

Quantum size phenomena in bismuth nanostructures

Konstantin Arutyunov^{1,2}

K.-P. Riihonen³, ***E. A. Sedov***¹

¹Moscow Institute for Electronics and Mathematics at National Research University High
School of Economics, Moscow

²Kapitza Institute for Physical Problems, Russian Academy of Science, Moscow

³*NanoScience Centre, University of Jyväskylä, Finland*



JYVÄSKYLÄN YLIOPISTO
UNIVERSITY OF JYVÄSKYLÄ

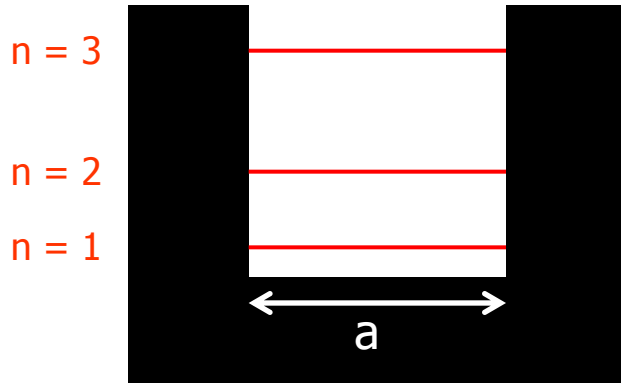


Outline

- **Introduction: Quantum Size Effect (QSE)**
 - **Existing experiments**
 - **Bismuth: properties and fabrication**
 - **2D films**
 - **1D nanowires**
 - **Conclusions**

Size quantization

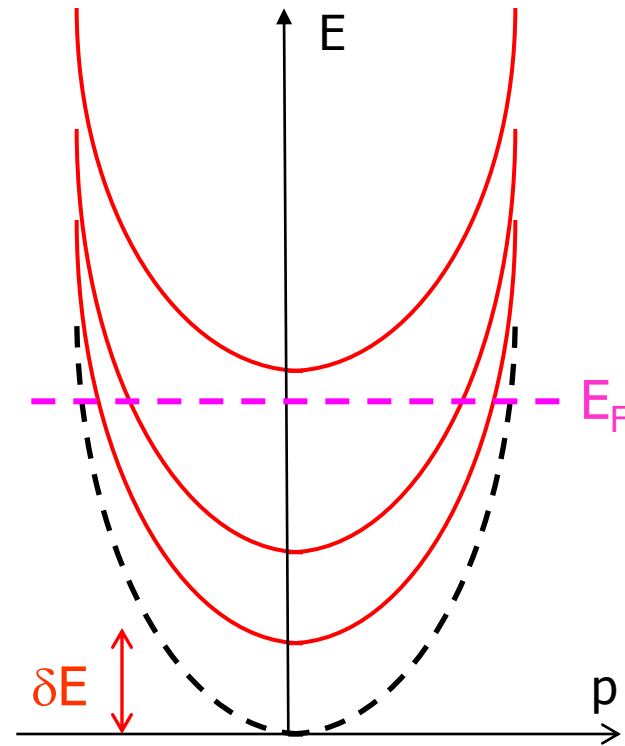
Particle in a potential 'box'



$$E_n = \frac{\hbar^2 \pi^2}{2a^2 m} n^2,$$

where $n = 1, 2, 3 \dots$

Conducting electrons
Size quantization



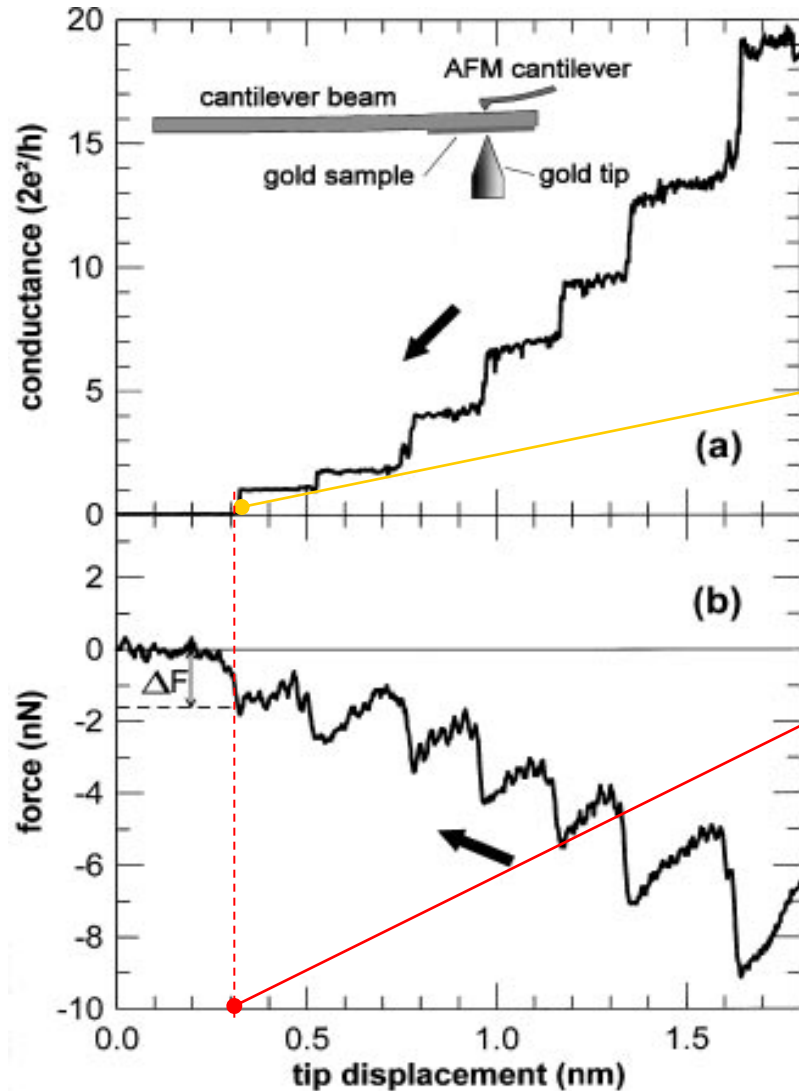
If Fermi energy E_F constant :

- properties should 'periodically' depend on the dimension a
- below a certain scale (de Broglie wavelength) $\delta E > E_F$: metal-insulator transition

For a 'good' metal ($E_F \sim 1$ eV, $m^* = m_0$) quantum size effects are important at scales of about 1 nm

Chewing gum experiment

G. Rubio, N. Agraït, and S. Vieira,
Atomic-Sized Metallic Contacts: Mechanical Properties and Electronic Transport
Phys. Rev. Lett. **76**, 2302 (1996)

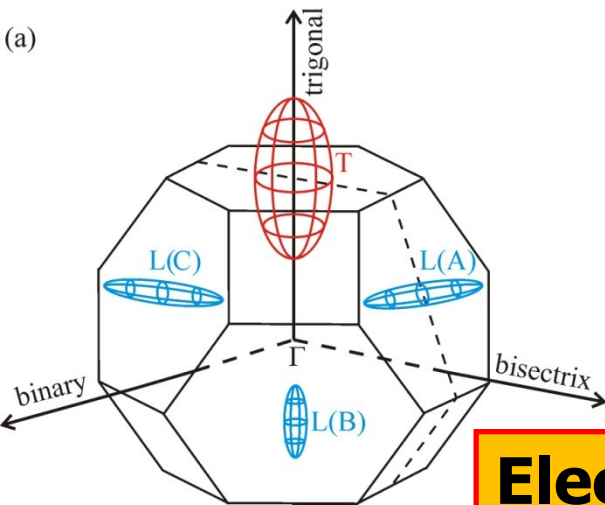


Electric conductivity turns to zero

Diameter ~ 0.3 nm

For gold 0.3 nm is about one interatomic distance...

Bismuth: unique material for solid state physics



Electron mass $m^* < 0.01 m_0$

Anomalously small $E_F = 28 \text{ meV}$

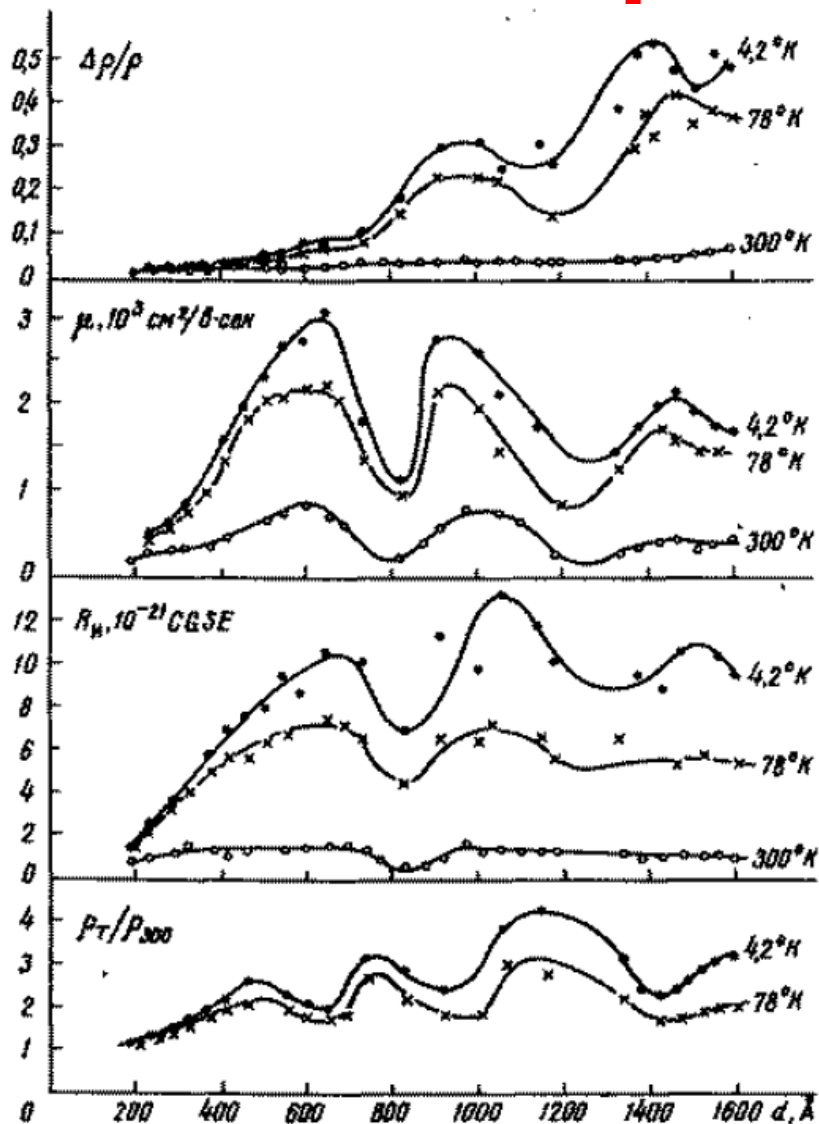
Electron concentration $n_e \sim 3 \times 10^{17} \text{ 1/cm}$

Electronic properties of Bi are strongly determined by the purity of the sample and its orientation vs. crystal axes

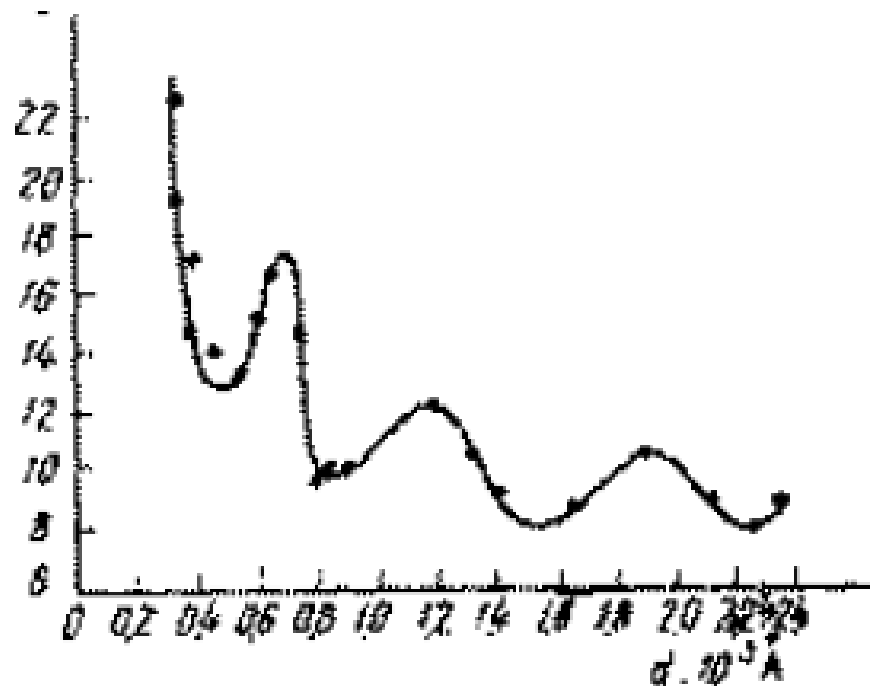
Good sample should be:

- pure (low electron concentration \rightarrow low E_F)
- single crystal (anisotropic energy spectrum)
- not mechanically stressed

First experiments on Bi films



Yu. F. Ogrin, V. N. Lutski and M. I. Elinson,
Pisma ZhETP 3,114(1966)

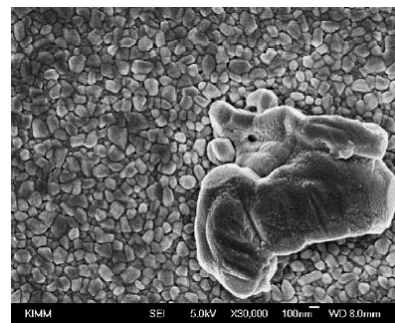
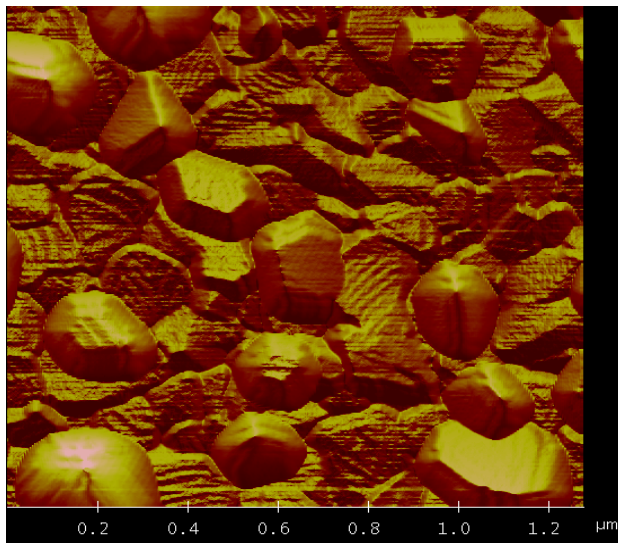


Yu. F. Ogrin, et. al., *ZhETP* 53,1218 (1967)

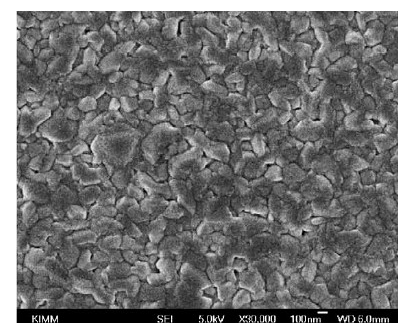
Qualitatively the effect is observed,
while theory interpretation is
problematic due to polycrystalline
structure of films with relatively random
orientation of grains

Bi film fabrication: optimization of substrate and deposition

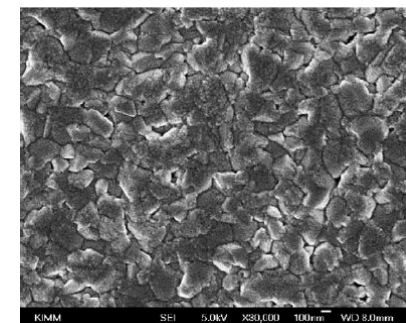
Substrate	Thickness nm	P _{evap} , 10 ⁻⁶ mBar	T _{evap} , K	Evaporation rate, nm/s	ρ _{ROOM} , 10 ⁻⁸ Ω * m	ρ _{77K} , 10 ⁻⁸ Ω * m	4.2 K		
							ρ _{4.2K} , 10 ⁻⁸ Ω * m	n _{4.2K} , 10 ¹⁸ , 1/cm ³	μ _{4.2K} , cm ² /Vs
Bulk Bi					150		450	0.3	2
MICA	40	3.1	~ 300	0.15	221	400	401	10	0.15
	150	5.1	~ 380	0.1	302	842	1106	9	0.07
	40	0.68	77	0.15	1588	2192	2300	20±4	0.0068
SiN	40	1.6	~300	0.16	600±30	1490±70	1510±90	60±20	0.0069
Si	40	1.6	~300	0.15	572	1320	1476	20	0.02



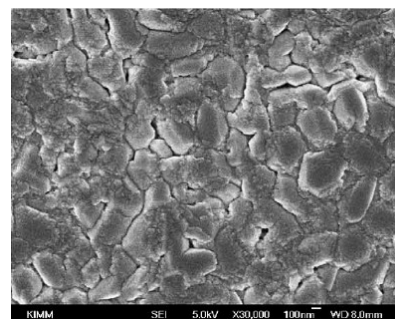
T = 373 K



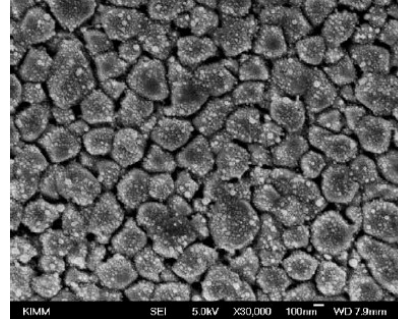
T = 393 K



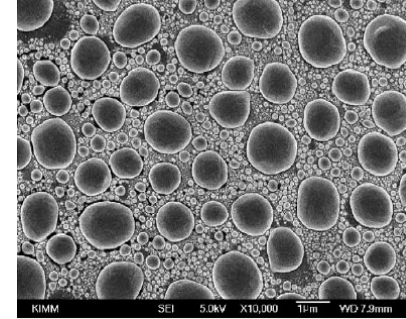
T = 413 K



T = 433 K



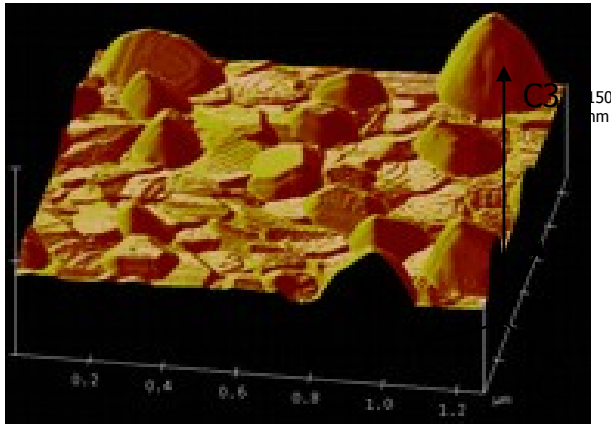
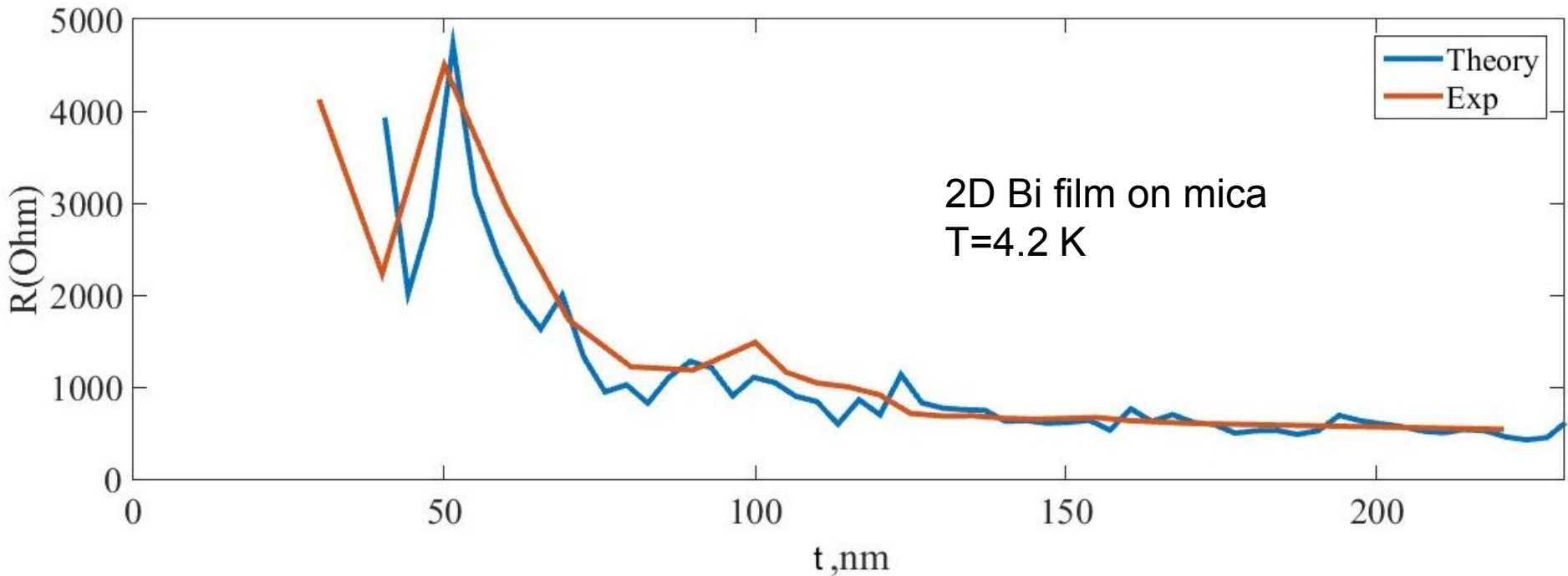
T = 448 K



T = 473 K

Bi film on glass deposited @ room T
With optimized deposition it is possible to obtain Bi film on mica with the grain size of about 1 μm.

2D bismuth film

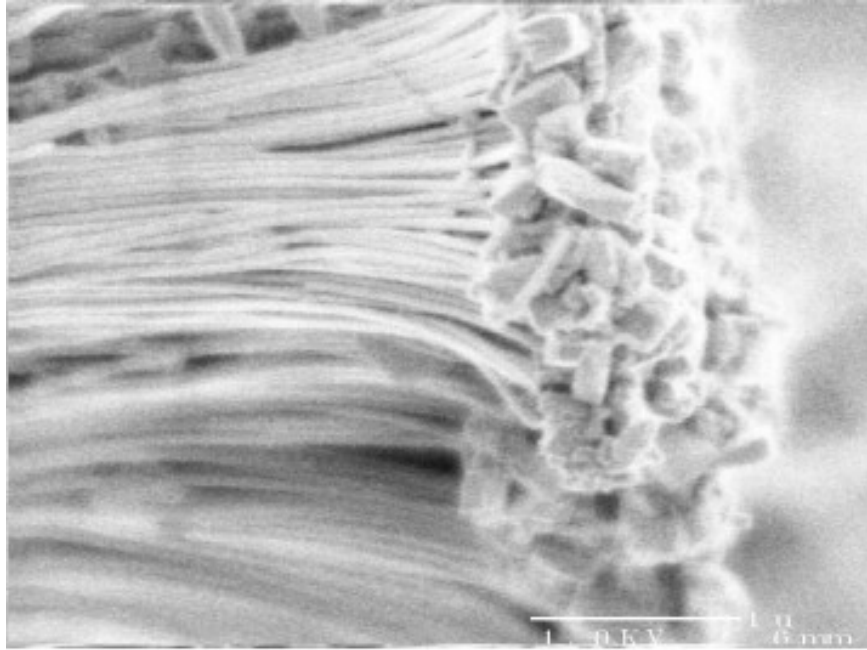


Simulated theory curve assumes wide bismuth film with trigonal axis C3 normal to the sample plane and random orientation of C2 axes in each grain

1D limit: Current status of experiments

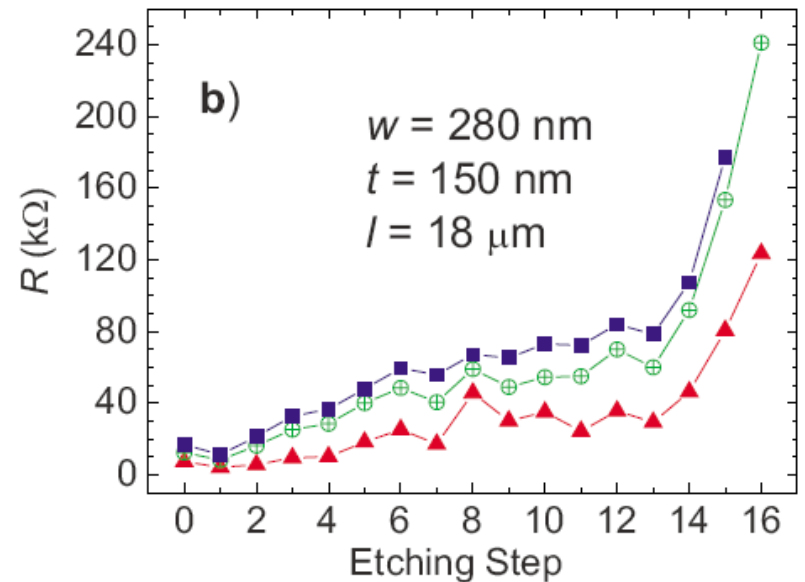
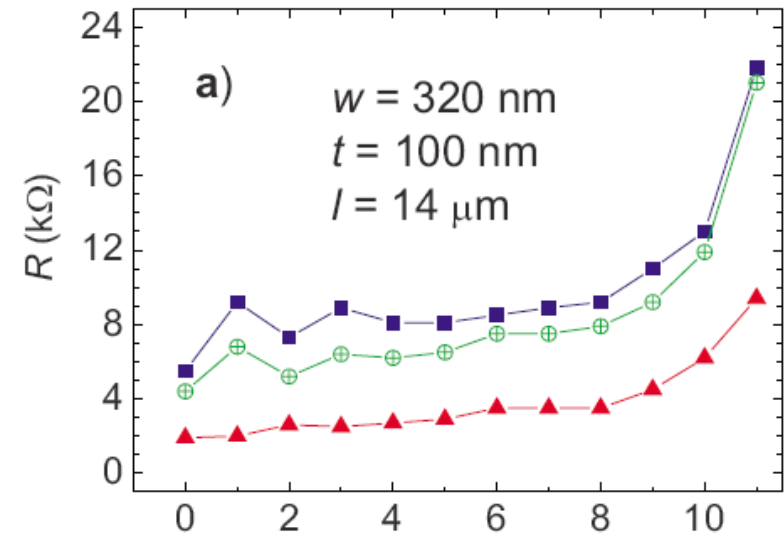
M.S. Dresselhaus, et.al., PRB **58**, R10091 (1998)

M.S. Dresselhaus, et.al., PRB **61**, 4850 and 2921 (2000)



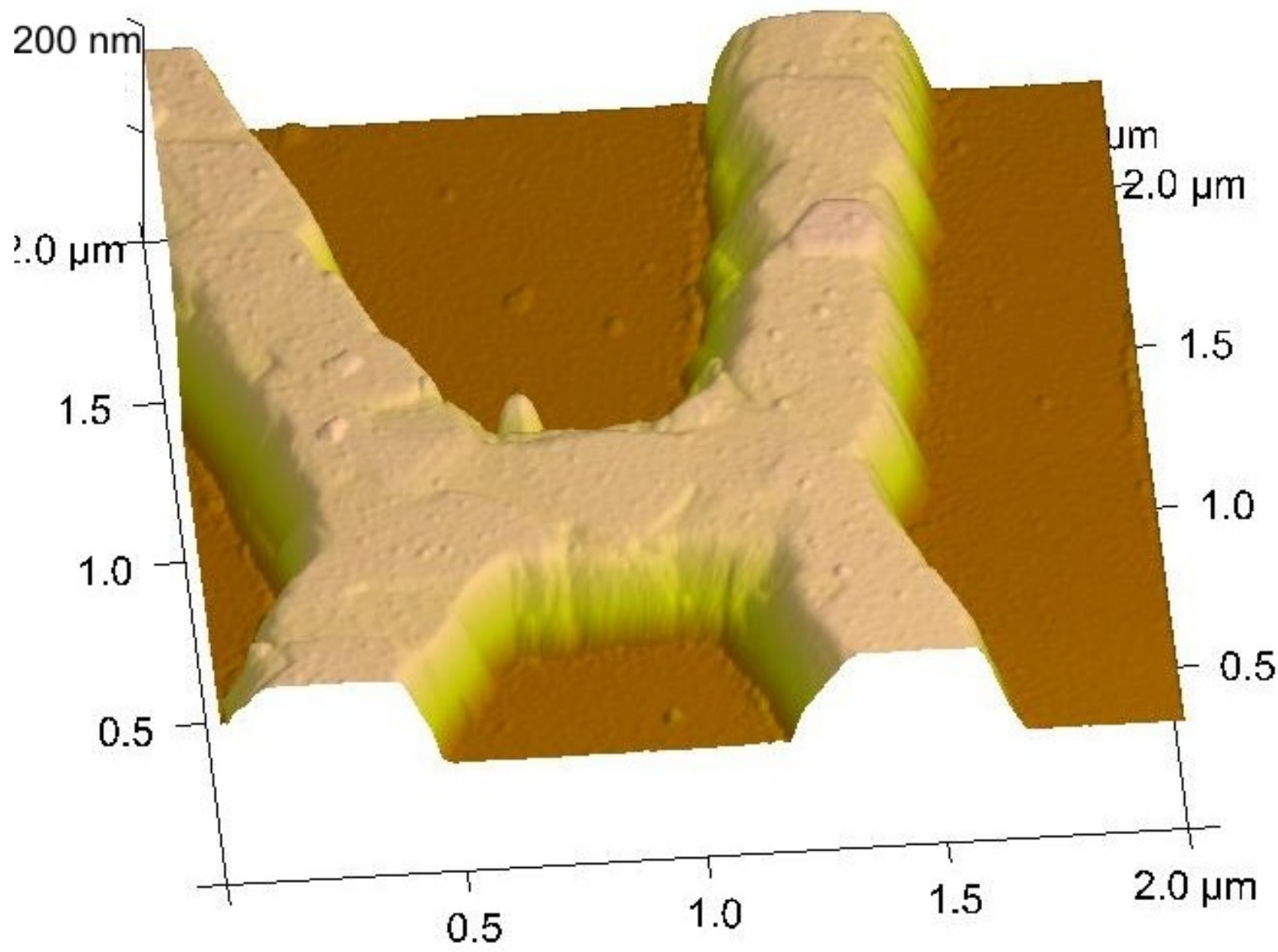
SEM image of a bundle of Bi nanowires after the alumina template has been dissolved in the H₃PO₄/CrO₃ solution for 4 days. The Bi chunks on the right of this image are the remnants of a thin Bi film left over from the Bi melt used to inject Bi into the pores [S.B. Cronin, PhD thesis, MIT 2002].

- not a single wire: array of 'corals'
 - dirty
- not well defined shape
 - stressed (?)
- non-Ohmic I-V (contact or structural problems?)
 - average diameter > 60 nm



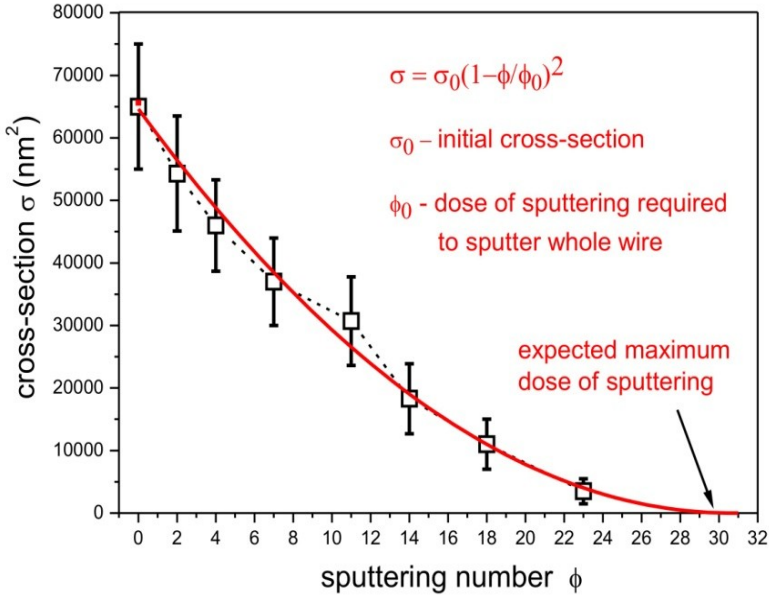
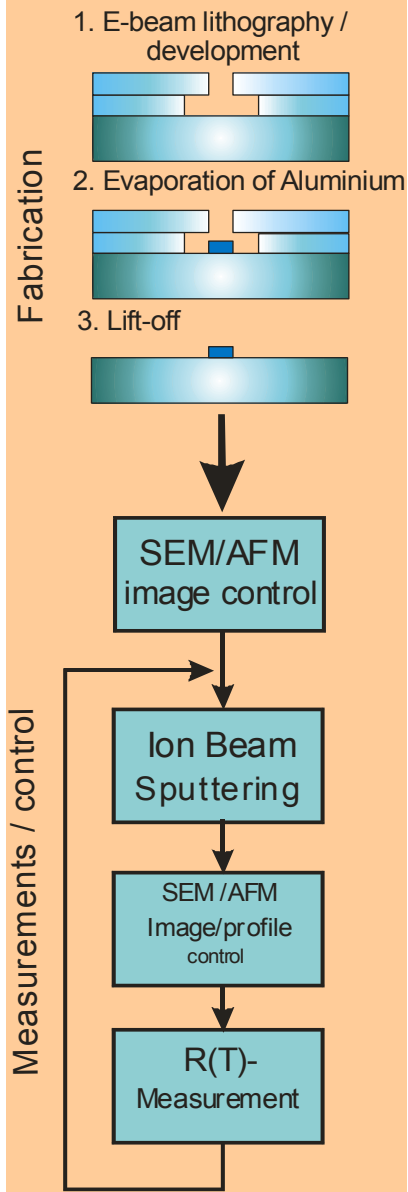
Long Bi nanowire formed of many grains, no theory fit is possible [Farhangfar S. PRB **76**, 205437 (2007)]

Single crystalline quasi-1D bismuth nanostructure



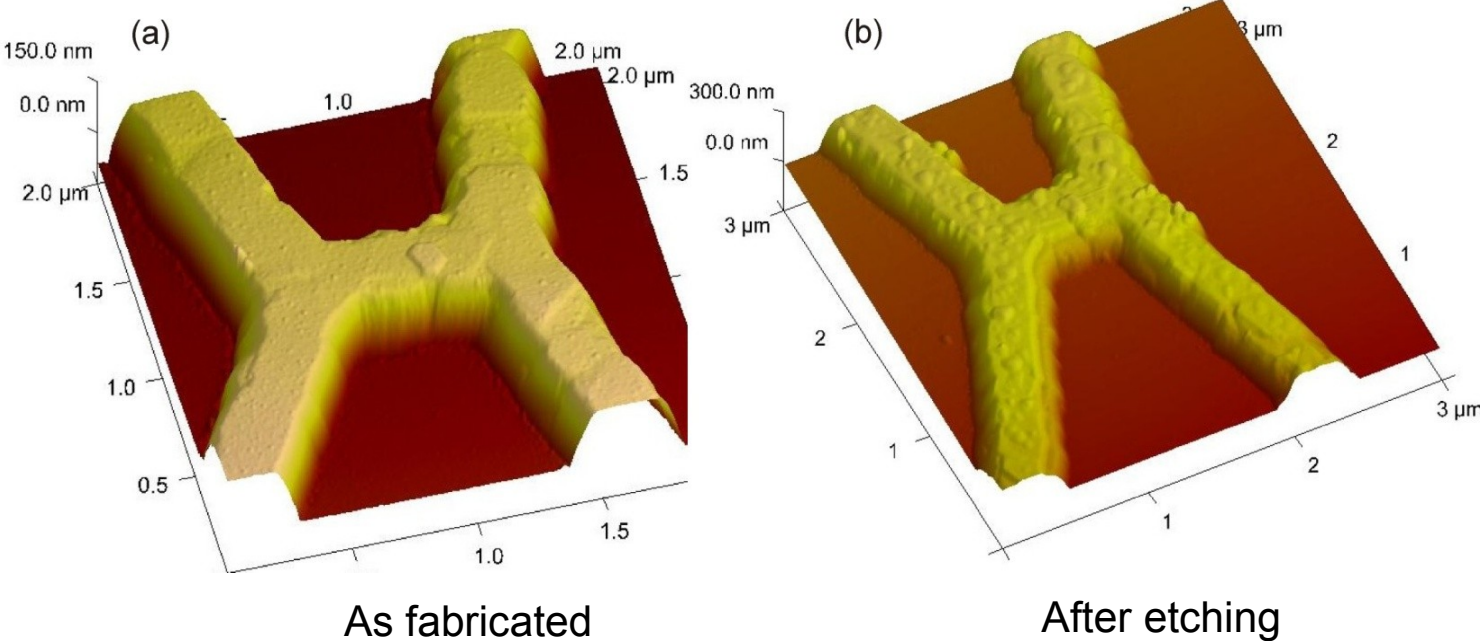
Progressive reduction of nanowire cross section by low-energy ion beam etching

RESEARCH FLOW-CHART



Penetration depth of 1keV Ar⁺ ions into Bi matrix is about 1.5 nm:
method is virtually non-invasive

M.Zgirski, *et. al.*, *Nanotechnology* 19 055301 (2008).
 K. Yu. Arutyunov, *patent* FI-122010.



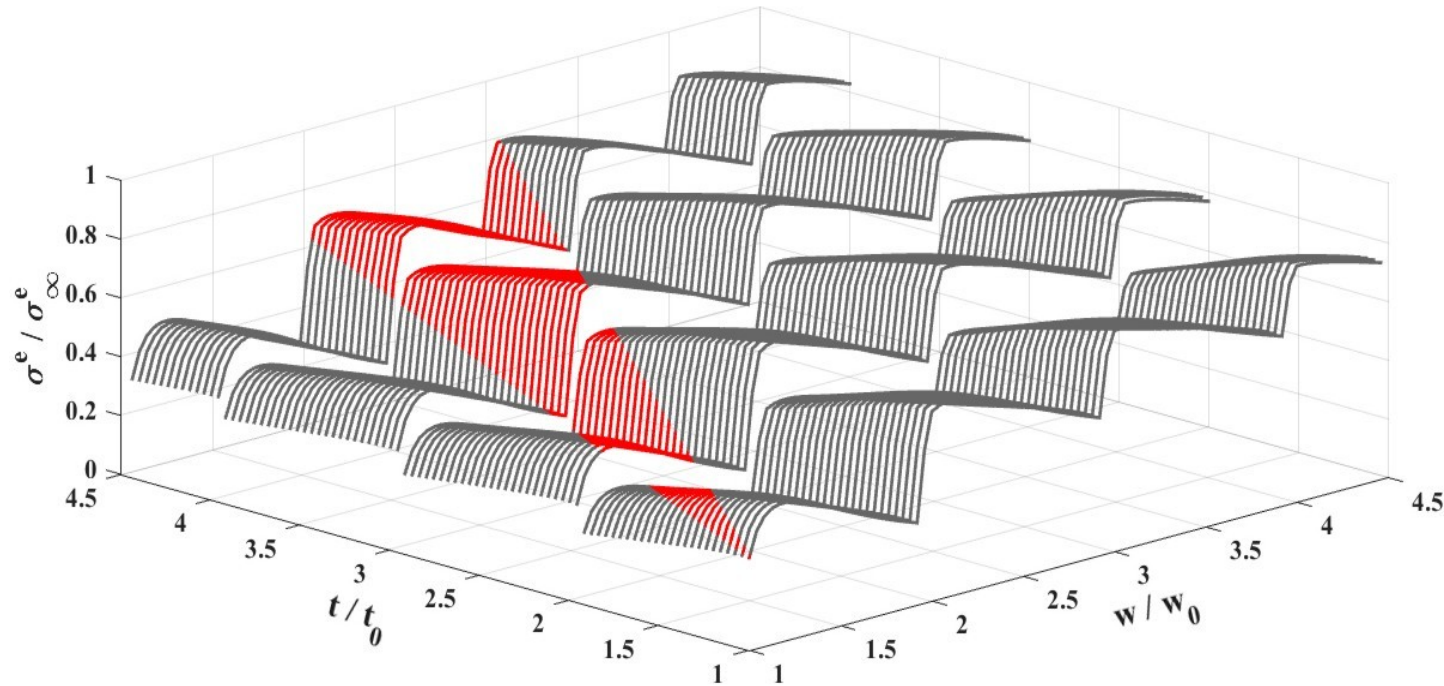
1D nanowire with rectangular cross section: theory

$$\sigma^e = \frac{2e^2}{\pi\hbar S} \frac{\mu_x^e}{m_z^e} \sum_{ij} \frac{[r_w][r_t]}{[\sum_{i'j'} \Lambda_{i'j'}^{ij} \sqrt{U_{i'j'}^e}]} (2\hbar/V_0)^2 \sqrt{U_{ij}^e}$$

$$\Lambda_{m'n'}^{mn} \equiv (2 + \delta_{mm'})(2 + \delta_{nn'})$$

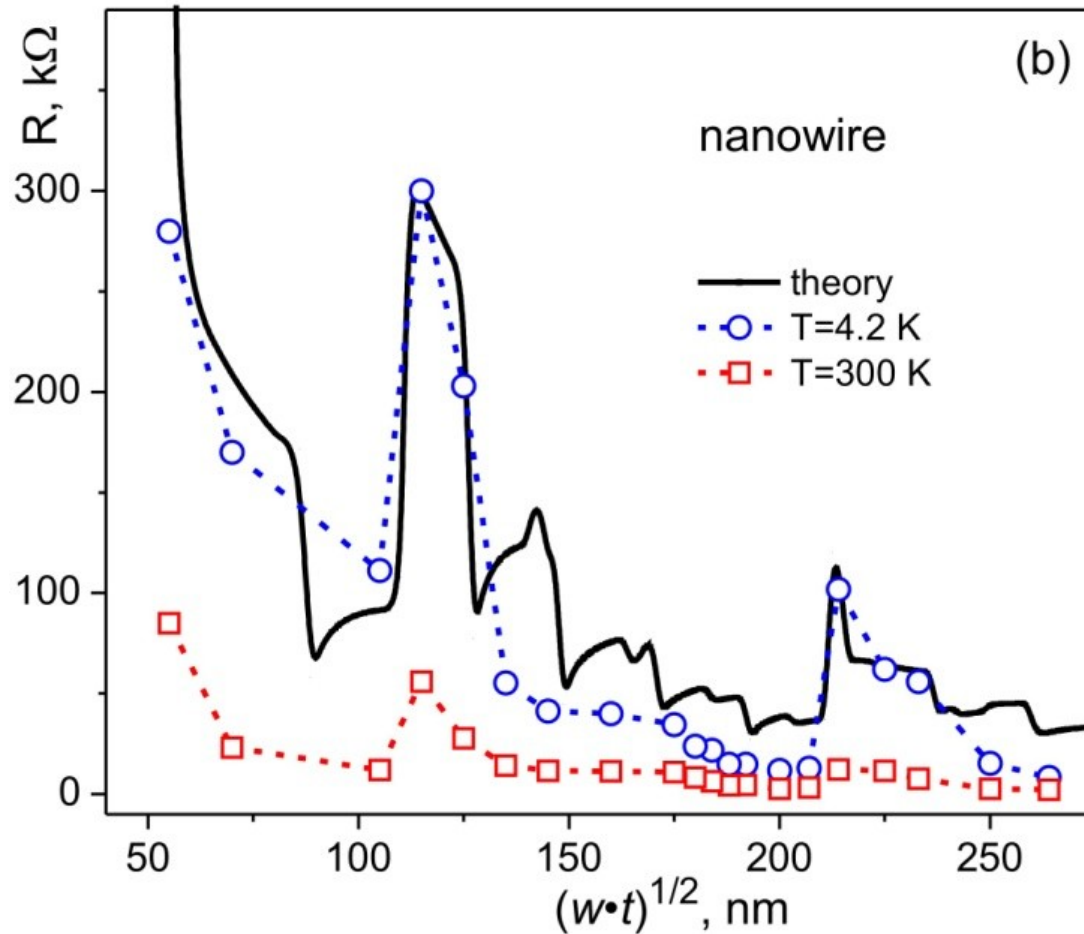
$$U_{ij}^e \equiv 1 - (i/r_w)^2 + (\mu_y^e / \mu_x^e) [1 - (j/r_t)^2]$$

S is the volume concentration of scatterers each of strength V_0 , Parameters $r_w \equiv w/w_0$ and $r_t \equiv t/t_0$ are width and thickness of nanowire, normalized by the relevant dimensions $w_0 = \hbar\pi(M_x\Delta_x)^{1/2}$ and $t_0 = \hbar\pi(M_y\Delta_y)^{1/2}$ corresponding to metal-to-semiconductor transition. Parameters S and V_0 are not known with necessary accuracy and are set by fits for 'bulk' sample $w \gg w_0$, $t \gg t_0$ [Farhangfar S. **PRB** 74, 205318 (2006)]



Calculated electronic conductivity of bismuth nanostructure cut along bisectrix axis. For nanowire of rectangular cross section ($w \cdot t$) the electronic conductivity σ^e exhibits oscillatory behavior as function of corresponding dimension(s). The bulk conductivity σ^e_∞ recovers at scales $w \gg w_0$, $t \gg t_0$, where $w_0 \approx 110$ nm and $t_0 \approx 25$ nm are the critical width and thickness corresponding to metal-to-semiconductor transition. Bright cone represents the range of studied samples.

1D nanowire: experiment

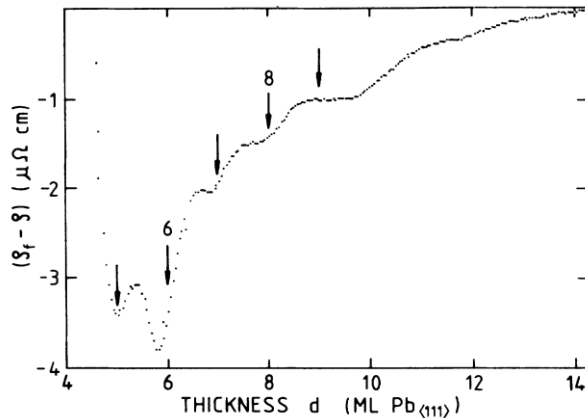


Dependence of bismuth nanowire resistance R on effective diameter $d_{\text{eff}}=(w \cdot t)^{1/2}$. Circles (\circ) correspond to liquid helium temperature $T=4.2$ K, squares (\square) stand for room temperature data. Dotted lines connecting experimental points are guides for eye. Theory fit (solid line) assumes trigonal axis $C3$ being normal to the sample plane and ~ 3 degree misorientation angle between the sample axis and the crystallographic bisectrix axis $C2$. Best fit 'trajectory' in coordinates $R(w, t)$ stands for reduction of $dw=1.87$ nm and $dt=1.69$ nm between successive points starting from a nanowire with initial width $w=300$ nm and thickness $t=265$ nm.

Other quantum size phenomena

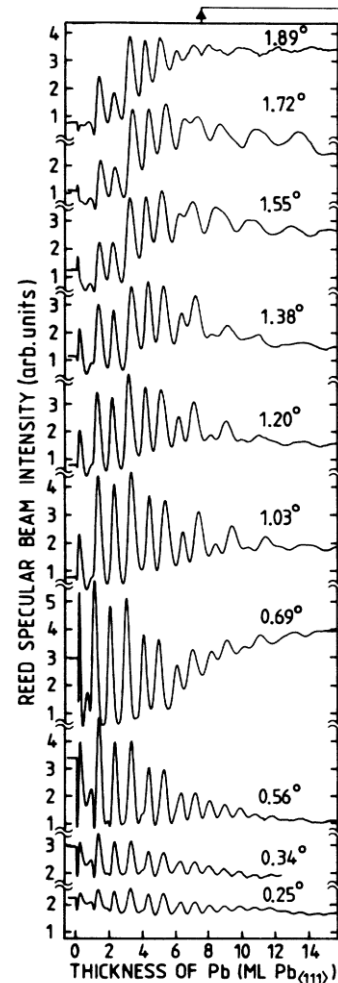
QSE should be observed in any low-dimensional system (e.g. film or wire) and should also affect properties other than electric conductivity.

2D conductivity

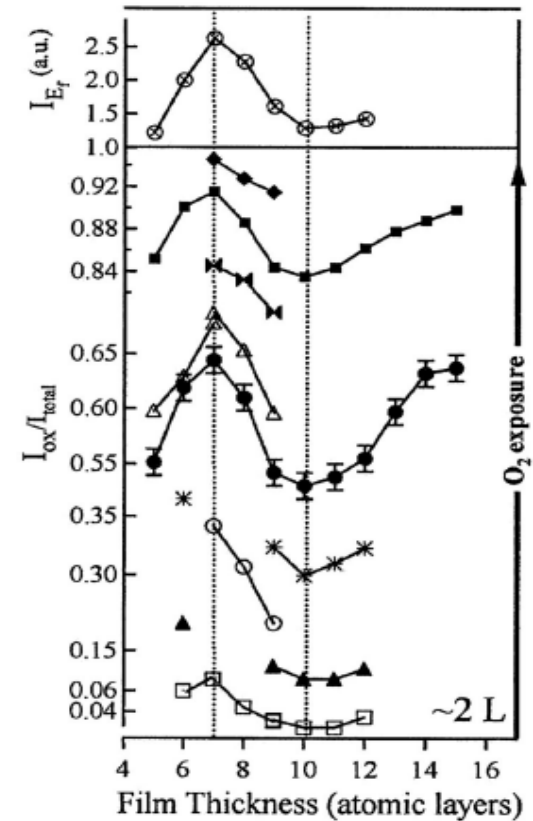


Epitaxial Pb films
M. Jalochovski, E. Bauer
PRB, 38, 5272 (1988)

Reflectivity of lead film



Surface chemical activity



Thickness-dependent variations in the oxidation rate of Mg film 17
L. Aballe, et.al. PRL 93, 196103 (2004)

Conclusion on quantum size effect in normal metals

- QSE is a universal phenomenon
- Observation of QSE in 'good' metals requires dimensions ~ 1 nm
- In semimetal like bismuth QSE can contribute already at 50 nm scales

Thank you !

Master degree

**“Quantum Information
Technology”**

2 year program in English to
start in September 2017

karutyunov@hse.ru