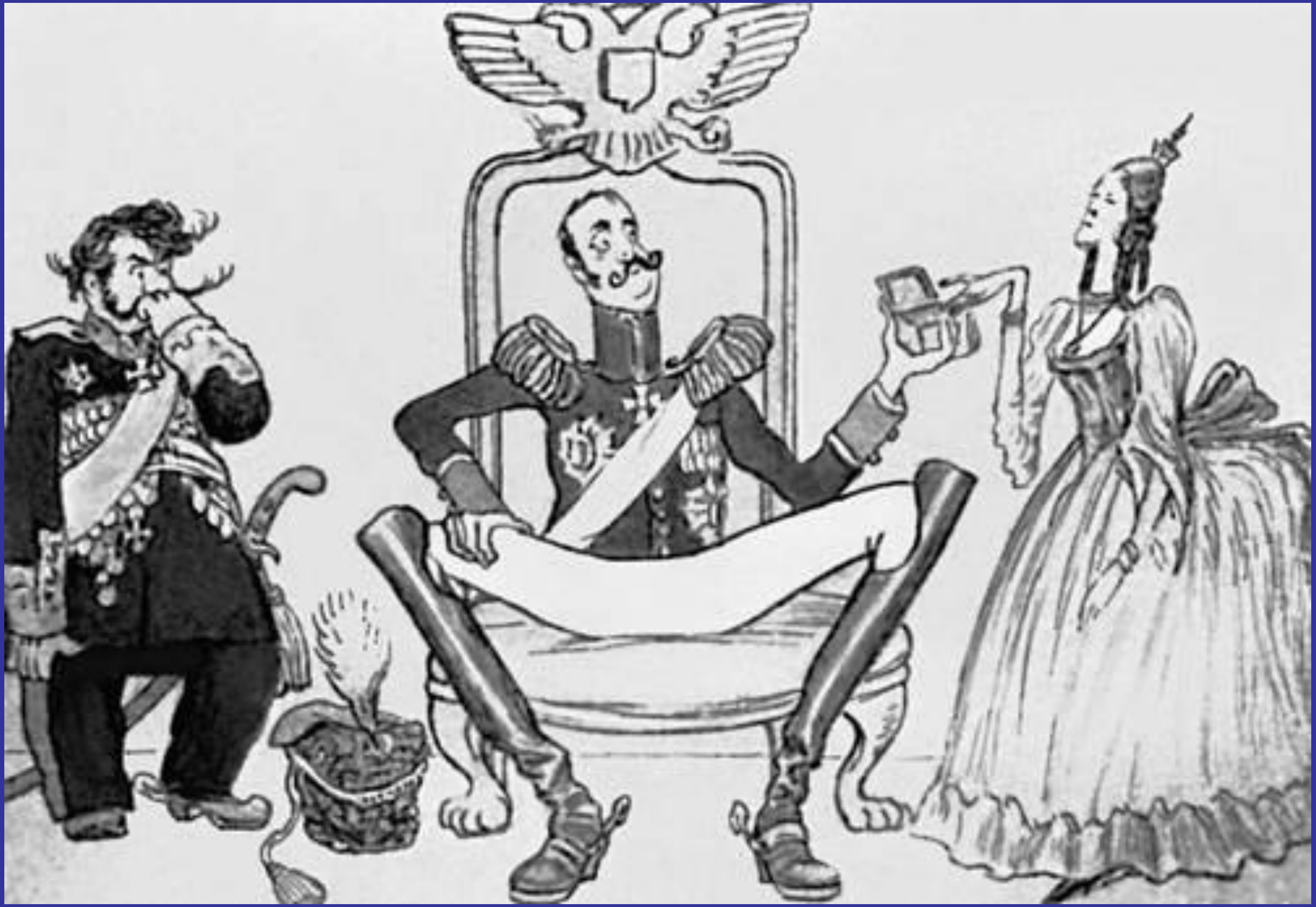
Каталитический рост нанопроволок и наносфер в квантованных вихрях сверхтекучего гелия: структура, строение и электрические свойства

Е.Б. Гордон,
Институт проблем химической физики РАН

«Проблемы ФТТ и ВД» 2010

Рассказ о том, как русский умелец сумел красиво испортить микромеханический механизм



Идея – похвастаться перед английской королевой – не изменилась до сих пор:

в России нет микроэлектронной промышленности –

некуда приложить полученные знания,

нет устройств для манипуляции с нанообъектами

Главный совет Левши:

не чистить ружья мелом

– пули выпадают

2003 год - Нобелевская премия по физике Алексея Алексеевича Абрикосова, Виталия Лазаревича Гинзбурга и Энтони Леггетта – вихри Абрикосова

2004 год – «Открытие» supersolidity

2006 год, июнь– статья Латропа и др.
визуализация кантованных вихрей

Quantized vortices in He II

- They appear only in superfluid phase assuring the superfluidity existence (rotons). Any perturbation causes the vortices, then they slowly decayed.
- They either form closed loops (smoker) or they are *pinned to protuberances (tornado).*
- Any impurity has affinity to vortex core – *few K per atom.*
- *They are practically one-dimensional features –*

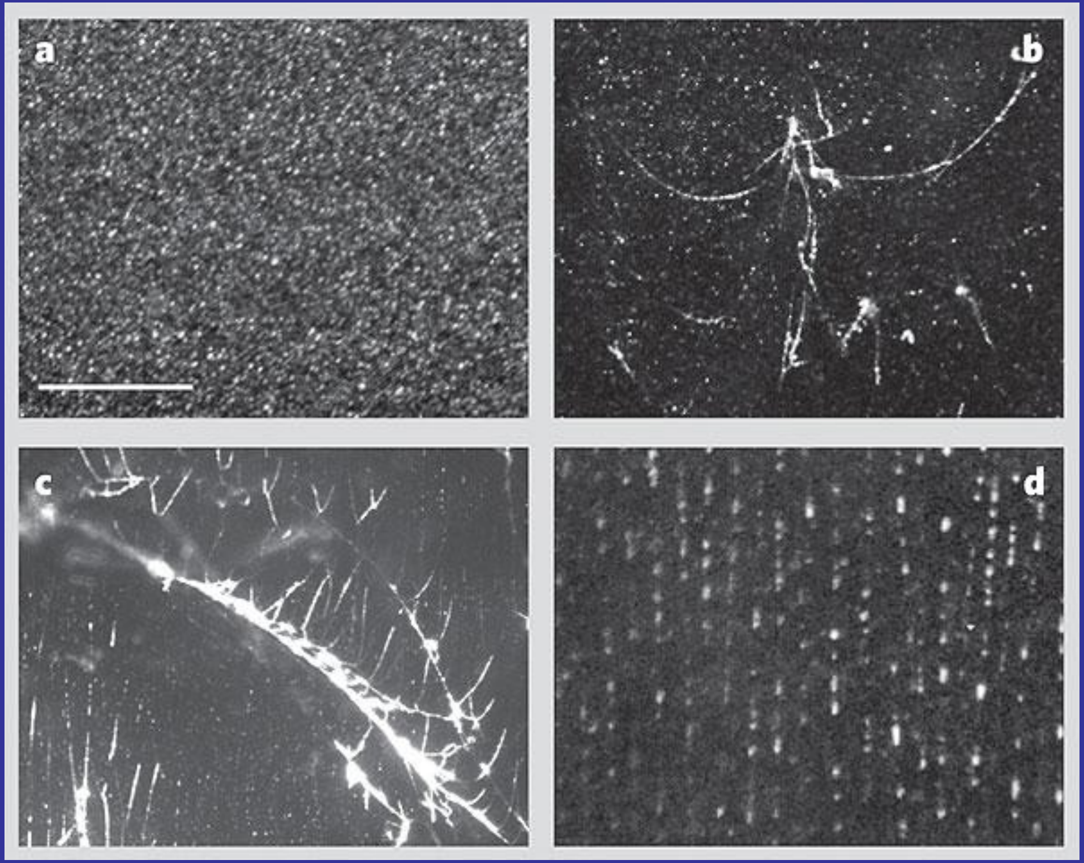
  $U = \ln(r/a)$ *, where* $a = 0.7Å$*,*

  whereas their length is up to few cm.

Nature 441, 588 (1 June 2006) | doi:10.1038/441588a

SUPERFLUID HELIUM: Visualization of quantized vortices

Gregory P. Bewley, Daniel P. Lathrop and Katepalli R. Sreenivasan



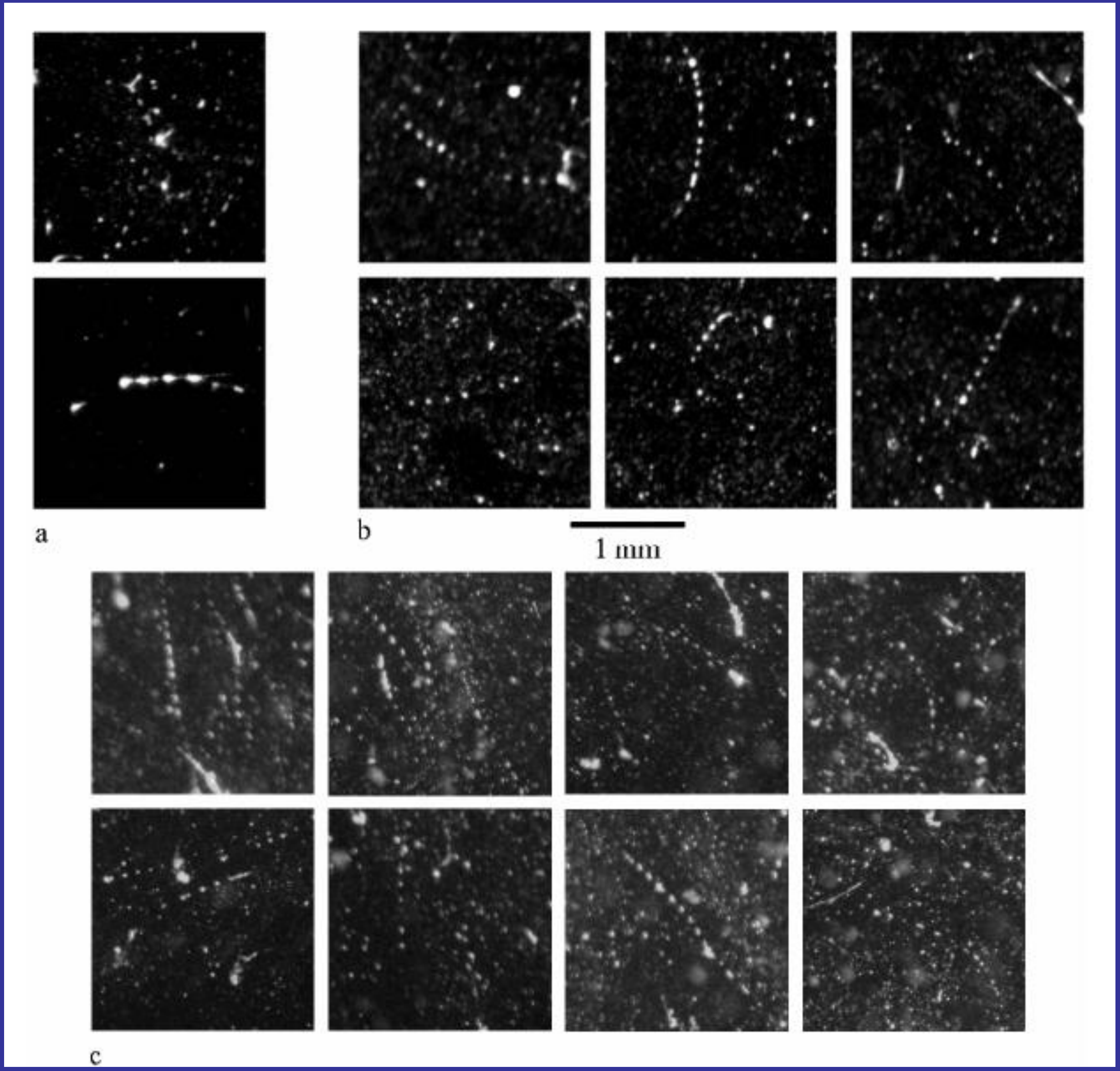
Quantized vortex cores in liquid helium.
a, just above the transition temperature, when they are uniformly dispersed;
b, c, on branching filaments at tens of millikelvin below the transition temperature; **d,** regrouping along vertical lines for steady rotation about the vertical axis.
In **b** and **c**, the particles on lines are evenly separated in small regions. Scale bar, 1mm.

The strong evidence for the interpretation is the Feynman rule validity :

The vortices should be directed along the cryostat rotation axes and their density should be proportional to angular velocity,

and that was really observed in experiment.

Bewley thesis: dotted lines

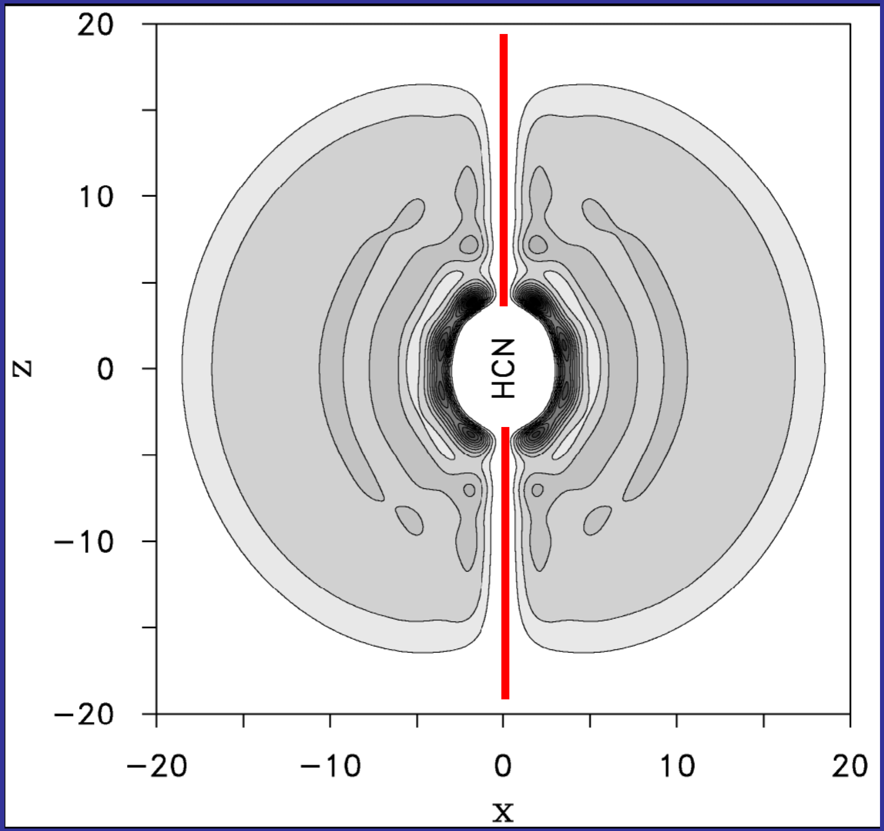


The hydrogen micron–sized grains in a vortex core seemed to repulse each other

VOLUME 85, № 5 PHYSICAL REVIEW LETTERS 31 JULY 2000

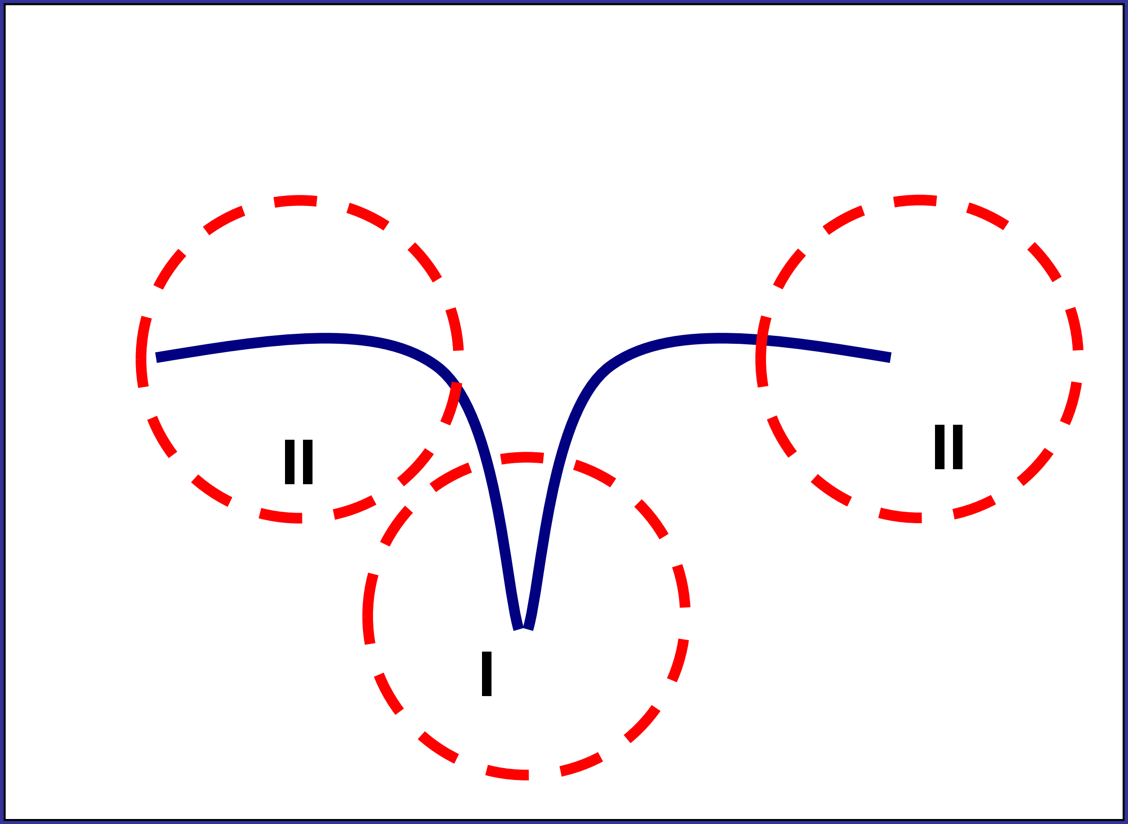
Pinning of Quantized Vortices in Helium Drops by Dopant Atoms and Molecules

Franco Dalfovo, Ricardo Mayol, Martí Pi, and Manuel Barranco



Density distribution in the *xz* plane for a HCN-He_{500} droplet hosting a vortex along the *z* axis. Lengths are in Å. Contour lines are drawn between 12 equally spaced intervals of density, where white is for density less than $7.5 * 10^{-3}$ Å^{-3},
and the darkest level corresponds to density higher than $9 * 10^{-2}$ Å^{-3}.

The vortex has a potential but there is no attractive force to it – too steep slope



Two states – one in a vortex core,

the rest is in the rest volume of liquid

The pinning impurity to a vortex proceeds only at their meeting (sweeping)

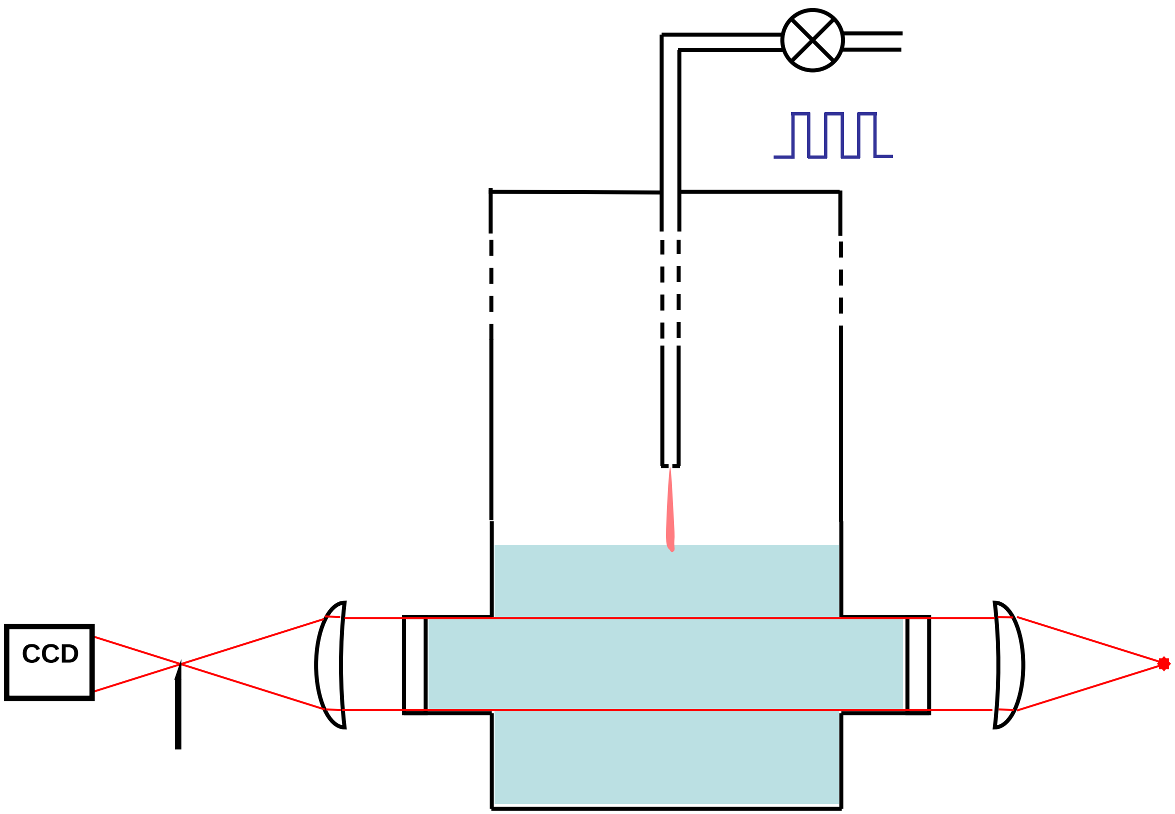
Что будет, если вводить в сверхтекучий гелий не крупинки, а молекулы водорода.

Мы знали, как это делать.

Эксперимент – Япония,

Токийский технологический институт

E. B. Gordon , R. Nishida, R. Nomura, Y. Okuda. Письма в ЖЭТФ, 2007, Vol. 85, No. 11, pp. 581–584



Schlieren technique

Depth resolution 3 см, space resolution 20 μ.

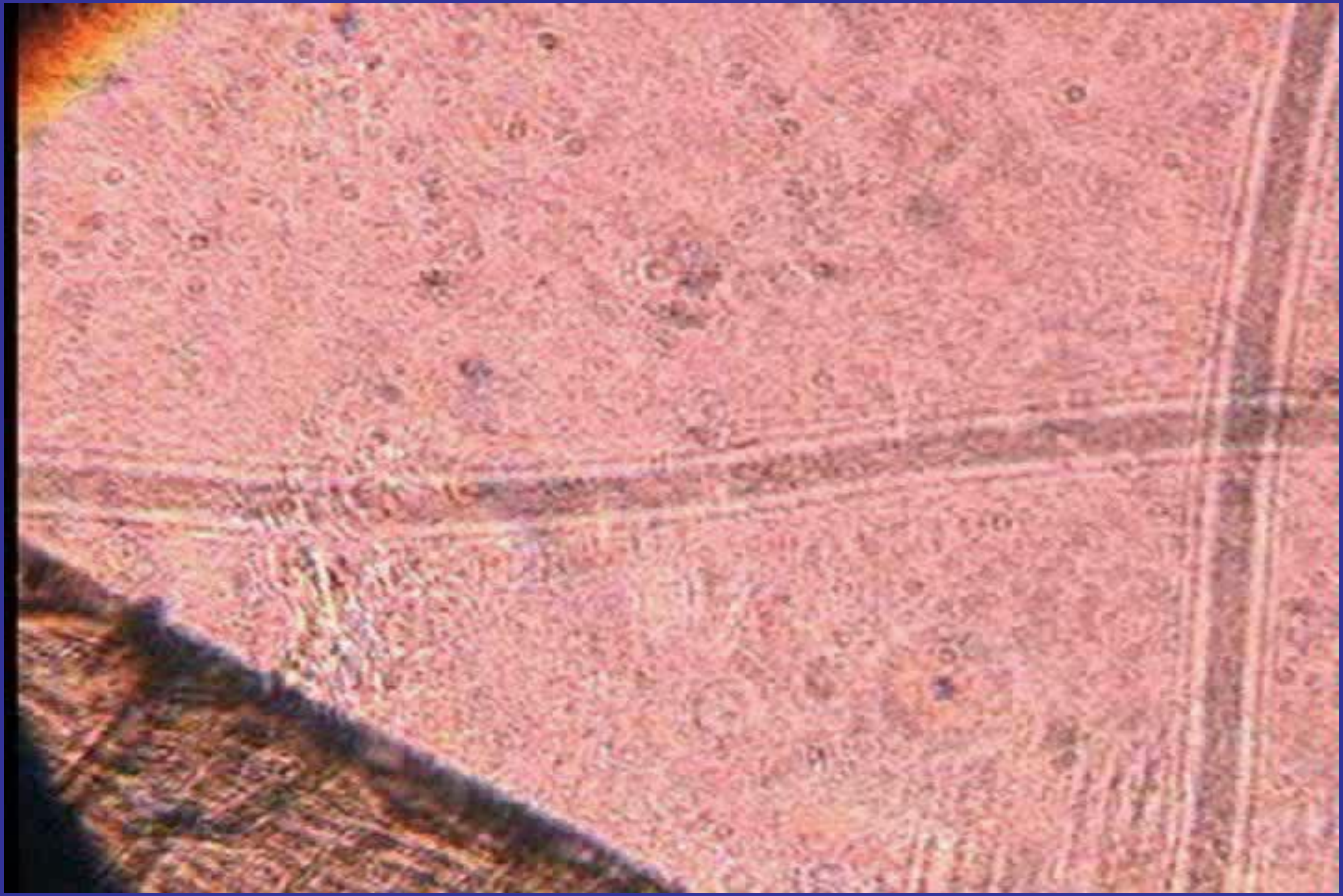
Helium-impurity jet through 0.3 mm orifice

Electromagnetic valve – pulse duration 80 ms, P = 6 bar

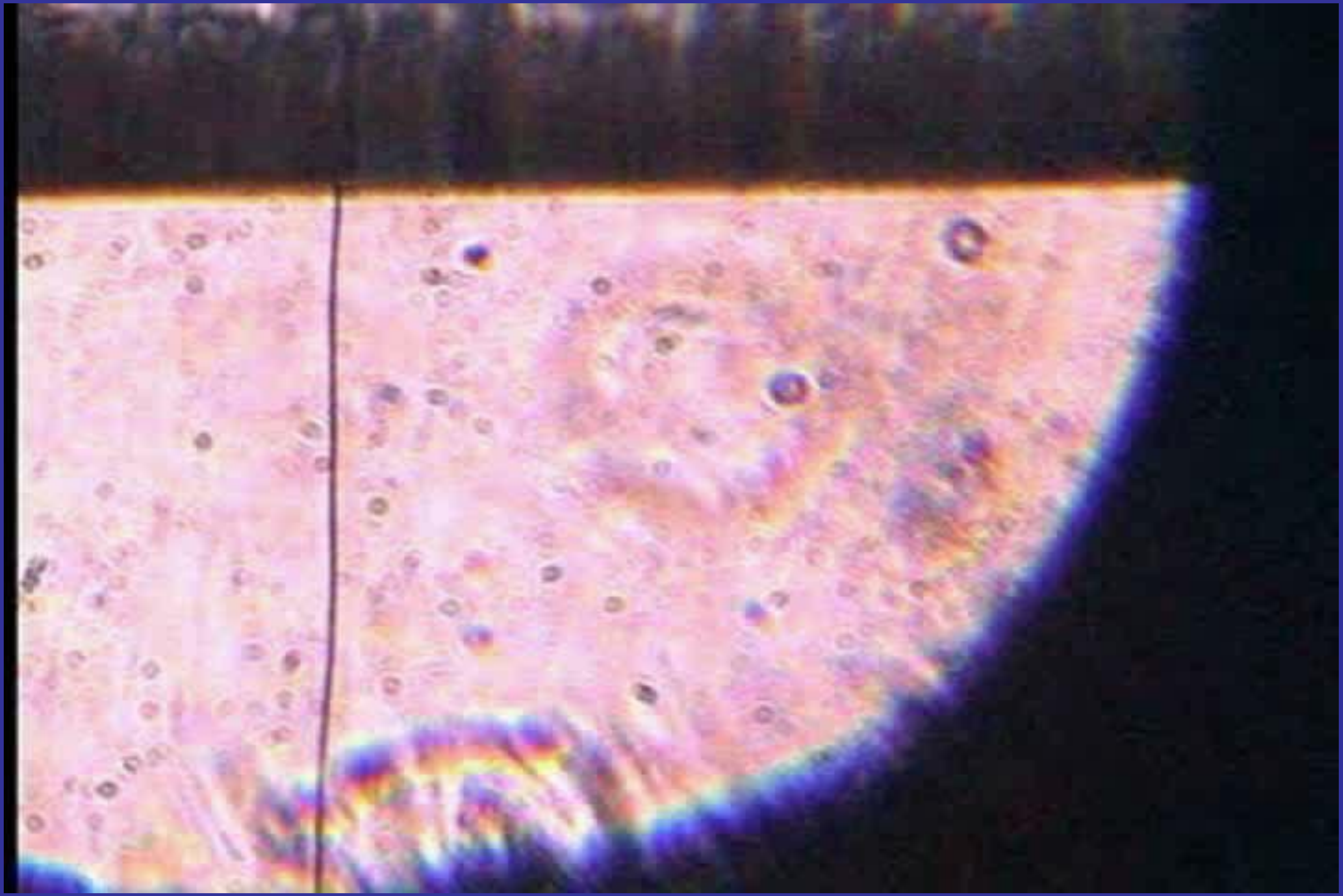
The fridge diameter 16 cm, interwindow distance 22 cm

Hydrogen-deuterium above λ-point (T = 2.3K)

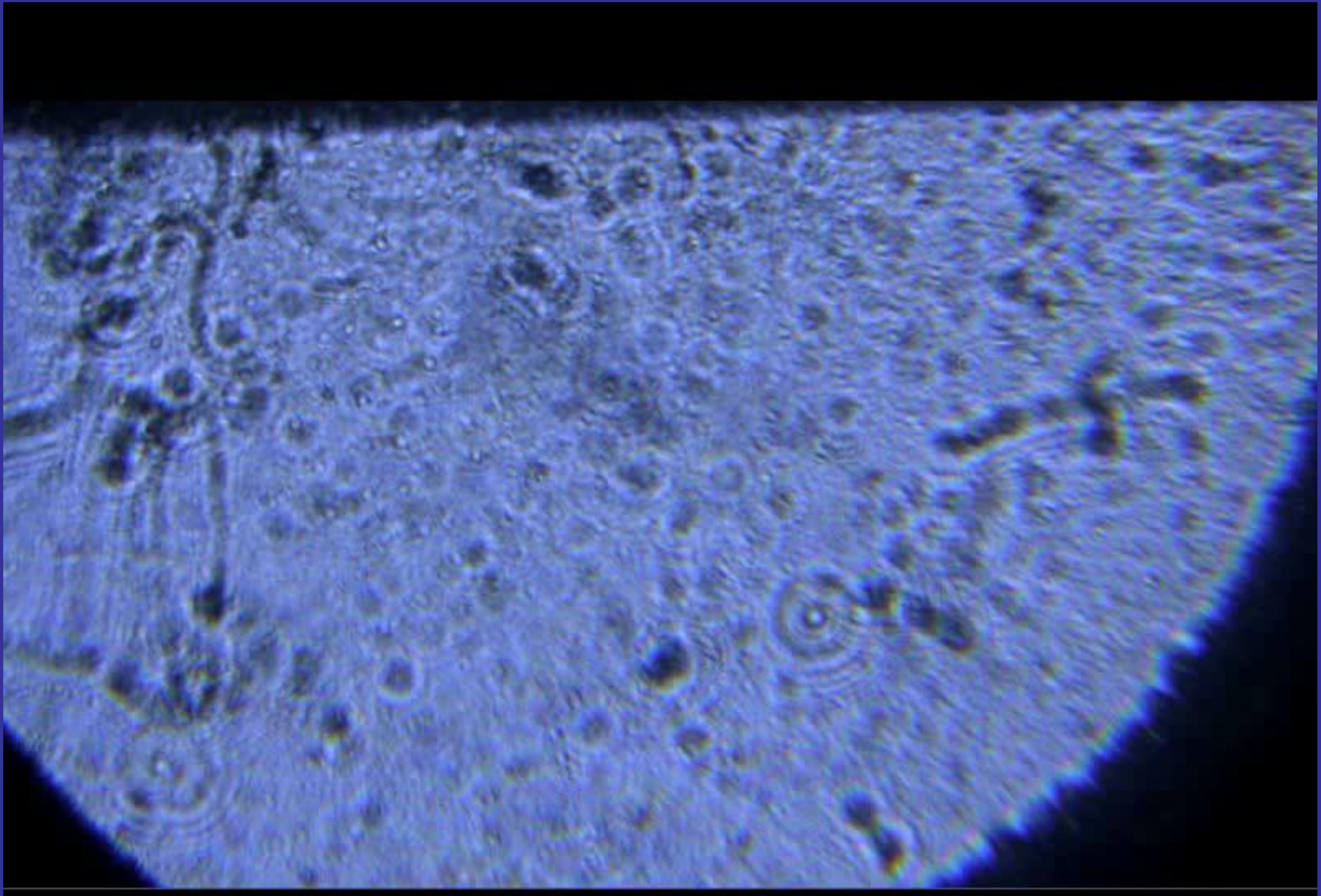
Hydrogen-deuterium below λ-point (T = 1.8K)



The vortex “pinned to protuberances”



Водород-дейтериевая веревка, сплетенная выше λ-точки из проволочек



Молекулярный водород образует
в нормальном жидком гелии «шарики»,
а в сверхтекучем - длинные нити, ведущие себя
подобно вихрям

New mechanism for impurities condensation in superfluid Helium

E. B. Gordon, Y. Okuda, JETP Letters, 85, 581 (2007), JLTP, 35, 209 (2009)

- Any guest particles have affinity to the core of quantized vortex.
- The particles captured there have enhanced rate of mutual collisions leading to coagulation.
- Resulting growth in its size increases the cluster lifetime in a vortex core and consequently their local density.
- Such self-accelerating catalytic process of condensation becomes to be prevailing .
- Due to the small (<1Å) thickness of a vortex core the primary condensation products should be extremely thin long filaments.
- Quantized vortex willingness of pinning to any protuberance may cause the filament growth just at needle electrodes

Образование металлических нанопроволок - лазерная абляция внутри HeII

Золото и медь – Fribourg (Швейцария)

Структура

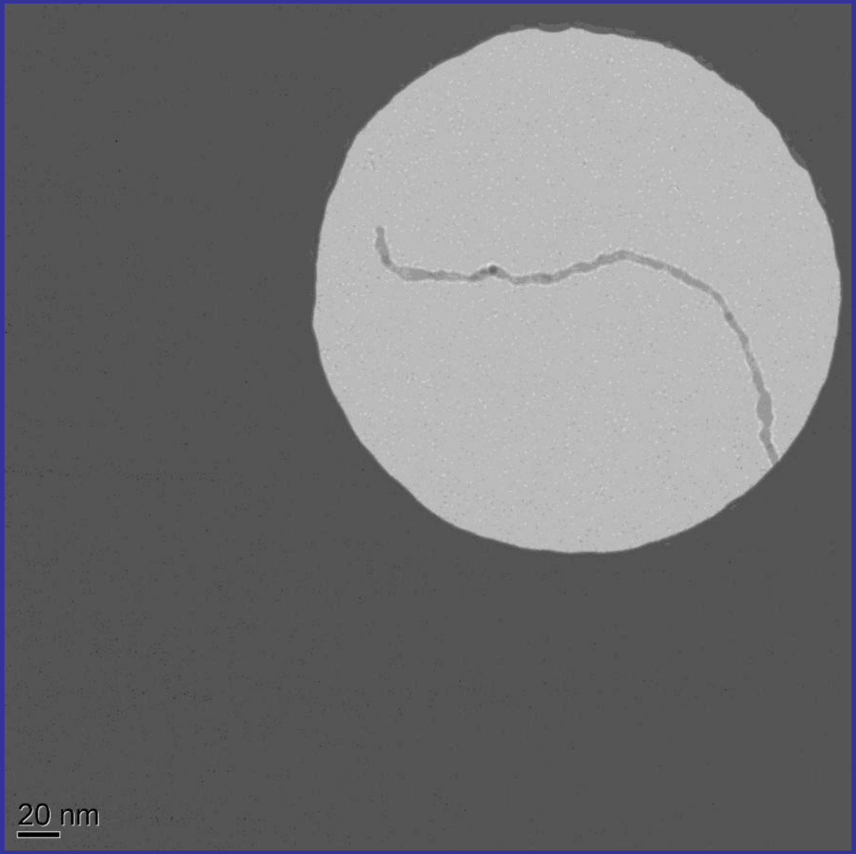
P. Moroshkin, V. Lebedev, B. Groberty, G. Neururer, E.B. Gordon and A.Weis, EPL ***90*** *34002 (2010)*

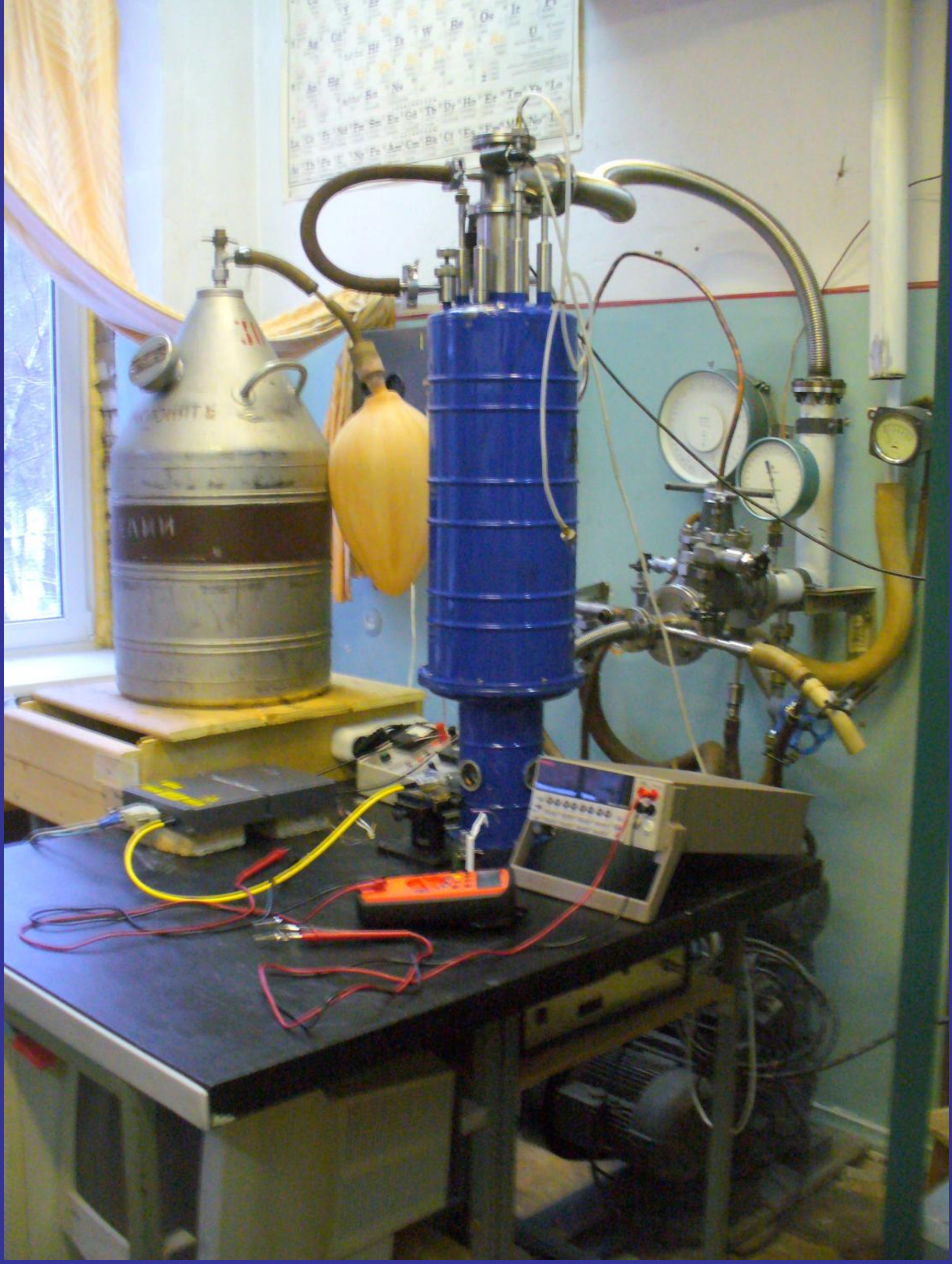
Никель, индий, свинец и олово – - Черноголовка (Россия)

Электрические свойства и структура

E.B Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov and I.I. Khodos, FNT, ***36*** *№ 7, p. 740 (2010)*

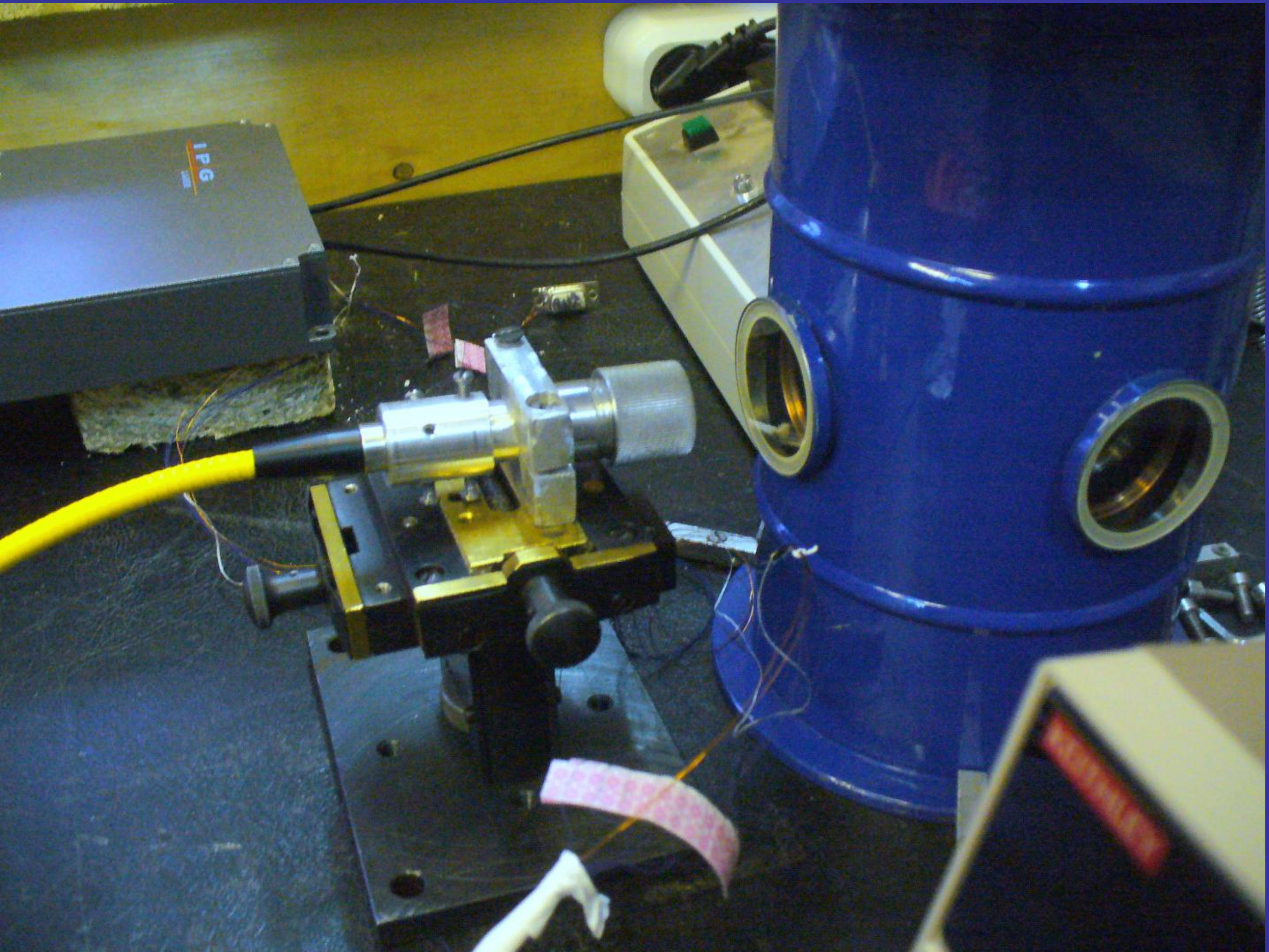
Уединенная золотая нанопроволока с d = 2 nm, выделенная диафрагмой, и ее дифрактограмма,





Экспериментальная установка в ИПХФ РАН

Количество материала для изготовления нанопроволок столь мало, что можно использовать маломощный волноводный лазер



Иттербиевый лазер

λ= 1.06 μ

E = 10^{-4} J

τ = 25 ns

f = 0.5 – 2 kHz

Обычно падающие из места их образования

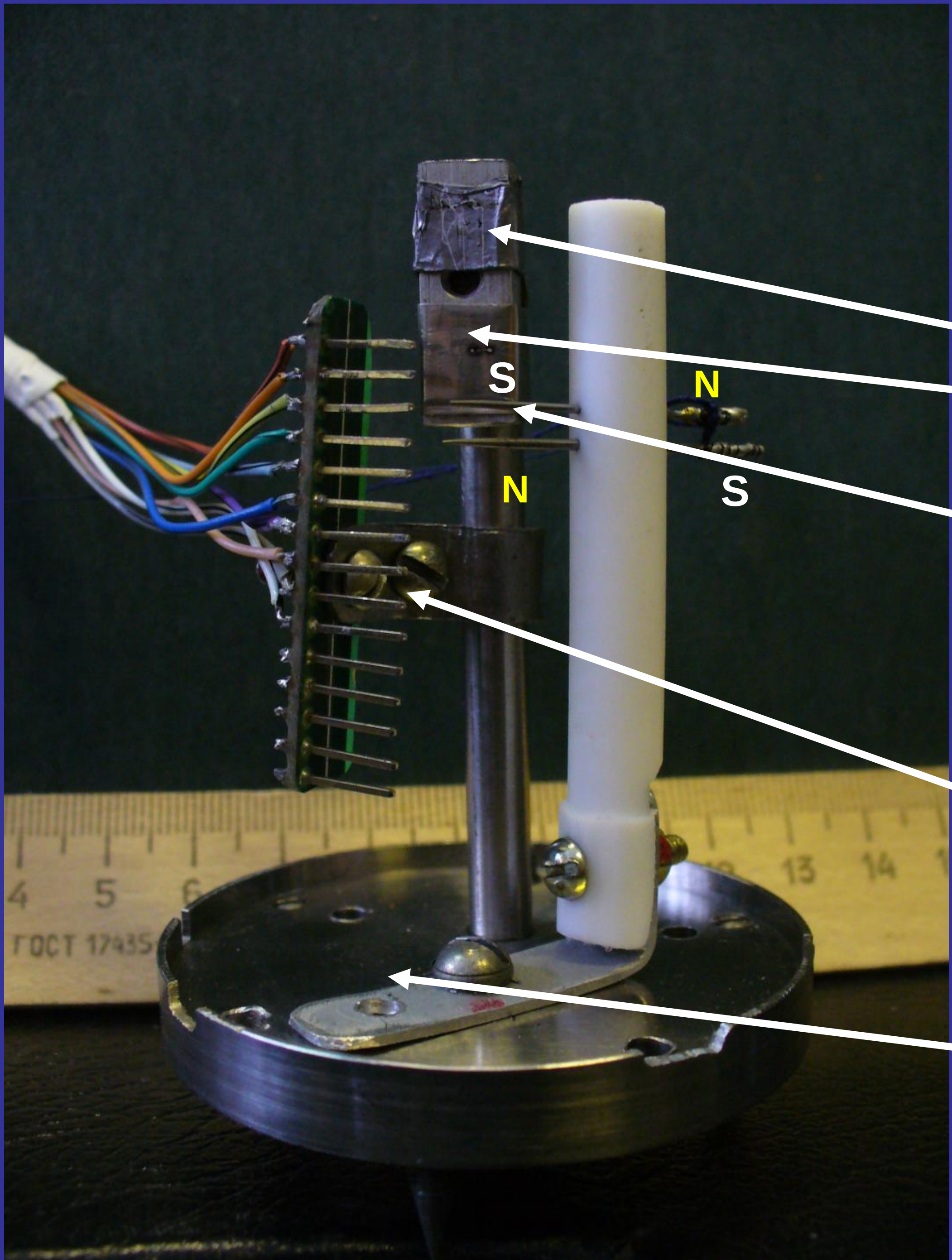
нанопроволоки пытаются поймать на решетку или сетку

При этом не удается создать надежный электрический контакт с электродами

Чтобы доказать способность нанопроволок прицепляться к остриям, мы использовали вертикальный ряд металлических контактов

При этом контакты оказались металлическими и прочными

Experimental cell



Metallic targets, the craters in laser focuses are seen

The pair of oppositely magnetized sewing needles are seen

Vertical row of gilded contacts, interelectrode distances are 3 mm each

Bottom, where fragments of filaments where collected

Процедура создания образца

1. Жидкий гелий откачивается до 6 торр, т.е. до $T = 1.6$ K; $T < T_\lambda = 2.17$K.
2. Включается лазер.
3. Лазерная абляция прекращается:
   а) после появления утечки электричества (при изучении полевой эмиссии электронов);
   б) после замыкания цепи (при измерении сопротивления).
4. После отогрева осадок с предметного стекла рассматривается в ОМ и собирается для ЭМ.

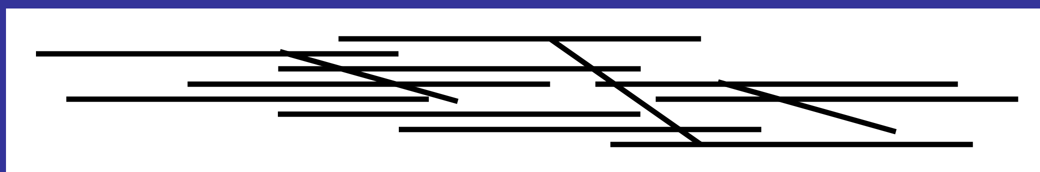
Не надо никаких приготовлений (помещения образца в зазор, обеспечения контакта с электродами и т.д.)

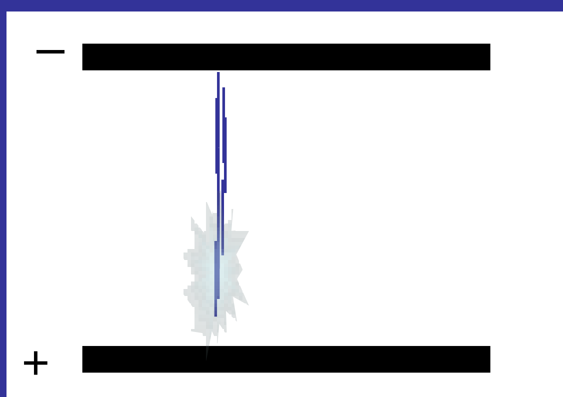
Образец

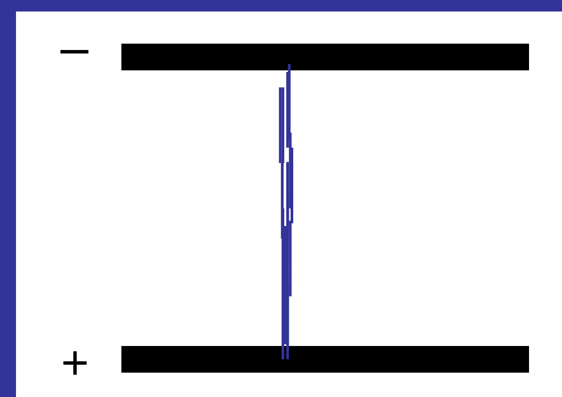
Пучок нанопроволок сантиметровой длины

(закон Ома при V= 0.2 В << φ – работы выхода)

с точечными контактами



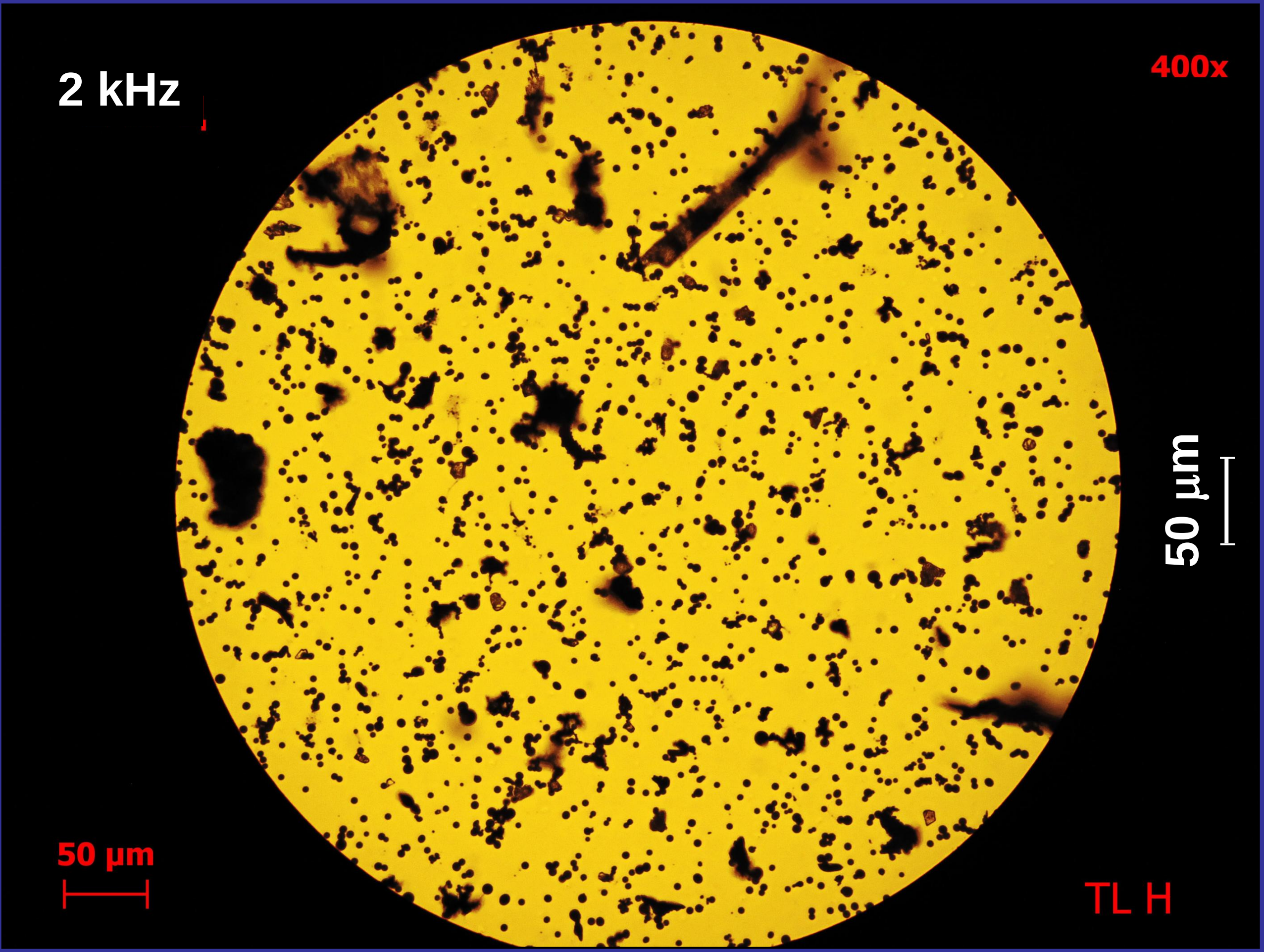




Нет контакта – полевая эмиссия электронов

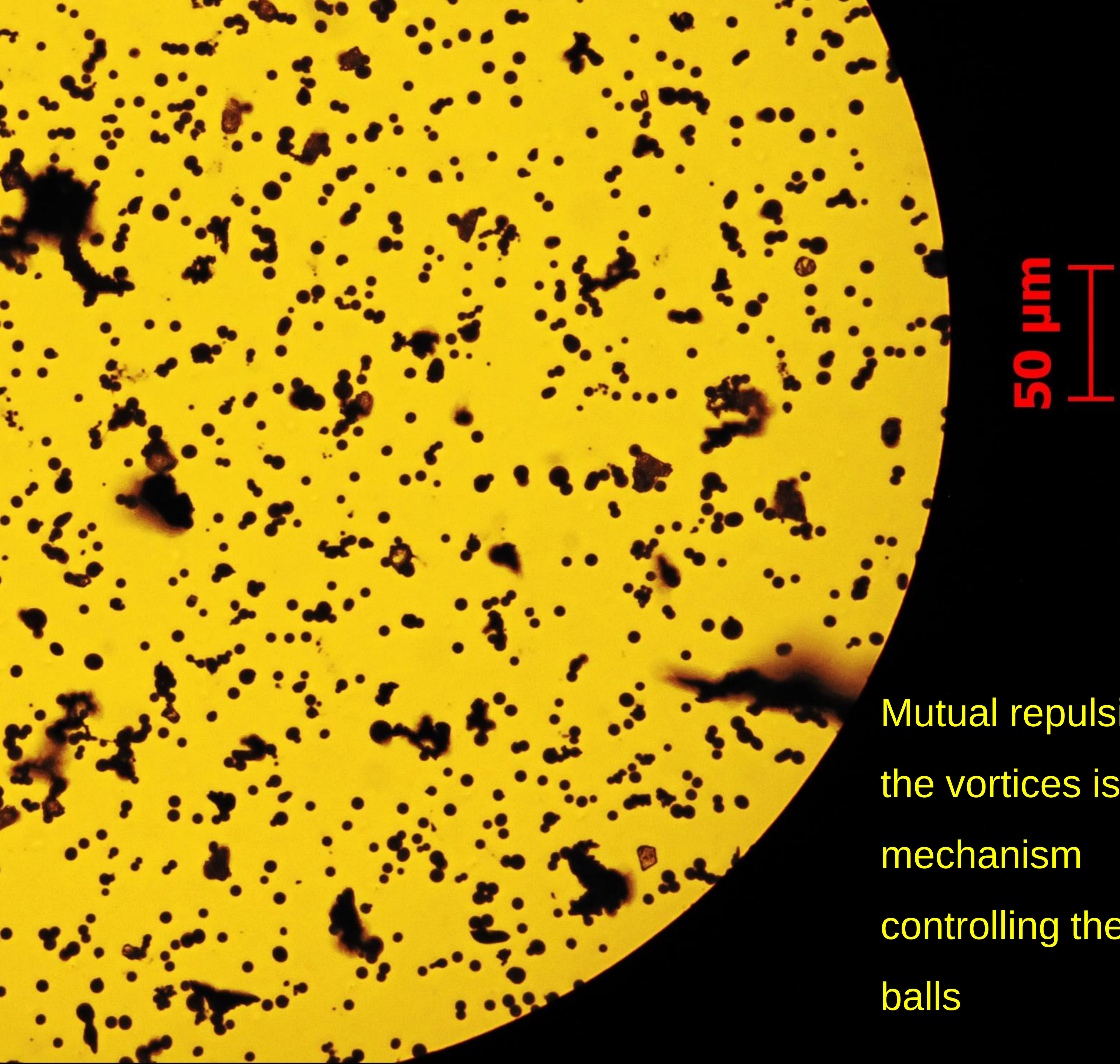
Есть контакт – омическое замыкание

OM: Sediment just beneath the target



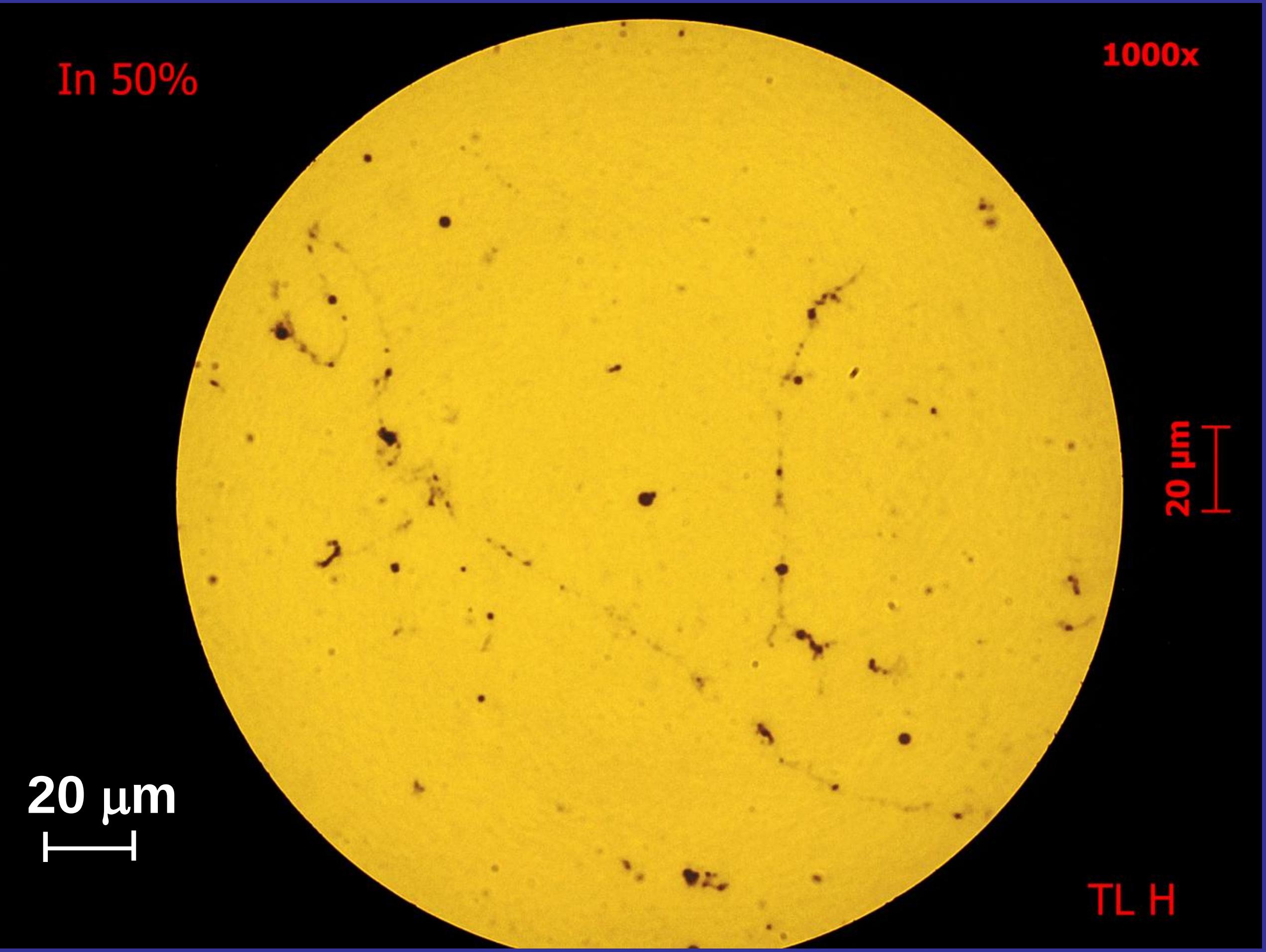
A lot of large (2 µm) metallic balls united to the beads –

possibly due to mutual repulsion as hydrogen large grains



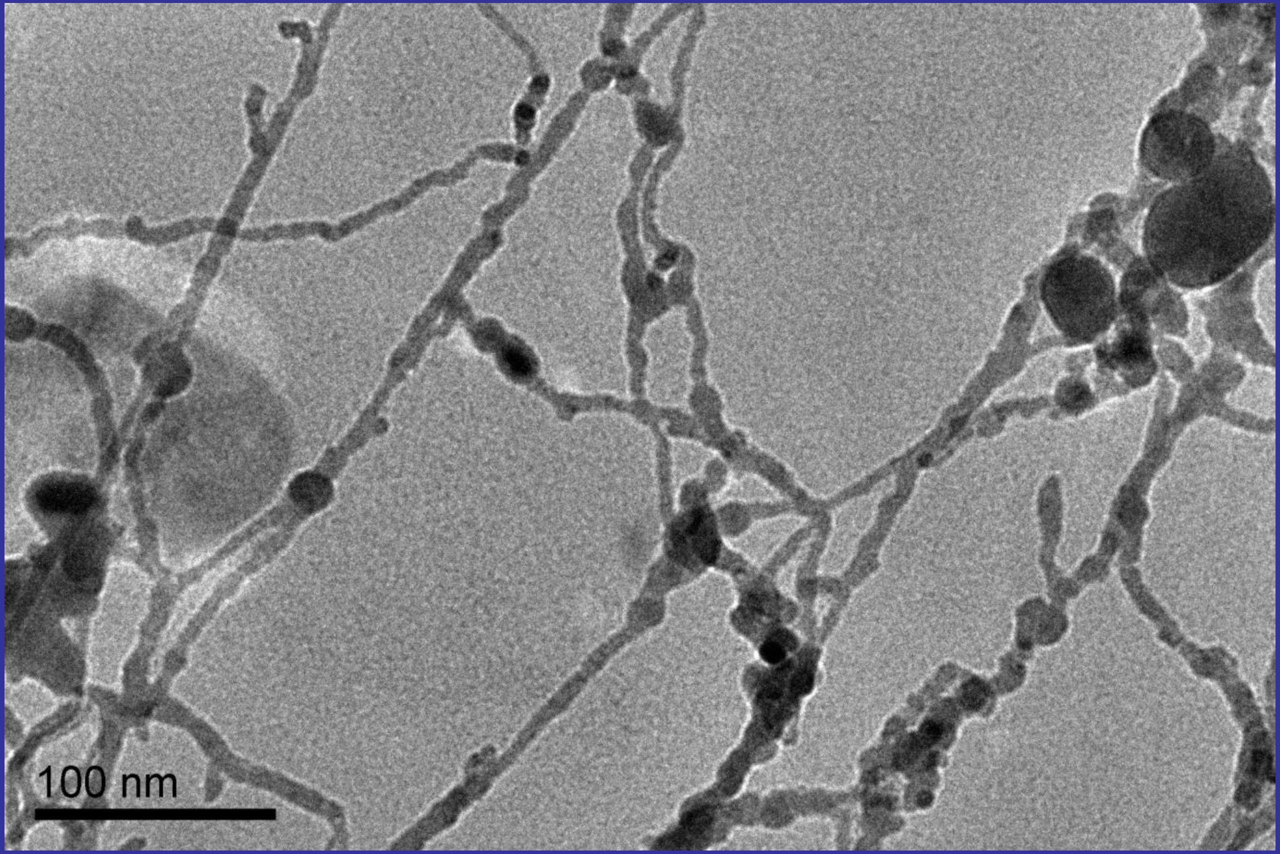
Mutual repulsion in the vortices is the mechanism controlling the size of balls

OM: Sediment at remote area beneath of the electrode arrray



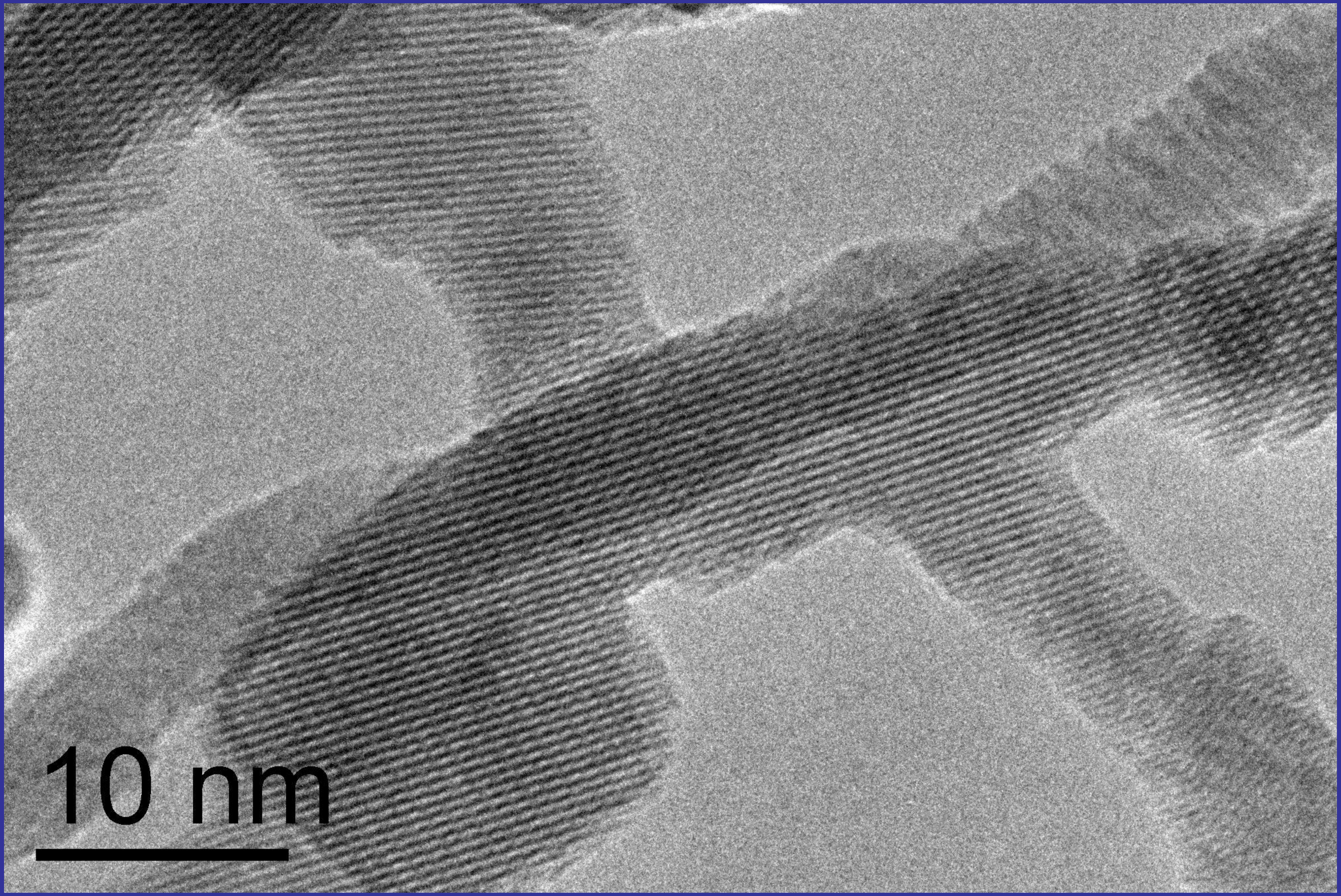
Compare with the length of common nanowires being about 1 micron

Fragment of Indium nanowire bundle (TEM)

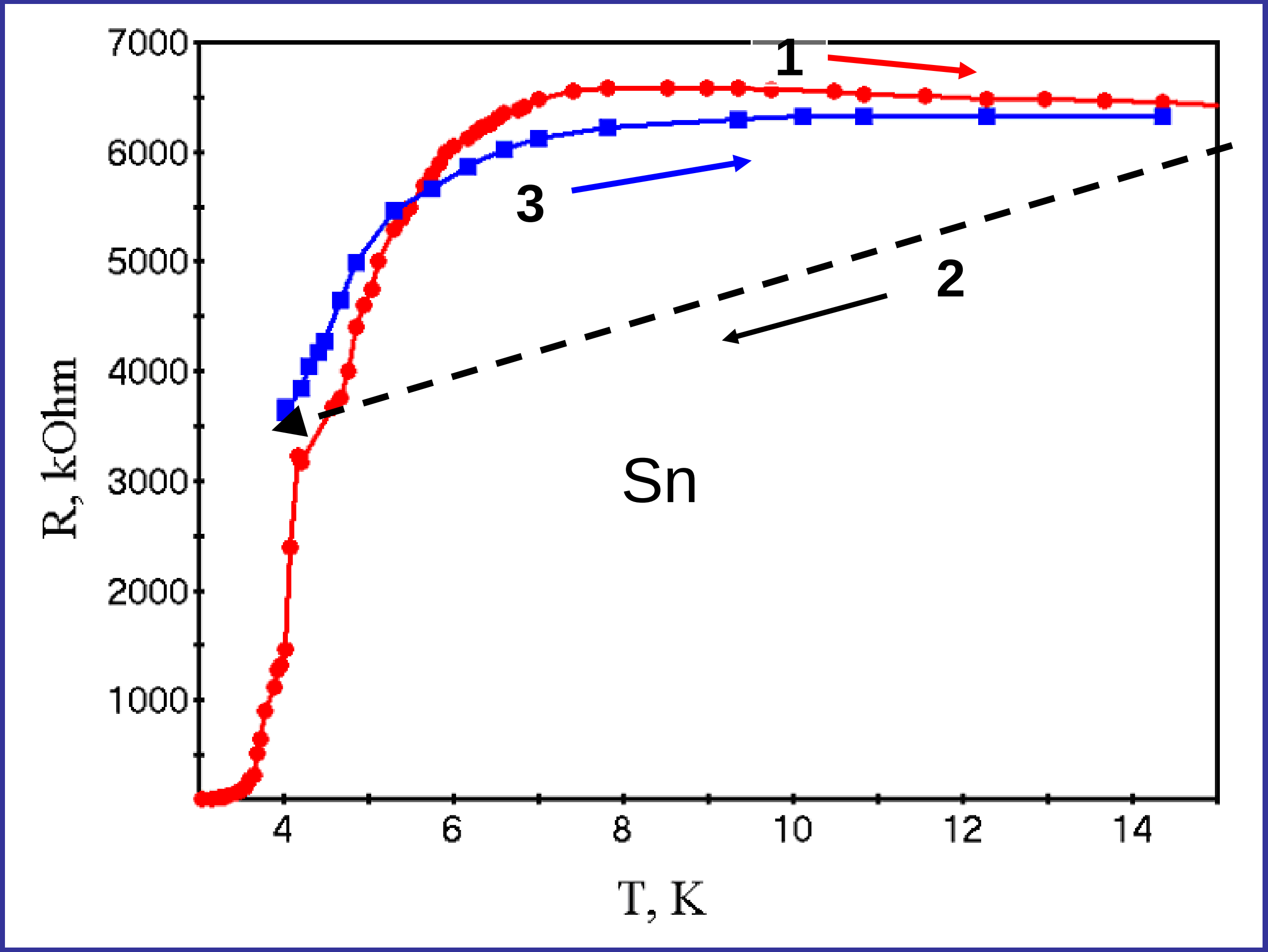


- **Rather thick – 8 nm in diameter**
- **Being inspected along individual wire displays monocrystalline structure**

Imposing the crystalline orientation in a knot (interference fringes direction and spacing)



The wires were monocrystals already in He II: reproducibility of transition from superconductive to normal state for bundle of tin nanowires (T_{bulk} = 3.7K)

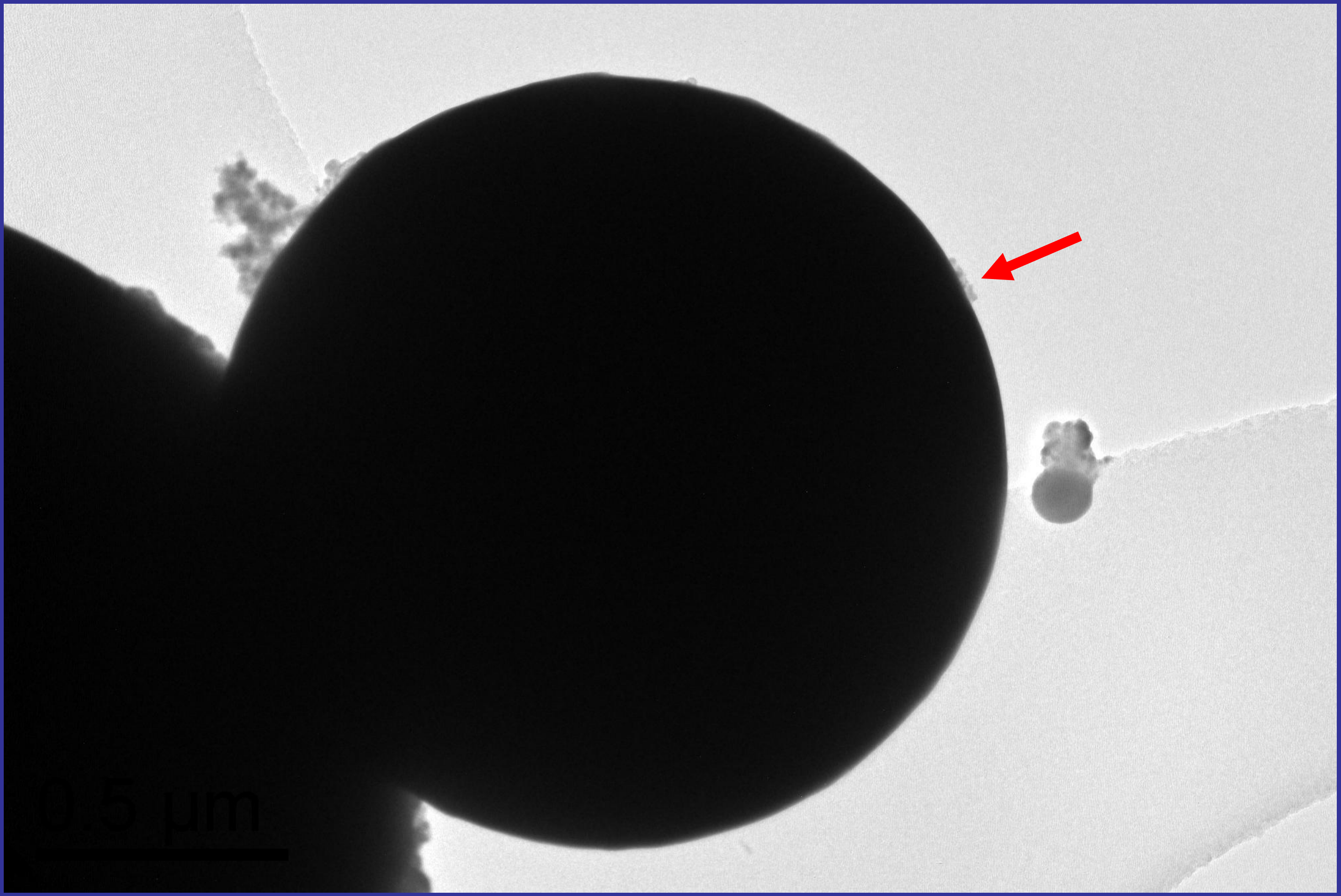


1 – passing λ-point, evaporating LHe, heating in a gas

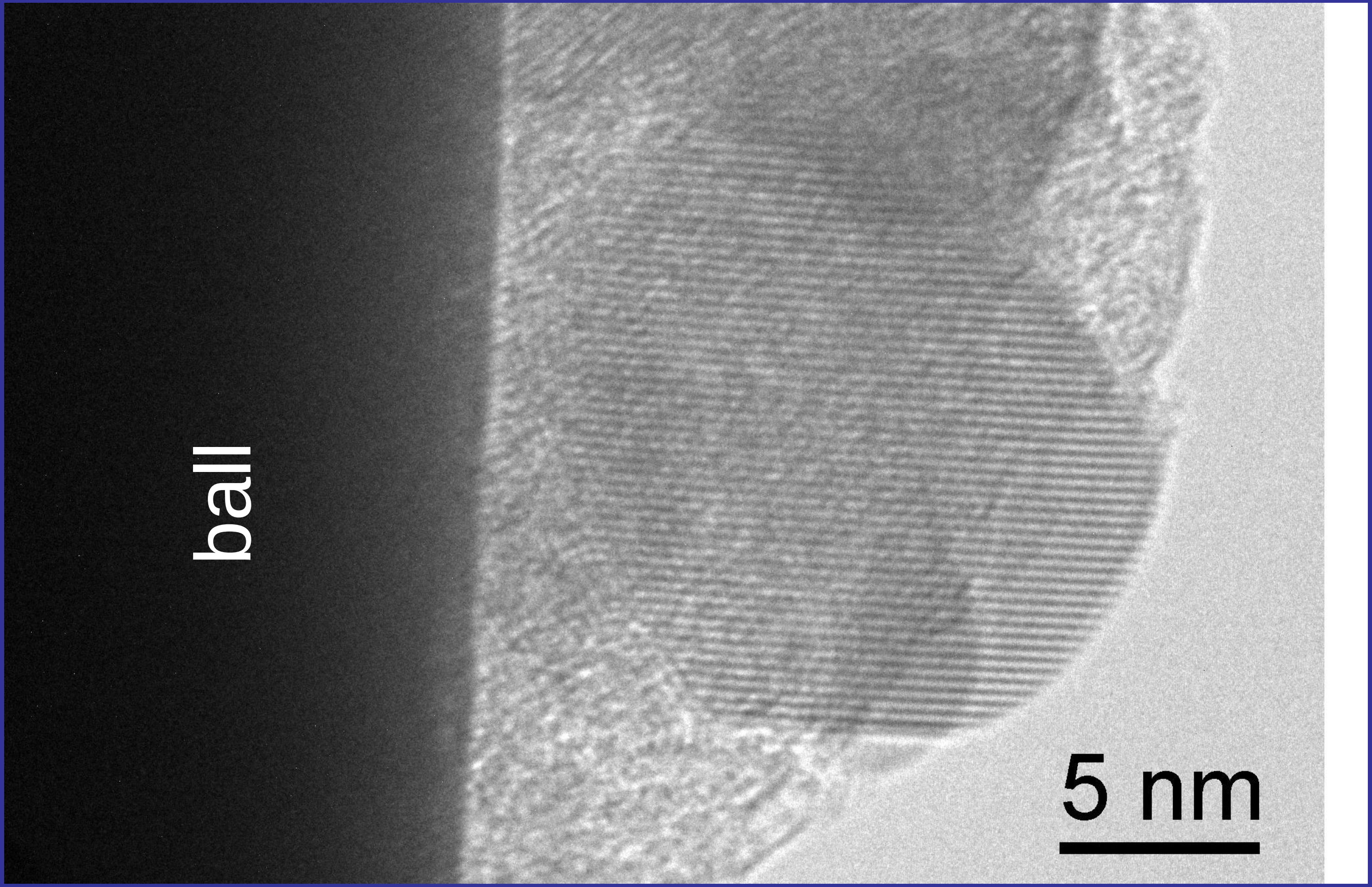
2 – cooling down submerging into LHe

3 – repeated heating with LHe evaporation

The metallic balls are ideal spheres, their radius was grown with increasing laser repetition rate



The edge of this sphere at high resolution



Accidentally sticking to the ball microcrystal demonstrates the scaling, interference fringes have 3Å spacing

– the ball surfaces are atomically smooth

The unambiguous conclusion:
both wires and balls are formed through

molten state

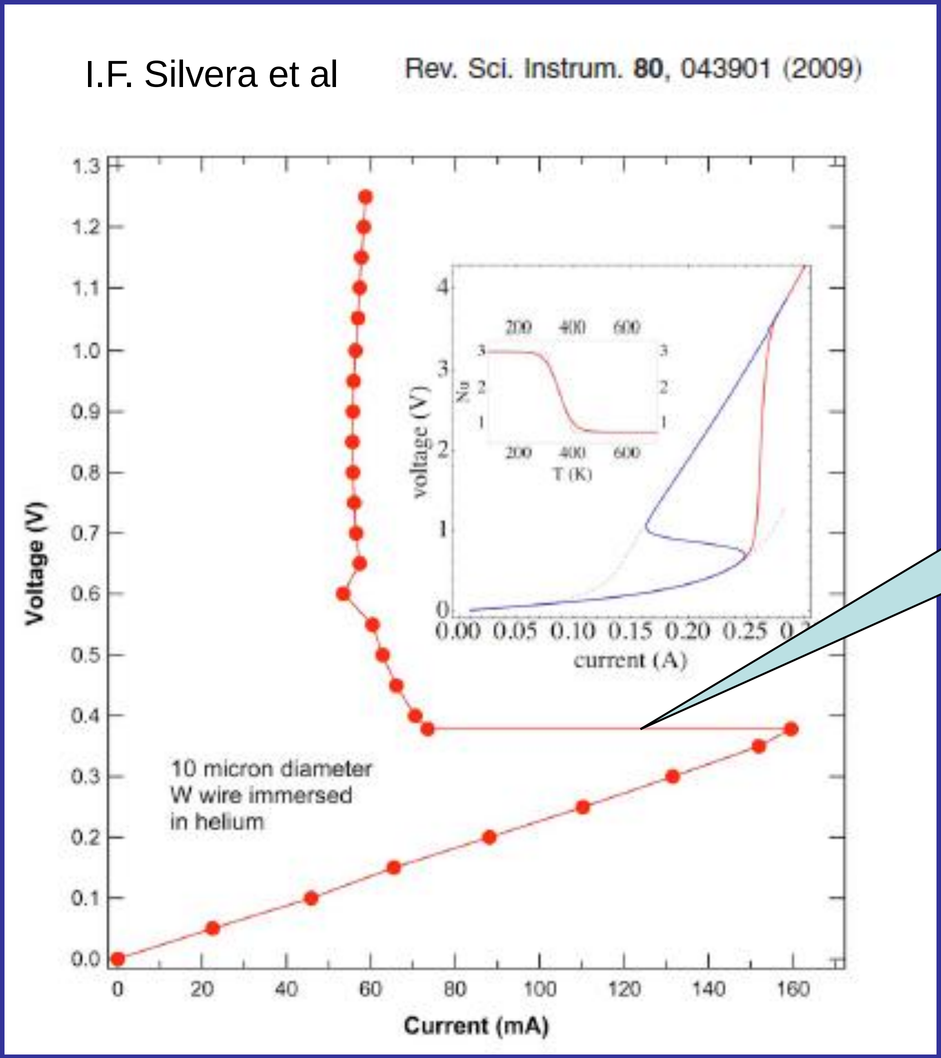
In superfluid helium !!!

HeII “possesses thermal conductivity 200 times higher than Copper”

But for very weak heat flow – less than **10 W /cm^2**;

We should remove more than **10^6 W /cm^2**

Heating 10 μ tungsten wire in HeII

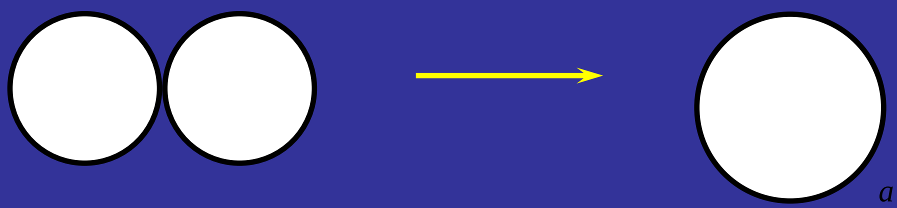


The wire temperature jump from 1.5 K to 1200 K took place at electrical power equivalent to 10 W/cm^2

"above a certain current a vapor sheath formed around the filament, insulating it from the liquid and it would glow at temperatures up to a few thousand kelvin"

In adiabatic conditions small cold metallic clusters are known to melt at merging

Simple model for estimating limiting radius of liquid ball and wire

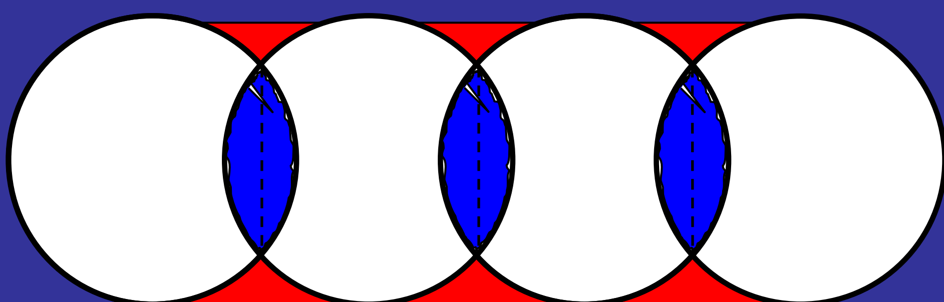


$$R \le R_s^{\max} \equiv 0.78\alpha a$$

$$\alpha \equiv Q_b / (CT_b + Q_m)$$

$$R \le R_w^{\max} \equiv \alpha a$$

a – **one-layer thickness**



Limiting sizes for melting spheres, R_s, and wires ,R_w

	α	R_s^{max}, nm	R_w^{max}, nm
In	7.66	1.8	2.3
Ni	3.05	0.7	0.9
Sn	7.12	1.6	2.1
Pb	4.34	1.0	1.3
Cu	3.28	0.78	1.0
Au	3.49	0.78	1.0
W	3.18	0.74	0.95
H_2	0.87	-	-
H_2O	0.77	-	-

In accordance with experimental results the radius of nanowire for casting metals is more than for refractory metals.

In hydrogen and water α <1 and melting is impossible.

How large atomically smooth metallic balls can be grown in HeII?

- At slow ablation rates the partners were cold. At high ablation intensities they have no time between collisions to cool down. The restrictions for liquidized spheres size becomes softer and then disappear.

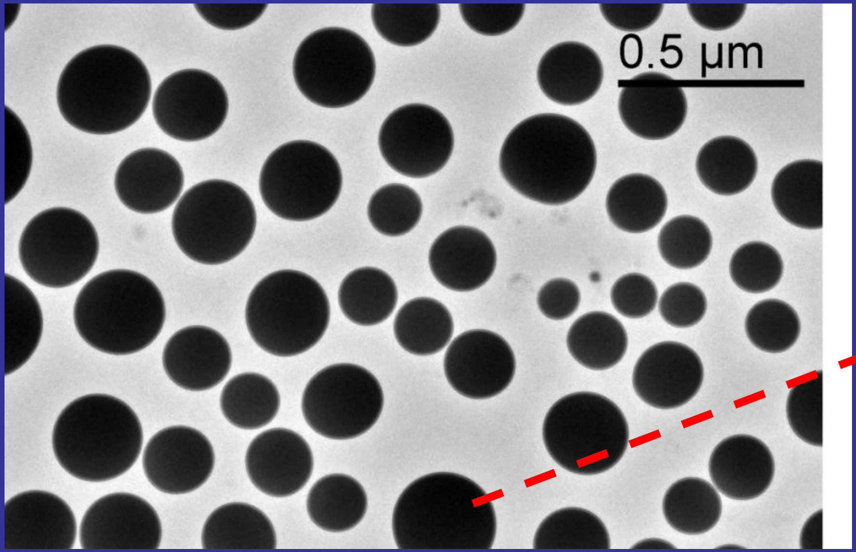
- For metals, in contrast with hydrogen, rare gases, water and most organics, the saturated vapor pressure at melting temperature is negligible and the powerful mechanism of cooling by evaporation is absent.

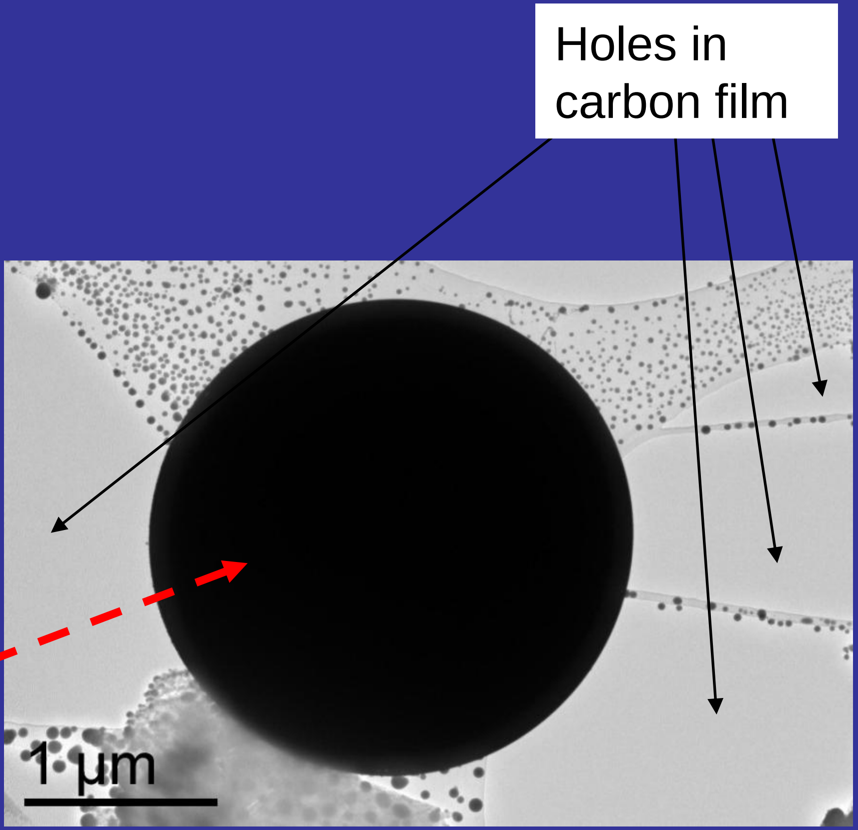
- The upper limit is the spheres mutual repulsion in quantized vortices. The spheres up to few μm size were grown.

This interpretation found its support in very interesting observation

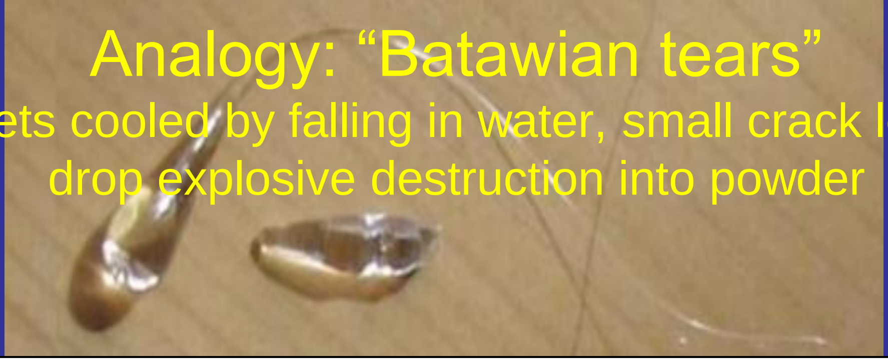
Sometime in TEM microscope (vacuum + T=300K) the ball exploded in a second after focusing electron beam on it. The negligibility of e-beam energy (ΔT_{av}= 0.2 K) was in a favor of its triggering action

Exploding ball outthrows the hundreds of small spheres

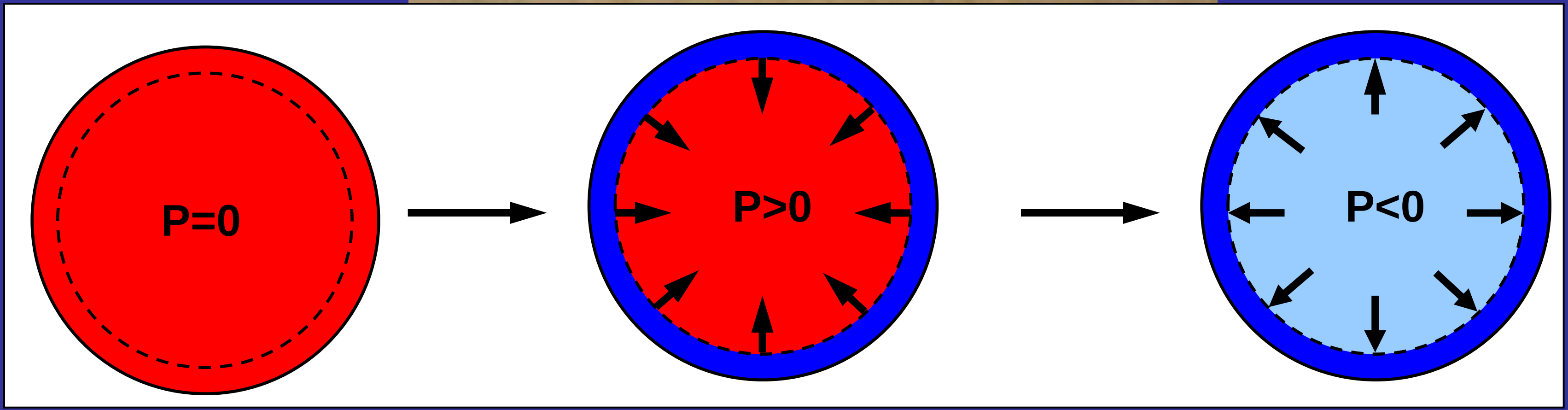




Analogy: "Batawian tears"



Glass liquid droplets cooled by falling in water, small crack led to the hardened drop explosive destruction into powder



Liquid hot drop size is higher then that of cold solid one

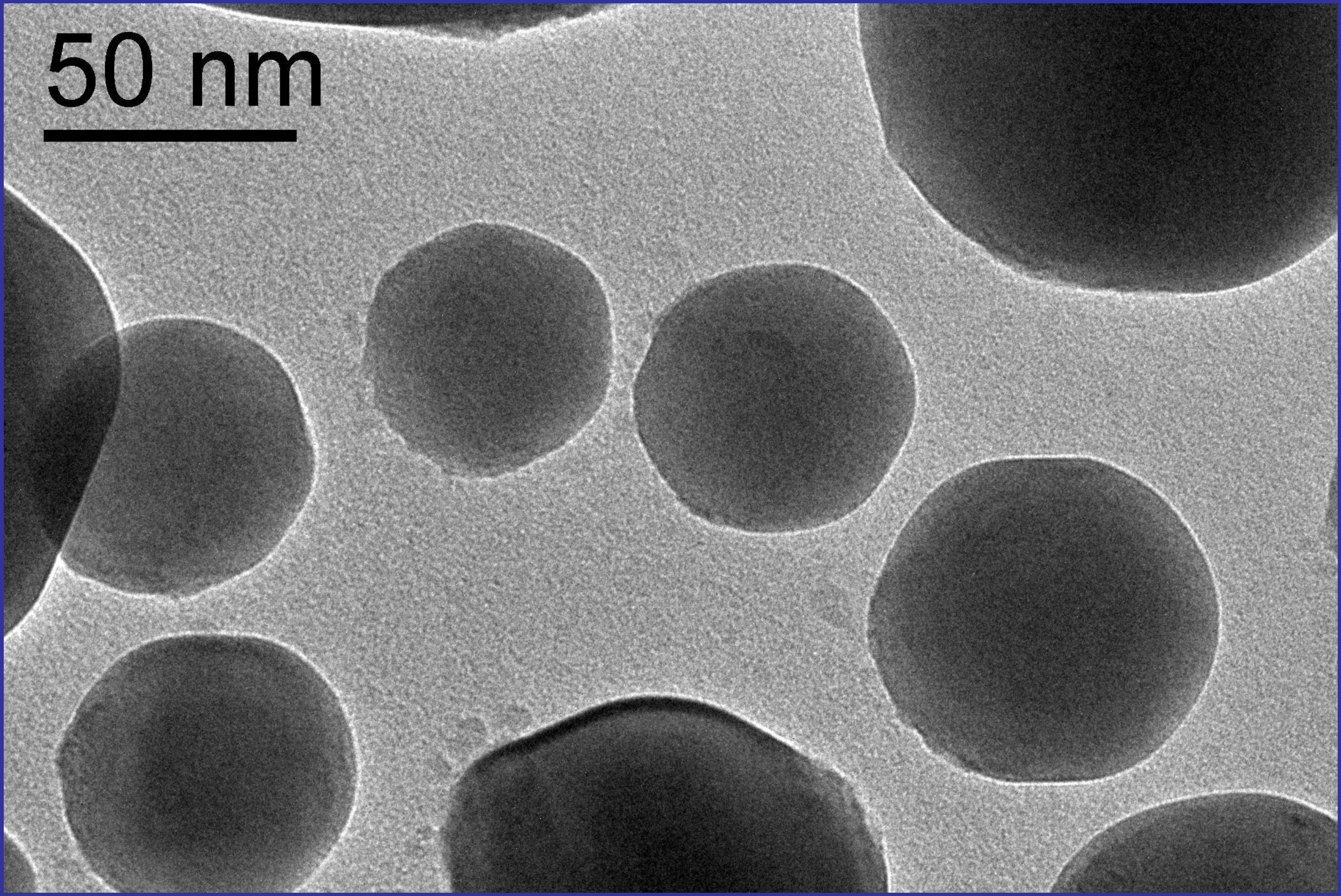
Fast cooling causes solid shell formation, which squeezed the liquid core

Further cooling leads to formatting solid core occupied the volume more then equilibrium one

The absence of dislocations and voids in micron-sized balls converts tensile metals, like indium,

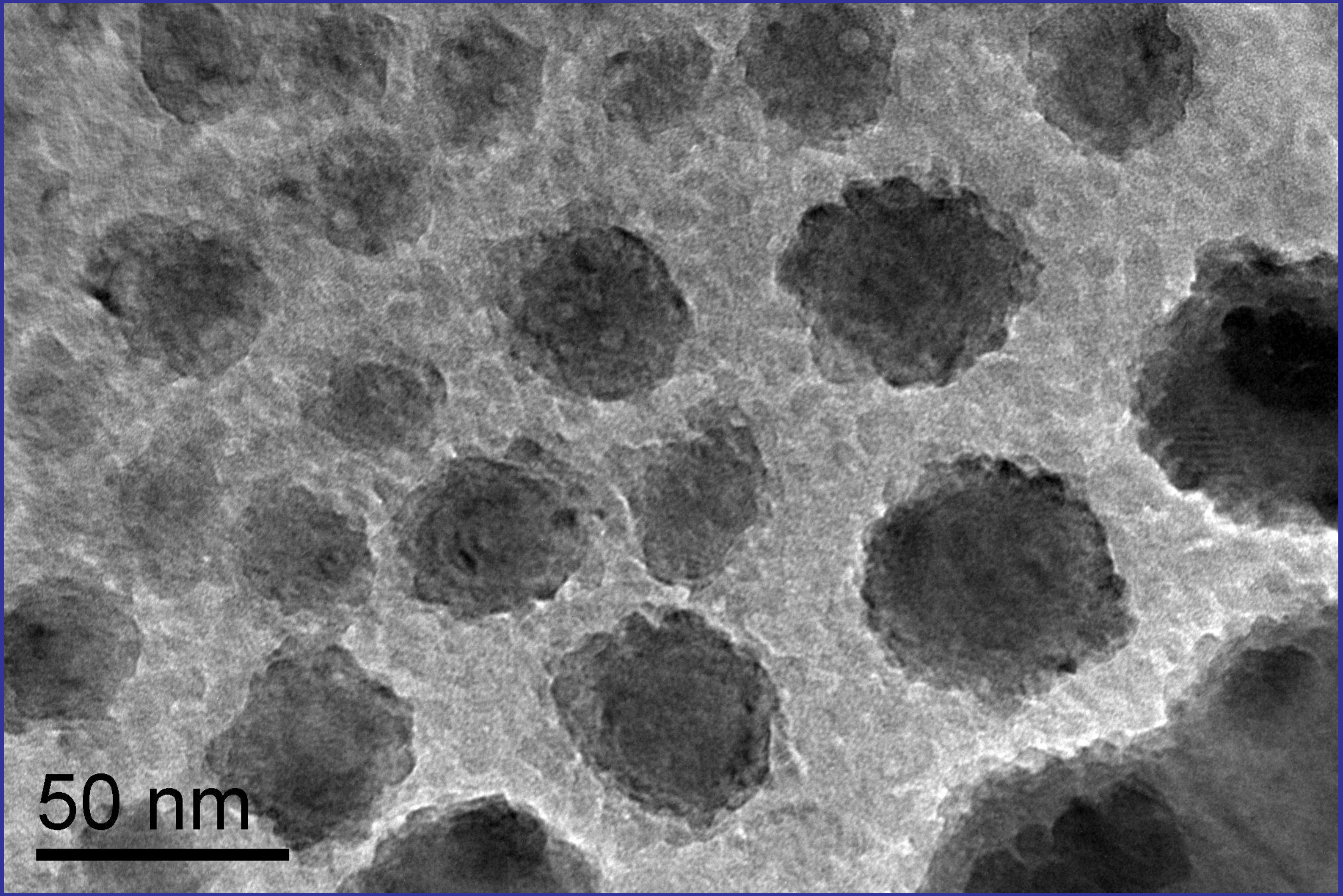
into hard elastic material as glass or steel

200 keV - electrons in TEM easily produce the microcracks inducing the decay

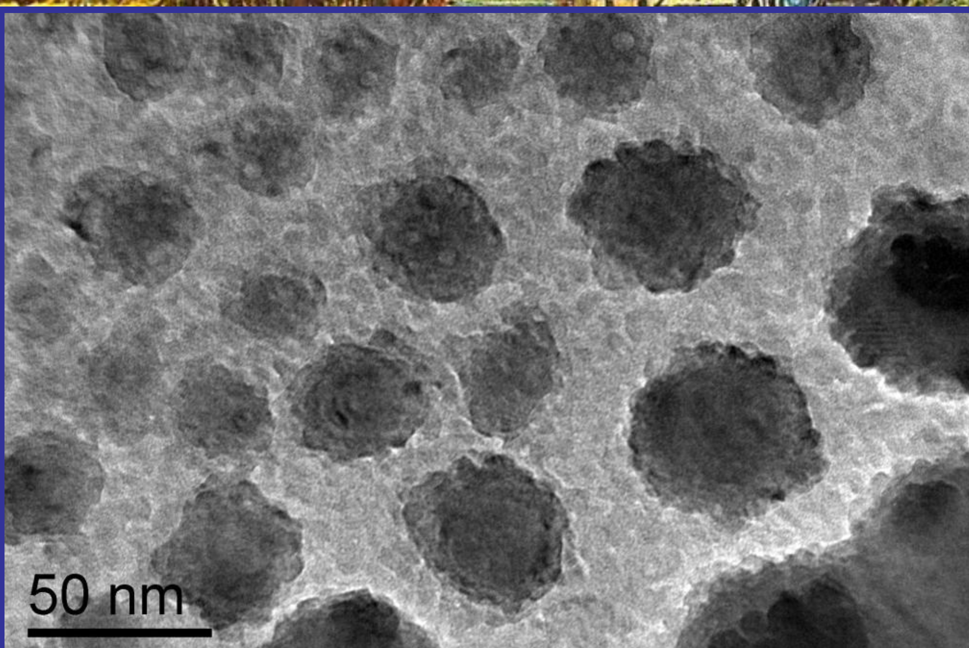


These small smooth monocrystalline spheres (quantum wells) are supposed to be the product of merging in vacuum of much smaller pieces

What was the size of primary dust particles formed in “tear” explosion ?

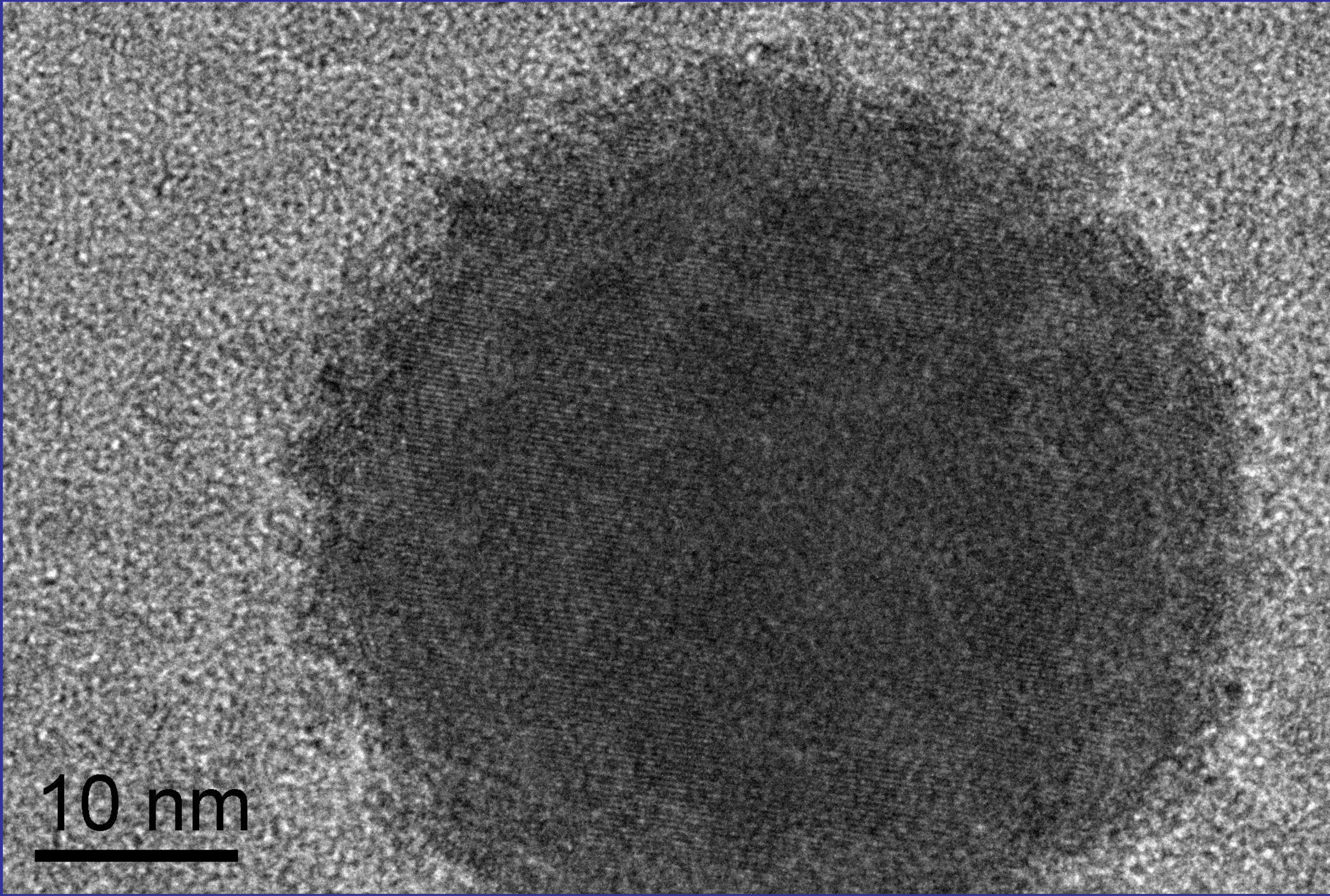


We were lucky to find the balls displayed threshold behavior, when the dust was too large to become molten under sticking. The dispersion of dust on size is rather narrow, because all of them are similar



Между «протозвездами» видны, как фон, исходные кластеры – готовые квантовые точки, которые можно распылить с регулируемой поверхностной плотностью на любой подложке

This protostar was definitely composed from crystals of 6 nm in diameter , interference fringes are seen

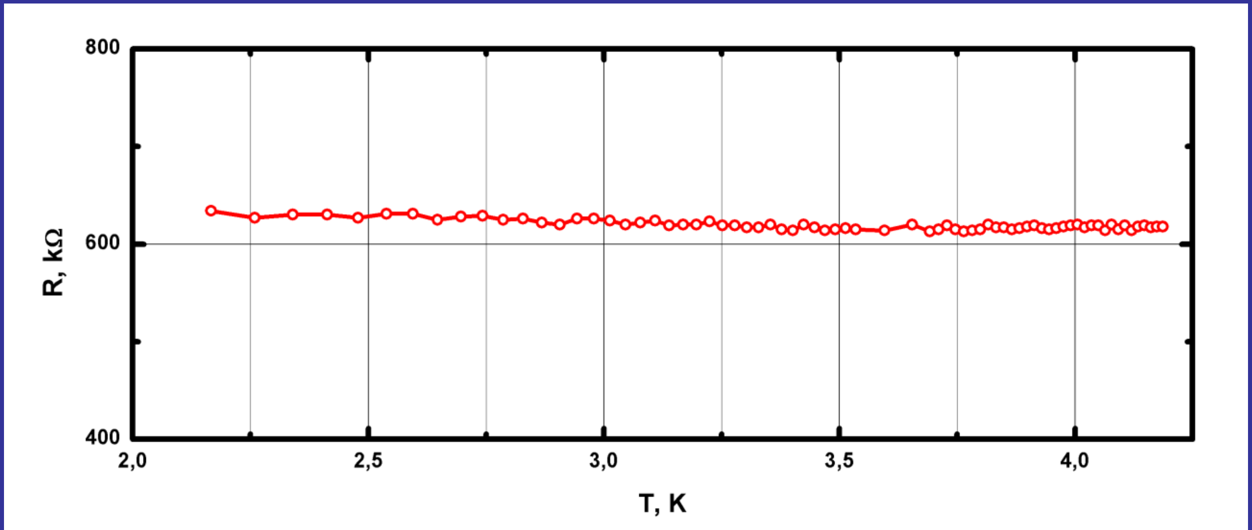


Conclusion

- Production of long thin metallic nanowires and strained metallic atomically smooth spheres was demonstrated in HeII, both of them displayed monocrystalline structure.
- The lowering ablative laser intensity was proved to improve quality of nanowires.
- The growth of HeII SVP from 10^{-2} to 25 bar should significantly diminish the yield of metallic balls comparatively to nanowires.
- Strong size effects inherent to electrical properties of nanowires have been demonstrated

Magic world of quasi 1D metals

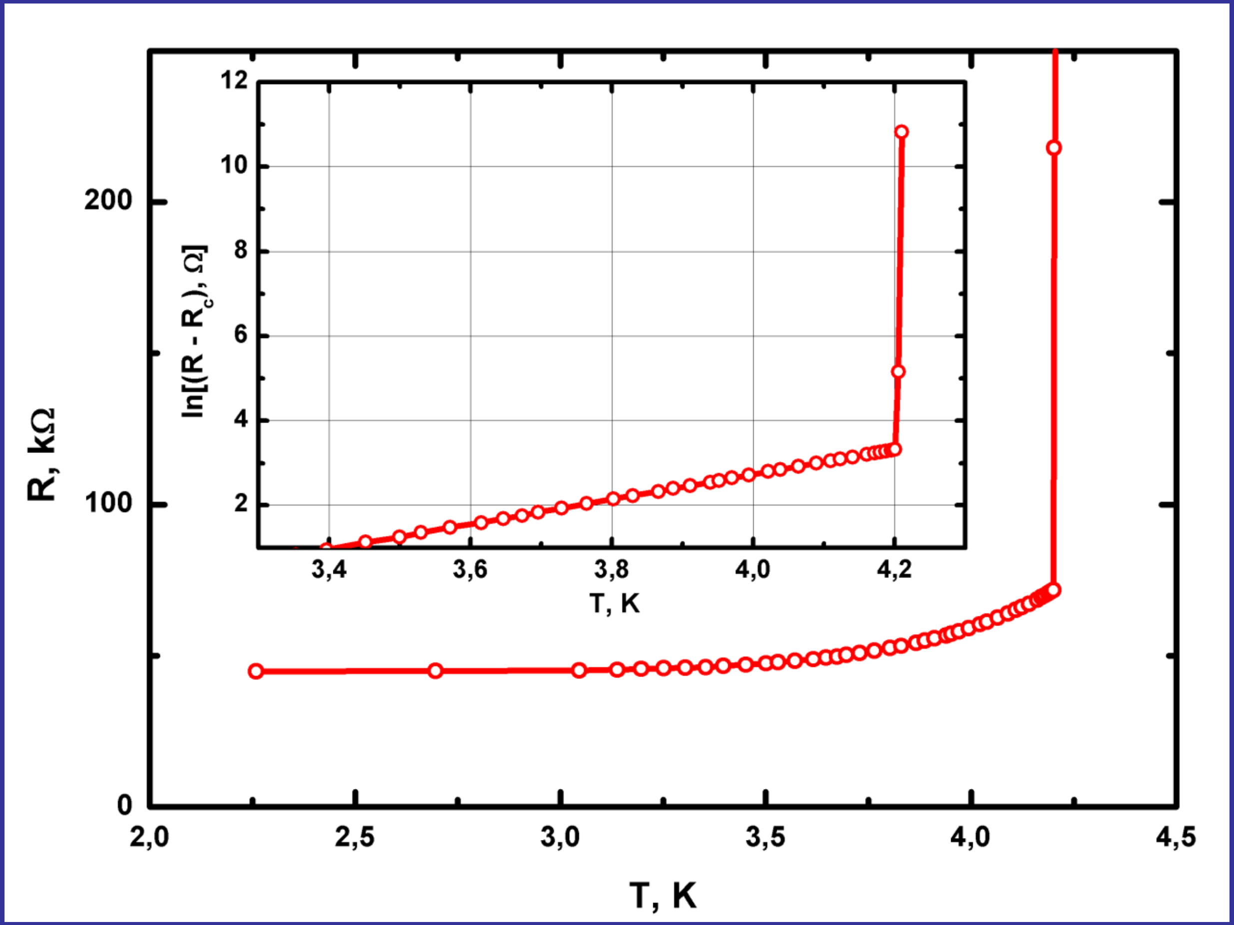
Nickel



- 10^3 times less specific resistivity , ρ, than in a bulk sample
- no temperature dependence of ρ value

E.B Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov , I.I. Khodos, FNT, 36 № 7, p. 740 (2010)

Magic world of quasi 1D metals



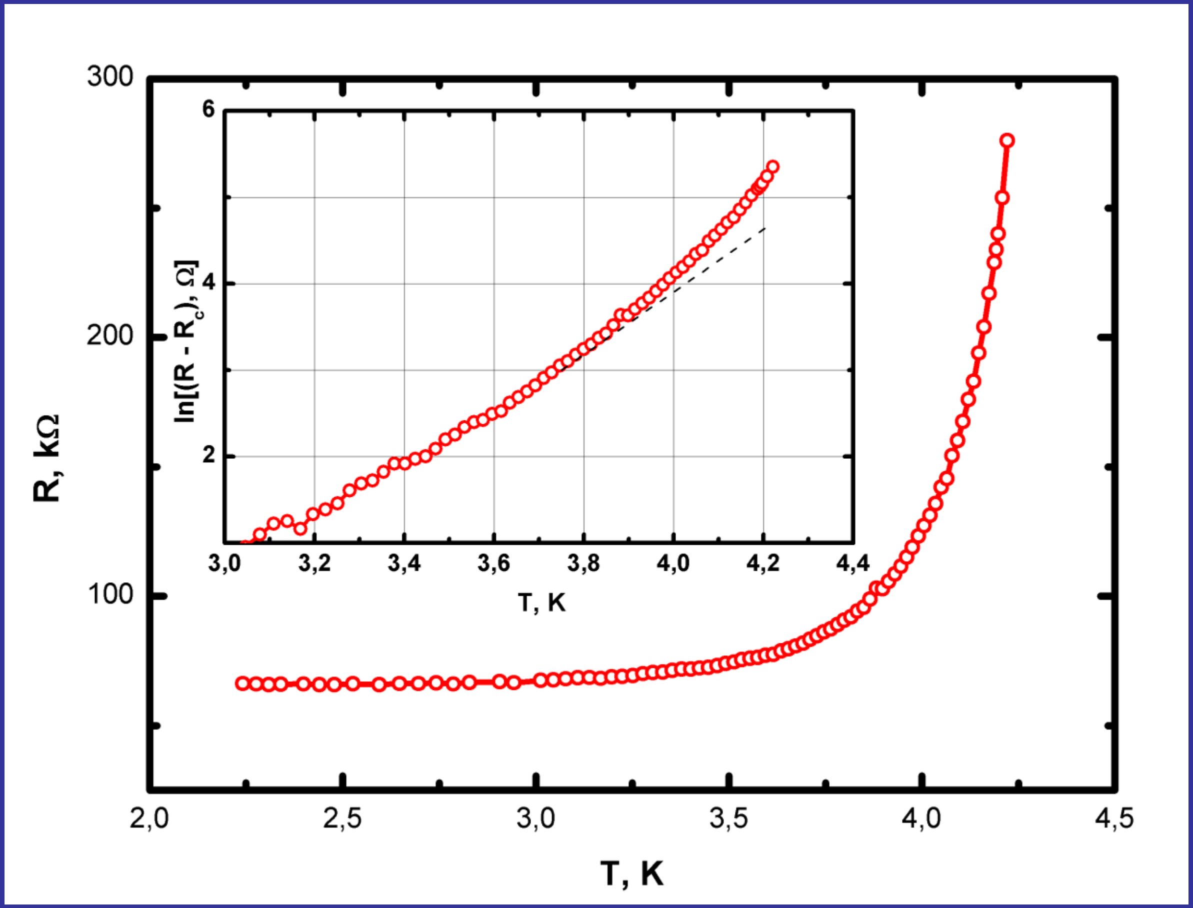
Lead

Superconductors:

The fall down of the temperature for superconductive - normal transition from T_{bulk} = 7.19 K to 4.3 K

E.B Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov , I.I. Khodos, FNT, 36 № 7, p. 740 (2010)

Magic world of quasi 1D metals



Indium

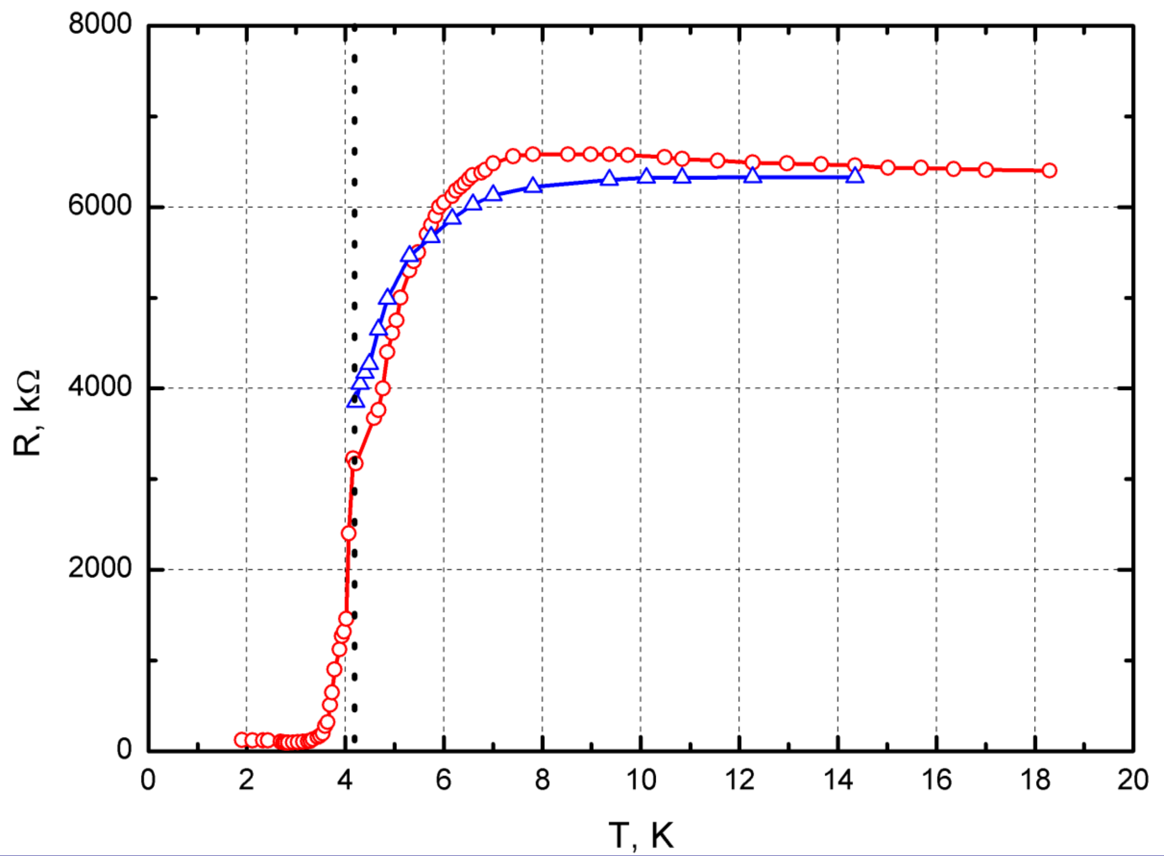
Superconductors:

The growth of the temperature for superconductive - normal transition from

T_{bulk} = 3.4 K to 4.45 K

E.B Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov , I.I. Khodos, FNT, 36 № 7, p. 740 (2010)

Magic world of quasi 1D metals



Tin

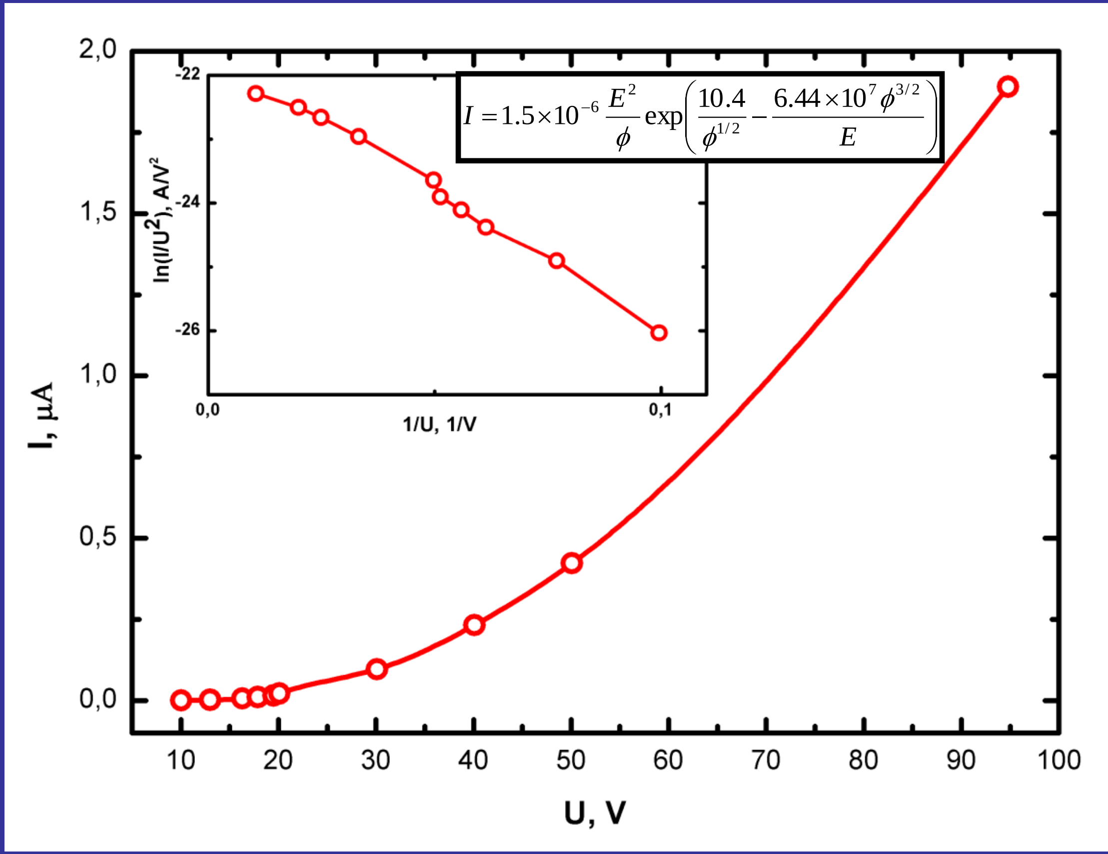
Superconductors:

The growth of the temperature for superconductive - normal transition from

T_{bulk} = 3.7 K to 6 K

E.B Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov , I.I. Khodos, to be published

Magic world of quasi 1D metals



Lead

Field-induced electron emission:

- **High efficiency – μA instead of common nA**
- **low voltage**

Large (3 mm) length of nanowire bundle - the prototype of cold cathode

E.B Gordon, A.V. Karabulin, V.I. Matyushenko, V.D. Sizov , I.I. Khodos, FNT, 36 № 7, p. 740 (2010)

Promises

- If the mechanism just proposed is true, the nanowires made of HTSC ceramics could be grown for the first time.
- The general pattern of impurity condensation in normal and superfluid helium could be revealed.
- Heat conductivity in quasi 1-D wires may be investigated.
- The polymer chains may be grown in HeII.

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