

Influence of near-surface inhomogeneity
on the optical properties
of II-VI compounds and their solid
solutions.

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Saint-Petersburg State University



The oldest Russian University was founded at 1724 in Saint-Petersburg.

Now it has 19 faculties and 13 research institutes.

In St. Petersburg State University get ready to become Bachelors or Masters of science or specialists more over than 30000 students. More over than 4000 Ph.D. student make their thesis, also university offers senior doctorate studies. The university has over 100 direct agreements of co-operation with universities of 50 countries.



Building of Twelve Colleges, a notable architectural landmark of the eighteenth century, become an emblem of our university.

Physics Faculty and Institute of Physics



The history of physics instruction in St. Petersburg State university start from 1746 year with first physics course in

Russian given by M.V. Lomonosov.

Now the physics education and scientific centre including 19 departments and 2 research institutes. The faculty programmes cover practically every field of modern physics, both theoretical and experimental. In the physics faculty study over 1200 undergraduate students and over 170 postgraduate students.

In the education and scientific centre works over 500 lectures and researches among them about 150 professors and 4 Academicians and Corresponding Members of the Russian Academy of Science.

*The faculty produced three Nobel Prize winners:
N Semenov, L.Landau, and A. Prokhorov.*



*Laboratory of
Optics of Solids*

Prof. B.V. Novikov

Optical and photoelectric properties of low-dimensional semiconductors systems, II-VI compounds.

Prof. V.F. Agekian

Magneto-optic properties of semiconductors. Time resolved spectroscopy.

Quantum wells.

Prof. S.V. Karpov

Raman scattering. II-VI quantum dots.

Prof. I.Kh. Akopyan

Superionic materials. Phase transitions in low-dimensional systems.

*Solid State Physics
Department*

Ultrasonic laboratory

Prof. E.V. Charnaya

NMR. Phase transitions.
Composite materials.

*The branch of the Solid State Physics
Department in the institute of the Russian
Academy of science*

Academian of RSSI A.A. Kaplianskiy

Electron and vibronic states in solids and related phenomena studied by means of optical spectroscopy.

Prof. A.V. Sel'kin

Photonic crystals. Bragg structure. Excitonic states in the near-surface and the near-interface region.

Solid State Physics Department.

In our department students can obtain the degree of Bachelors (by specialization physics) and Masters by following specializations:

1. Solid State spectroscopy (Prof. B.V. Novikov and Prof. A.V. Selkin)
2. Coherent phonons and NMR in Solids (Prof. E.V. Charnaya)

Now in our department study about 50 students.

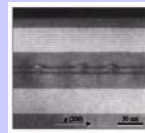
Solid State Physics Department

Group of Prof. B.V. Novikov

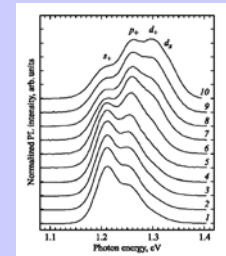
The main subjects of research:

The basic research methods are worked out on a base of exciton spectroscopy

1. Quantum dots and quantum molecules.



In the InAs/GaAs QD and QM are study the electron structure and luminescence processes in depends on growth conditions.



2. II-VI compounds and their solid solutions.
(exciton photoluminescence, reflectance and photoconductivity)

3. The near-surface region.
(study and modeling exciton reflection spectra)

4. Superionic materials

Our group is in close collaboration with Ioffe Physico-Technical institute of Academia of science, with universities of Leipzig and Ilmemaу (Germany). In last time is established collaboration with group of Prof. Perez-Rodriguez.

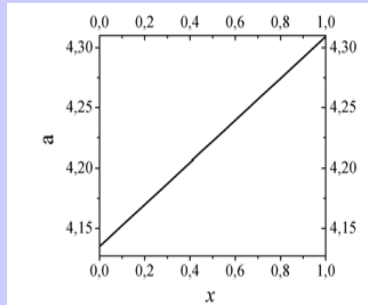


Influence of near-surface inhomogeneity on the optical properties of II-VI compounds and their solid solutions

- Solid solutions (compositional disorder)
- Peculiarities of II-VI compounds (structural disorder)
- Optical properties of $\text{CdS}_{1-x}\text{Se}_x$
- Self-assembled near-surface potential well in $\text{CdS}_{1-x}\text{Se}_x$.

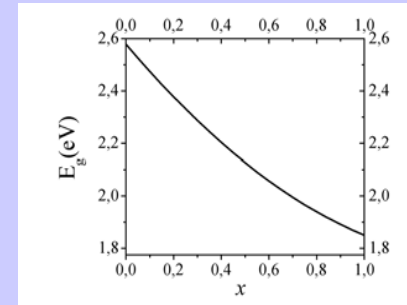
Solid solutions (general properties)

*Lattice constant versus concentration x
(Vegard law)*

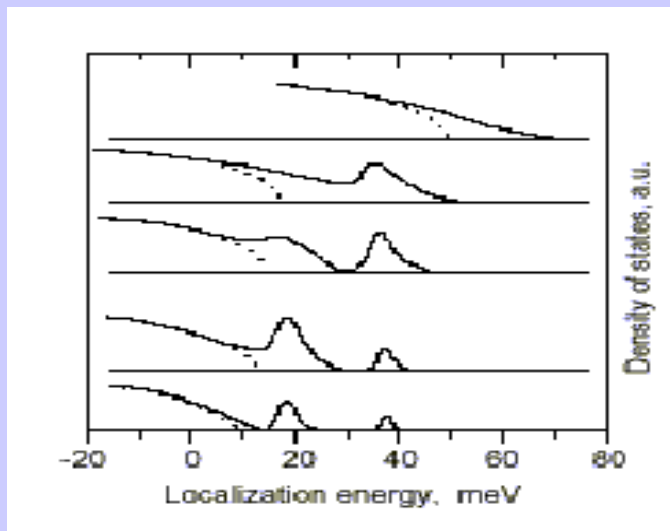


Energy gap versus concentration x

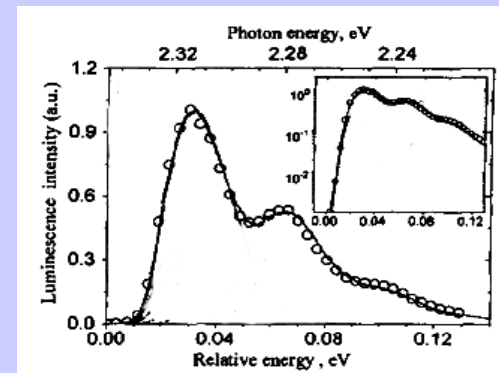
$$E_g(x) = E_g^A(1-x) + E_g^Bx - bx(1-x)$$



*Compositional disorder:
the density of the states*



photoluminescence

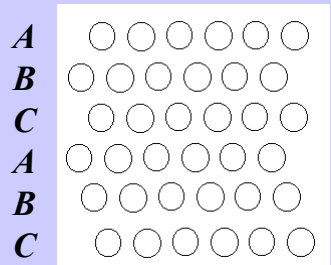


Peculiarities of II-VI compounds

Two basic crystal structures

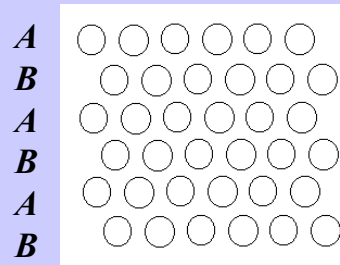
(sequences of close packed planes (111) along [111]-direction)

zinc-blende



T_d^2
3C

wurzite.

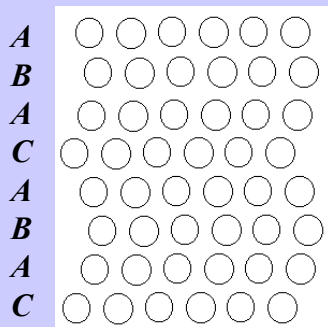


C_{6v}^4
2H

Intermediate structures

ordered

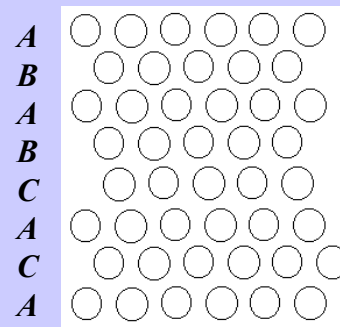
4H polytype



nH -hexagonal
nR - rhombohedral
n - period of
the repetition

disordered

stacking fault intrinsic type-I₂



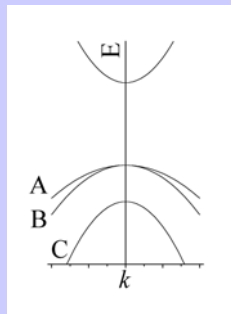
C_{3v}
anisotropy parameter:
 $\alpha = n_h / (n_h + n_c)$
2 types of intrinsic stacking
faults and 1 type of extrinsic
stacking fault.

Peculiarities of II-VI compounds

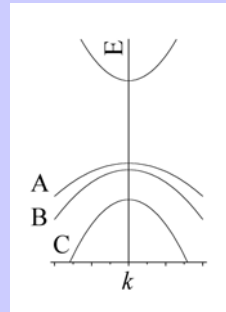
Phase transitions from zinc-blende to wurzite in dependence of concentration x

Transformation of electron structure near Γ -point

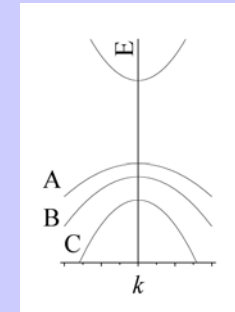
zinc-blende



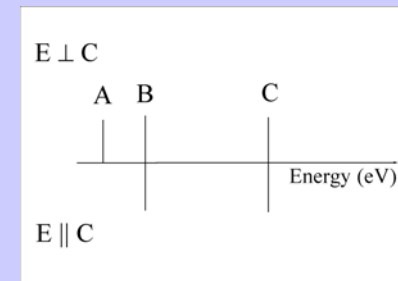
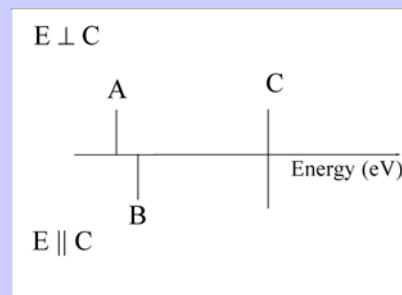
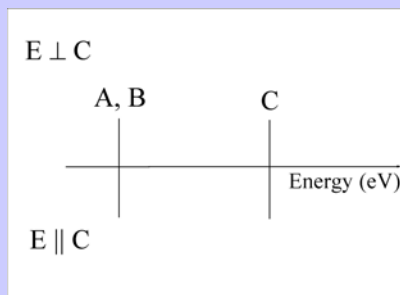
structures with stacking faults



wurzite



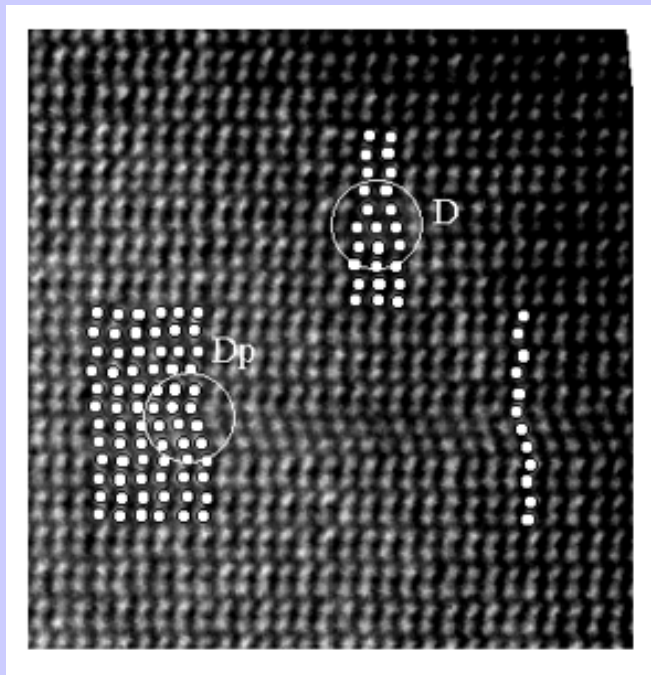
Schemes of exciton optical spectra with different α



CdS_{1-x}Se_x crystals

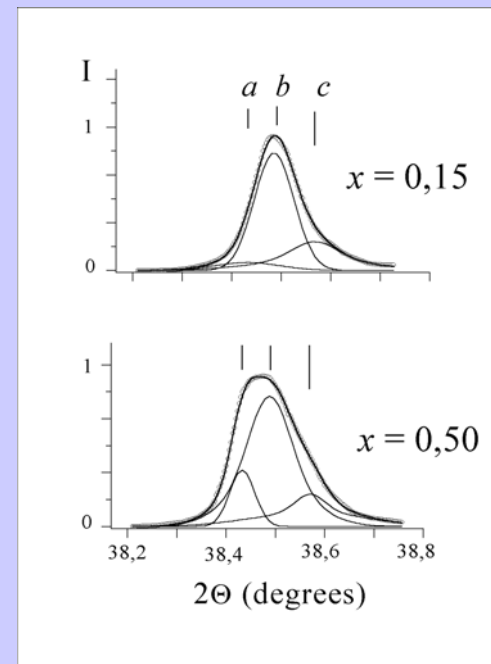
Structural peculiarities of the CdS_{1-x}Se_x crystal

Experimental HRTEM lattice image viewed from the [110] direction showing an intrinsic stacking fault of type I₁ within the hexagonal CdS_{1-x}Se_x (x = 0.5).



B.V. Novikov et al
J. Crystal Growth **233** (2001) 68

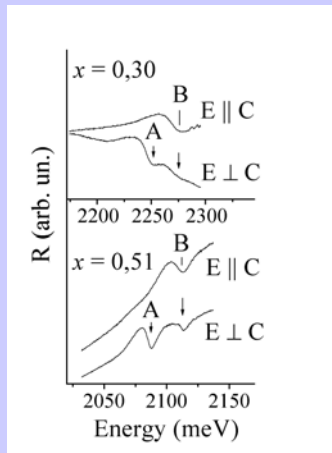
(220) reflection profiles obtained with CuK_α radiation on CdS_{1-x}Se_x



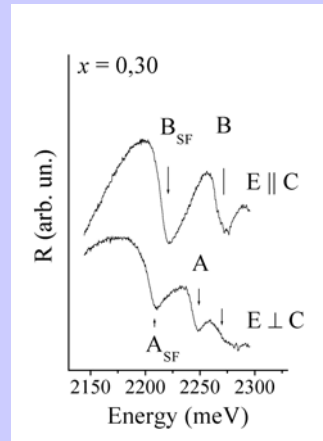
N.R. Grigorieva et al,
Phys Sol St **42** (2000) 1613

Optical spectra of $\text{CdS}_{1-x}\text{Se}_x$ crystals

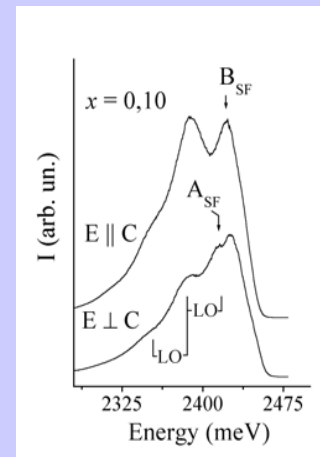
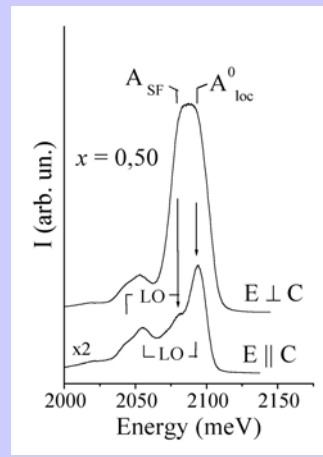
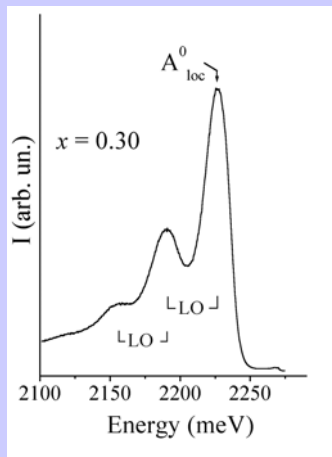
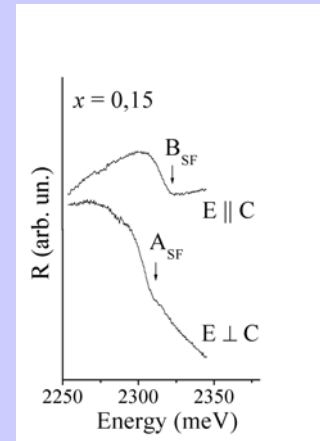
Group I
wurzite structure



Group II
co-existence of wurzite
structure and structure with
stacking faults



Group III
structure with
stacking faults



1. B.V. Novikov et al, JETP LETTERS **70** (1999) 222

2. N.R. Grigorieva et al, J of Crystal Grows, **214-215** (2000) 457

3. N.R. Grigorieva et al, Phys Sol St **42** (2000) 1613

CdS_{1-x}Se_x crystals

Areas with different spectral structure of luminescence

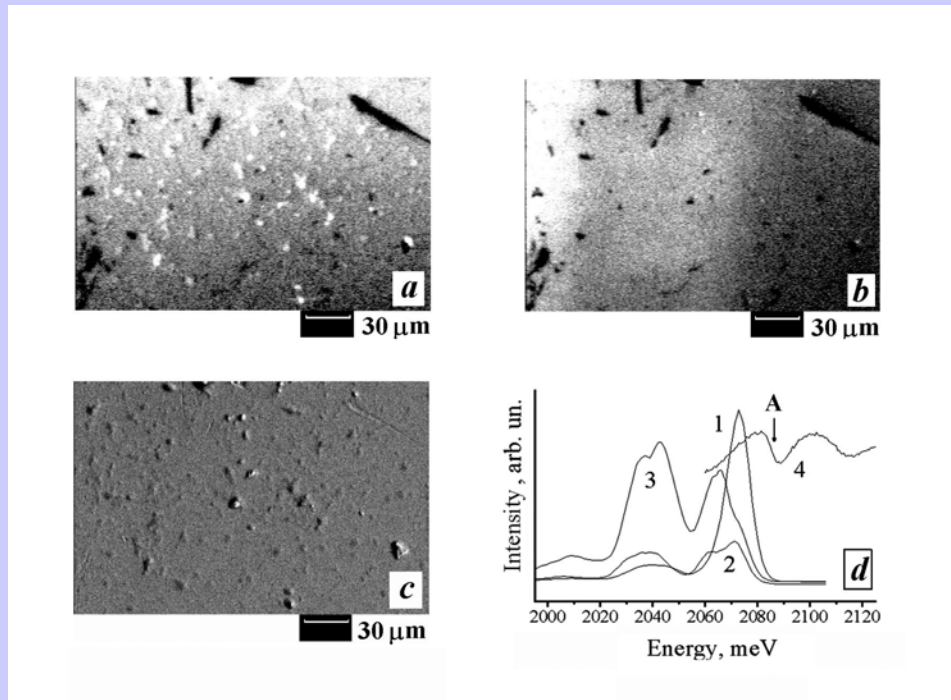
CL- and SE-images and CL and reflection spectra obtained from CdS_{0.5}Se_{0.5} crystal:

a – CL-scanning at E = 2073 meV;

b – CL-scanning at E = 2063 meV;

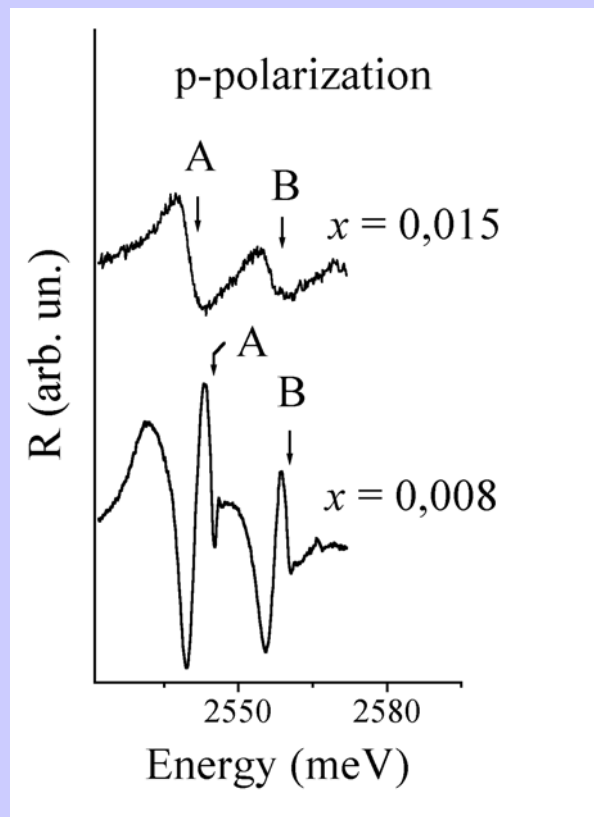
c – SE-image;

d – CL- and reflection spectra: 1 – from bright micro-areas (micro-hills); 2 – from light zone; 3 – from darker zone; 4 – reflection spectrum.



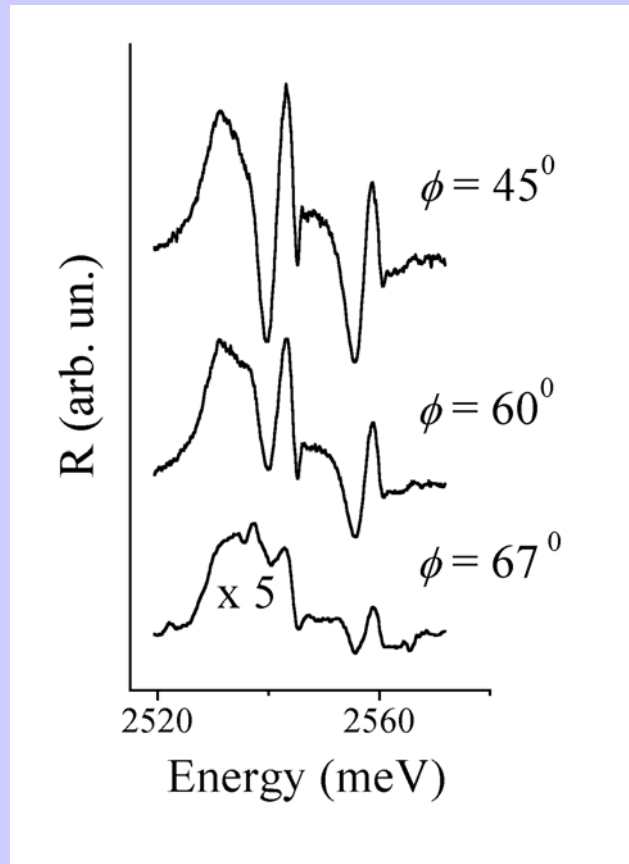
$\text{CdS}_{1-x}\text{Se}_x$ crystals with low Se concentration self-assembled quantum well in the near surface region

Reflection spectra of $\text{CdS}_{1-x}\text{Se}_x$ crystals with normal (dispersion) and anomaly shape of exciton line. $T = 2 \text{ K}$, p-polarization $\mathbf{E} \perp \mathbf{C}$.



$\text{CdS}_{1-x}\text{Se}_x$ crystals with low Se concentration self-assembled quantum well in the near surface region

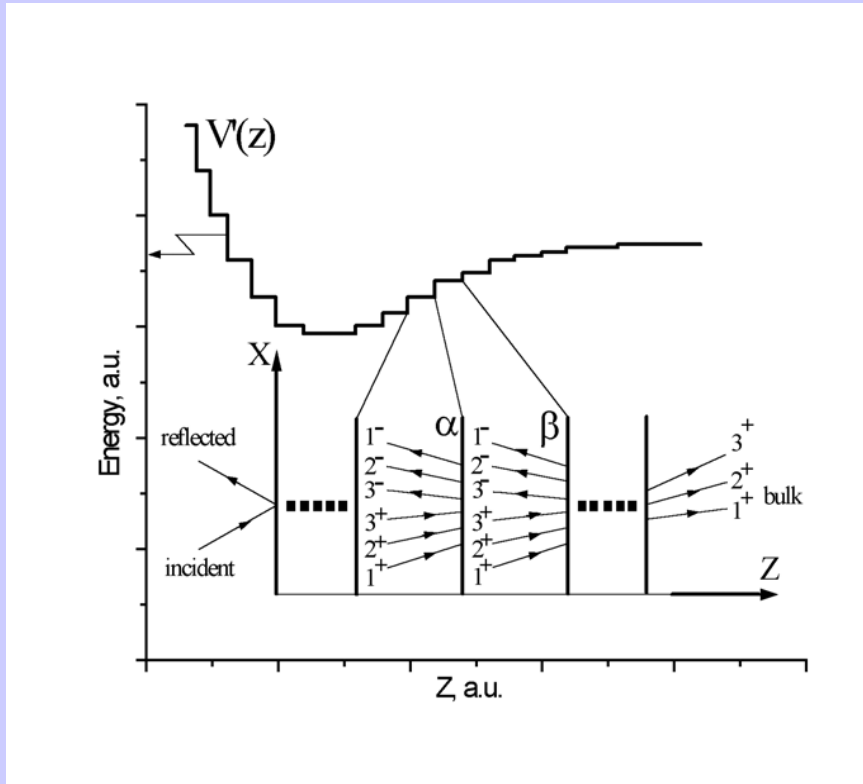
Reflection spectra of $\text{CdS}_{1-x}\text{Se}_x$ crystals ($x=0.008$)
at oblique incidence of light. $T=2\text{ K}$,
p-polarization $\mathbf{E} \perp \mathbf{C}$.



H. Azucena-Coyotecatl, N.R.
Grigorieva, F. Perez-Rodriguez,
A.V. Sel'kin et al, Thin solid films
373 (2000) 227

CdS_{1-x}Se_x crystals with low Se concentration self-assembled quantum well in the near surface region

Multistep model for near-surface potential well



The relationship between the excitonic polarization \mathbf{P} and electric field \mathbf{E} at light frequency ω near bulk resonant frequency ω_T :

$$\left[\frac{\hbar\omega}{M} \nabla_{\mathbf{R}}^2 - \omega_T^2 + \omega^2 - i\omega_T\Gamma_0 + \frac{2\omega_T}{\hbar} V^*(z) \right] \mathbf{P}(\mathbf{R}, \omega) = \beta_0 \omega_T^2 \mathbf{E}(\mathbf{R}, \omega)$$

$V^* = V' + iV''$ - exciton potential.

The real part describes the coordinate dependence of local resonant energy.

The imaginary part describes a z -dependence of the damping parameter $\Gamma(z) = 2V''(z)/\hbar$.

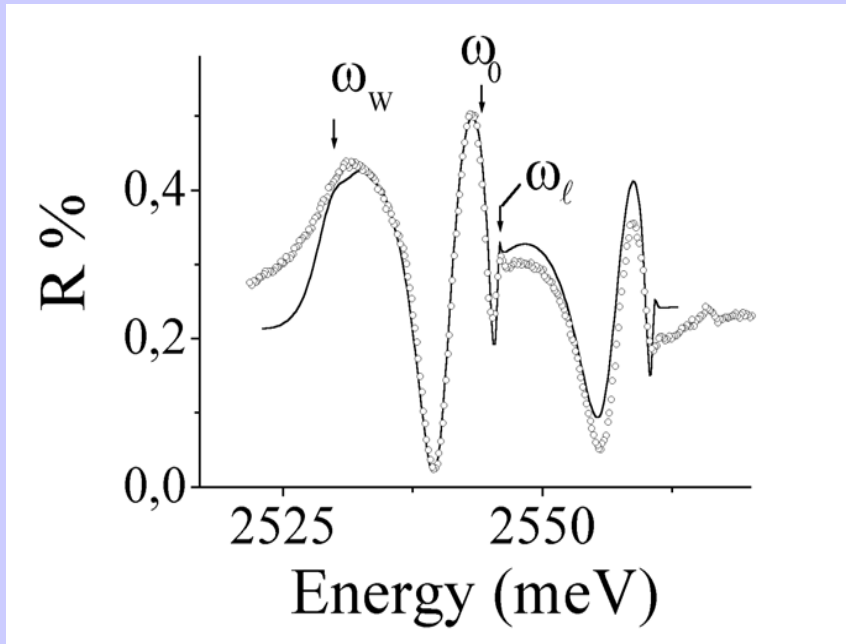
Used potential:

$$V(z) = U_1 e^{-(z-z_1)/L_1} - U_2 e^{-(z-z_2)/L_2} + iU_3 e^{-(z-z_3)/L_3}$$

1. H. Azucena-Coyotecatl, N.R. Grigorieva, F. Perez-Rodriguez, A.V. Sel'kin, et al, Thin solid films **373** (2000) 227
2. H. Azucena-Coyotecatl, N.R. Grigorieva, F. Perez-Rodriguez, A.V. Sel'kin, et al, Superficies y Vacio **9** (1999) 313

CdS_{1-x}Se_x crystals with low Se concentration self-assembled quantum well in the near surface region

The experimental reflection spectra of CdS_{1-x}Se_x ($x=0.008$) obtained at $T=2$ K, p-polarization $\mathbf{E} \perp \mathbf{C}$ in comparison with theoretical ones.



The best fit parameter values corresponding to the theoretical reflectance curve (b) and potential curve (a) are as follows:

$U_1 = U_2 = 0.903$ meV, $U_3 = 0.53$ meV,
 $L_1 = 12.9$ nm, $L_2 = 41.8$ nm, $L_3 = 99.3$ nm,
 $Z_1 = 88.9$ nm, $Z_2 = 19.6$ nm, $Z_3 = 42.5$ nm;
 $\hbar\omega_T = 2543.7$ meV, $\beta_0 = 1.173 \cdot 10^{-3}$, $\hbar\Gamma_0 = 0.105$ meV.
 The background dielectric constant $\epsilon_b = 9.4$ was taken to be the same for the transition layer and the bulk. The number of elementary homogeneous layers was chosen to be $N=100$. A

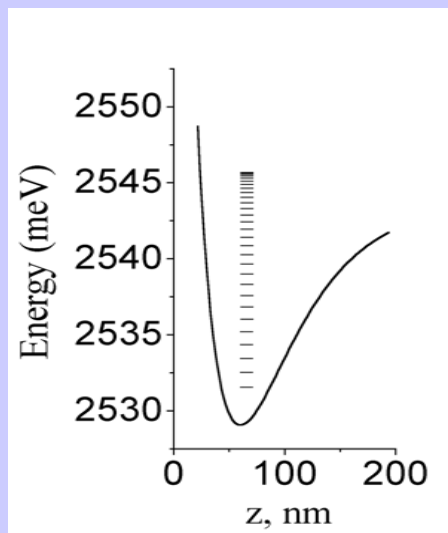
1. N.R. Grigorieva, B.V. Novikov, A.V. Sel'kin, et all, Physics of Solid State **41** (1999) 1437
2. N.R. Grigorieva, B.A. Kazennov, B.V. Novikov, A.V. Sel'kin, Vestnik SPbGU, Ser. 4, №25 (1999) 39
3. H. Azucena-Coyotecatl, N.R. Grigorieva, F. Perez-Rodriguez, A.V. Sel'kin, et all, Thin solid films **373** (2000) 227

CdS_{1-x}Se_x crystals with low Se concentration self-assembled quantum well in the near surface region

Generalized Morse near-surface excitonic potential:

$$U = \begin{cases} U_1 e^{-(z-z_1)/L} + U_2 e^{-2(z-z_2)/L} & z > z_0 \\ \infty & z < z_0 \end{cases}$$

The model Morse near-surface excitonic potential
close to the used potential



The parameter values of this
potential are:

$$U_2 = 2U_1, U_1 = 14.6 \text{ meV},$$

$$L_2 = 2L_1, L_1 = 25 \text{ nm},$$

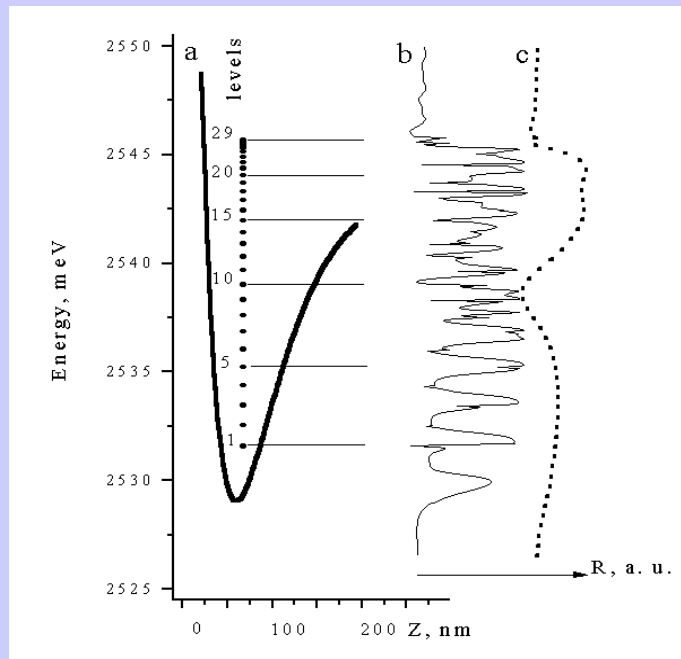
$$Z_1 = Z_2 = 60 \text{ nm}.$$

Longitudinal exciton quantized energy levels are
marked (1 to 29) by lines.

1. H. Azucena-Coyotecatl, N.R. Grigorieva, F. Perez-Rodriguez, A.V. Sel'kin et al, Thin solid films **373** (2000) 227
2. H. Azucena-Coyotecatl, N.R. Grigorieva, F. Perez-Rodriguez, A.V. Sel'kin et al, Superficies y Vacio **9** (1999) 313-315

$\text{CdS}_{1-x}\text{Se}_x$ crystals with low Se concentration self-assembled quantum well in the near-surface region

The model Morse near-surface excitonic potential (a) close to the used potential and the corresponding theoretical reflectance spectra for p-polarization at $\varphi=45$ degrees: b -- low damping, c -- high damping. Longitudinal exciton quantized energy levels are marked and numbered.



Low and high exciton
damping parameters:

$$\text{b: } U_3 = \hbar\Gamma_0/2 = 0.001 \text{ meV,} \\ L_3 = 100 \text{ nm, } Z_3 = 19.6 \text{ nm}$$

$$\text{c: } U_3 = \hbar\Gamma_0/2 = 0.051 \text{ meV,} \\ L_3 = 34.6 \text{ nm, } Z_3 = 19.6 \text{ nm}$$

1. H. Azucena-Coyotecatl, N.R. Grigorieva, F. Perez-Rodriguez, A.V. Sel'kin et al, Thin solid films **373** (2000) 227
2. H. Azucena-Coyotecatl, N.R. Grigorieva, F. Perez-Rodriguez, A.V. Sel'kin et al, Superficies y Vacio **9** (1999) 313