 60876002**;**

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