

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

212 2012-03-15

周五论坛

低维 / 纳米半导体的曼光谱学与物性

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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

北京大学 物理楼212 2006年11月3日





Raman Spectroscopy and its Application

in Name



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CONTENTS

I. Basic Feature of Raman Spectra and Nanostructures

II. Raman Spectral Feature of Nanosemiconductors

III. Abnormal Raman Spectral Feature Relative to Conventional Raman

Spectroscopy.

IV. Abnormal Raman Spectral Feature Relative to Nanostructure Raman Spectroscopy

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I. Basic Feature of Raman Spectra and Nanostructures

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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

ω_{S} , $\omega_{Rad} = \Delta \omega$	Name	Property	
<mark>> 1 cm⁻</mark> 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



W

(1) Intensity I • $I_{\text{Raman}}/I_{\text{Incident}} < 10^{-6-12}$ $(I_{\text{Rayleigh}} / I_{\text{Incident}} < 10^{-3})$ • $I_{\text{Stokes}} / I_{\text{Anti-Stokes}} \approx \exp(\hbar \omega_k / kT)$ >> 2) Frequency ω_s $\omega_{\rm s}$ Independent of $\omega_{\rm s}$ **Energy** conservation $|\omega_{\text{Stokes}}| = |\omega_{\text{Anti-Stokes}}|$ **<u>Time inversion symmetry</u>**

(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 > $1 \sim 2 \text{ cm}^{-1}$.

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

 $\omega_{\rm S}$ Independent of $\omega_{\rm i}$

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

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 ~ µ m) 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



cluster

nano flowers

graphne

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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 (OCE)



Energy (Raman frequency) changes with sample sizes a

(II) FSE on Symmetry

1. Spatial symmetry - translation symmetry



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

(III) FSE on Momentum

1. Uncertainty relation

 $\Delta \mathbf{k} \Delta \mathbf{r} \leq \hbar$ i=x,y,z $\Delta k_i \Delta r_i \leq \hbar$

When the size *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 Δq , rather than q = 0are 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 0 and Δq 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!

II-3 Observed Raman Spectra

- Examination of above predictions of Raman features

(I) Superlattices (SLs)



- 5 TARLE . Strampergaranteers as detined in the text Processimple
- h S6 and S8 the parameters have been estimated from the growt conditions.

2		d (Å)	\overline{x}	<i>n</i> ₁	п
4	<i>S</i> 2	29.2	0.123	6	
9	\$5	51	0.147	9	· · ·
7	\$7	54.4	0.141	12	
2	\$9	81.4	0.145	17	13



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



(II) Nanomaterials (NMs)

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

> Early works: Consisted of two Bulk Raman spectra ??: Not match the prediction based FSE!



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

Aanalyses and measurement for PS Raman spectra

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



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



2. Si and diamond NMs



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 !

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



-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).



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 $\Delta \neq 0$

⊿ values of CNTs and perfect graphite - HOPG

Sample	MW-CNT	SW-CNT	HOPG	HOPG _{Au}
<i>W</i> _{AS} -	<i>W</i> _S ∣ +7	+7	/	-7.7
Δ	≠ 0	≠ 0	= 0	≠ 0

∆ ≠ 0 Related with tubular structures !
∆ ≠ 0 Related with defected materials !

Inspect CNT structure:



CNTs is a defect structure; Defects ~ d.
 Δ ≠ 0 may from tubular structure itself!

Expectation: Larger the <d> , Smaller the ⊿

Experimental confirmation



Confirmed experimentally



Calculate Δ by double resonance $q = (E_1 - h\omega_{ph})/v_1 \text{ or } (E_1 - h\omega_{ph})/v_2$ (1) $\omega_{ph}(q) = f(q)$ (2)



Confirmed theoretically

Brief summary

- The RSSE is an embody of FSE, i.e.,:
 RSSE FSE
- The |𝒫As| |𝒫s| ≠ 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.

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IV-1 Abnormal Feature of Raman Frequency

APPLIED PHYSICS LETTERS

VOLUME 81, NUMBER 23

2 DECEMBER 2002

<u>Vesietien af Barear fortum se resitation wowalcosthic pilling a secondiance</u> Shullin Zhang,⁴¹865 Ding, Yan Yan<u>, Jiang Qu, Biles Li</u>, Lessu Li, Kweklie Yue, <u>.</u>

<u>eg_SiConnarade "assisting af smaller groins, we experit</u> 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



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





(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).



Suggested Origin 2 : Not in resonance

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



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:

		E of laser (nm/eV)							
Sampl e	Eg (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	1	0	1.3	33.3
A _{1T}		1.3	1			
A _{1L}		1	1.3	2.4	1.3	
<i>E</i> ₂ (H)		1	0	1.2	0.3	
E _{1T}		1	0			
$E_2(L)$	ТО	/	2.5	2.4	0.3	8.3
		Γ-Σ	Γ–Α			

Red numbers: Much dispersive values. Not all are little dispersive



(I) Sample: Nearly Uniformed ZnO NPs samples









27.4± 1.8nm

 $\textbf{5.7} \pm \textbf{ 0.6nm}$



7.5± 0.9nm



18.2± 1.7nm





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

350 400 450 500 550

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 LOExperimental XYXXTheoreticalXY/

B-2 Interface (IF) Modes of (GaAs)₄/(AsAl)₂ SLs

Т

(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
heoHuang	0			0		0	0	
	e -	e	<u>e</u> _	S =	e	e	e -	e :

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 is confined in QWs.

2. Parity γ is definite.

The origin may be the sample not match the preconditions.



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)

$$I_{\alpha\beta,\gamma\delta}(\omega) = \sum_{b} C_{b \alpha\beta,\gamma\delta} \left[(1+n(\omega))/\omega \right] D_{b}(\omega)$$

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

$$I(\omega) = \int \frac{\frac{MCM}{d^3 q C(0,q)^2}}{(\omega - \omega(q))^2 + (\frac{\Gamma_0}{2})^2} \qquad I_{\alpha\beta,,\gamma\delta(\omega)} = \sum_b C_b^{\alpha\beta,,\gamma\delta} [(1 + n(\omega))/\omega] \underline{D}_{\underline{b}}(\omega)$$



Can't fit by MCM:

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



Wavenumber (cm⁻¹)

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 $|_k < |_{k-1}$

A. Superlattices

Sample: (CdSe)4/(ZnTe)4 SLs
 Observed results of micro-IF MP modes



2. Interpretation We note a paper:







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 1780 ZnO NPs 1760 4 1742.9 TP 1739.1 1740 3 1714.5 1720 1711.2 2 1200 300nm 250 1180 ົ້ອ 1140 170 1162.8 DP 1159.8 27.4 18.2 7.5 5.7 1143.5 1140.0 5 620 SP 600 587.1 585.9 3 580 Č 2 5⁷⁷.3 574.9 560 5 10 15 20 25 150 200 250 300 0 0 d (nm) 2 MP Order 3 1 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 $\omega_{1:}$

 $\omega_k = k\omega_1$

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

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

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

 $\omega_k k\omega_1$

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

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

<u>RSSE</u>

• ZnO nanoparticls and tubes



FSE



300 400 500 600



(2) Acoustics phonon

CdSe NRs

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



Table 1. R	adial Breath	ning Mode	Frequency	of CdSe	е
Nanorods		0	1		

sample dimensions	$\omega_{\rm RBM}, {\rm ~cm^{-1}}$
$3.5 \text{ nm} \times 20 \text{ nm}$	29.8
$4 \text{ nm} \times 25 \text{ nm}$	21.9
$4 \text{ nm} \times 30 \text{ nm}$	21.7
$6 \text{ nm} \times 35 \text{ nm}$	20.6



• ZnO nanoparticles

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



(II) Calculated regular paten

Atomic structure in cluster model

ZnO/InSb	Atom	Sizes (nm)	
	Number	ZnO	InSb
Miller warden Billing	512	2.12	2.42
MMA MANNE BANKE	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

······································	Alle States Filler		Atom	Sizes (nm)	
Will.		Mille.	number	Si	diamond
			216	1.49	0.98
3333333	5555555	344	1.76	1.16	
512	Atoms:216 atoms	344	512	2.08	1.34
		E ^{DI} IIII	1000	2.57	1.69
		Eze IIII	1728	3.12	2.05
			2198	3.39	2.23

728 2198 Atoms: 1000

1



d (nm)

 9 10 100 200 300 400 *d* (nm)



Non-polar semiconductors

Polar semiconductors



 non-polar semiconductors polar semiconductors
Acoustic phonons

Optical phonons

electric neutrality ionicity Deformation (no charge) interaction 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 $\omega_{1:}$

 $\omega_k = k\omega_1$

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

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

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

 $\omega_k k\omega_1$

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

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





Dependence of relative intensity *I*

(II) Confirmation of suggested origin

1. Fröhlich interaction $H_{\rm F}$ and predication for Raman spectra

 $H_{\rm F}$ with phonon wavevector q and the sample volume V can be expressed as approximately²¹

 $H_{\rm F} \sim q^{1} V^{1/2}$

•At q 0 of the Brillouin zoon, Fröhlich interaction plays a key role.

•Since the V of nano-semiconductors is very small, $H_{\rm F}$ will be critical.

For frequency of single and multiple phonon: the scattering of OPs in polar nano-semiconductors occur at q = 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





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.

ifferent 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.

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