

14.09 : землетрясение



15.09 : торнадо

16.09 : ?????



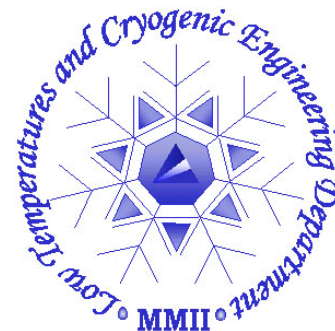
*XI Конференция молодых ученых
"Проблемы физики твердого тела и высоких давлений"
г. Сочи, пансионат "Буревестник" 10-19 сентября 2008г*

Поиски физики в нанофизике и нанофизики в физике: неупорядоченные системы, квантовые спиновые цепочки и наноматериалы на основе оксида ванадия



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НАНО ФИЗИКА

Наличие нанометрового масштаба в системе.

Наномасштаб играет существенную роль, определяя физические процессы.

Хорошо известные наносистемы:

КРИСТАЛЛЫ

$$\hat{H}(\vec{r} + \vec{a}) = \hat{H}(\vec{r})$$
$$a \sim 0.3 \text{ нм}$$



И. Кеплер
1611



СВЕРХПРОВОДНИКИ II рода
с высокими H_{c2}

$$\xi = [\Phi_0 / 2\pi H_{c2}(0)]^{1/2}$$

$$H_{c2}(0) = 100 \text{ кЭ}$$

$$\xi = 5.7 \text{ нм}$$



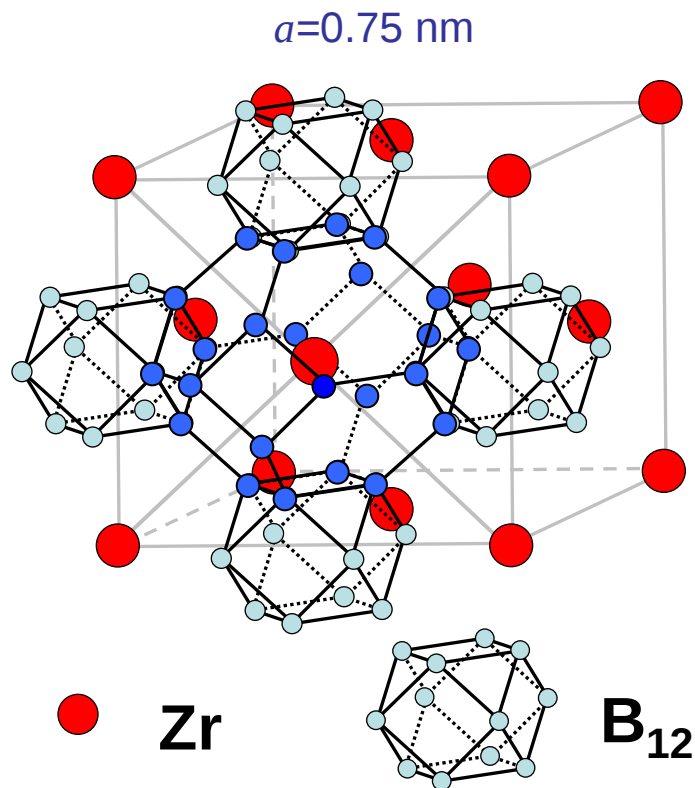
Л.В.Шубников
1937



А.А.Абрикосов
1957



НАНОФИЗИКА в КРИСТАЛЛАХ



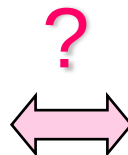
Додекаборид циркония, ZrB_{12} :
сверхпроводник с нанокластерами бора.

Переход в сверхпроводящее состояние
при $T_c=6.1\text{K}$

B.T.Matthias et al.,
Science, 159, 530 (1968)

Каков механизм электрон-фононного
взаимодействия?

Эйнштейновская (локальная) мода
R.Lortz et al.,
Phys. Rev. B, 72, 024547 (2005)



Широкий спектр (модель Дебая)
V.A.Gasparov et al.,
Phys. Rev. B, 73, 094510 (2006)

phys. stat. sol. (b) 243, No. 11, R72–R74 (2006) / DOI 10.1002/pssb.200642300

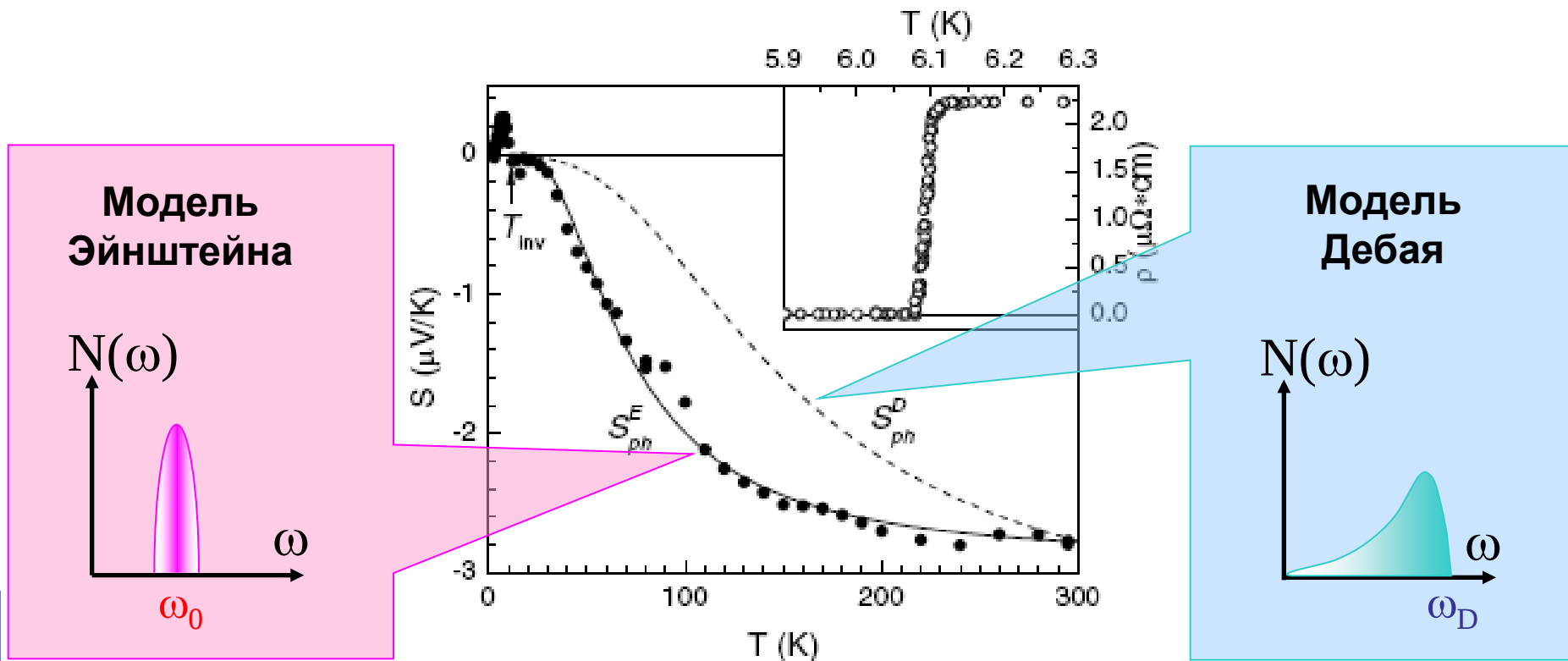
Phonon drag induced by
Einstein mode in ZrB_{12}

V. Glushkov^{*,1}, M. Ignatov¹, S. Demishev¹, V. Filippov², K. Flachbart², T. Ishchenko¹, A. Kuznetsov⁴,
N. Samarin¹, N. Shitsevalova², and N. Sluchanko¹

pss +++rapid
research
letters +++
www.pss-rapid.com



Термоэдс в ZrB_{12} определяется электрон-фононным взаимодействием (эффект фононного увлечения).

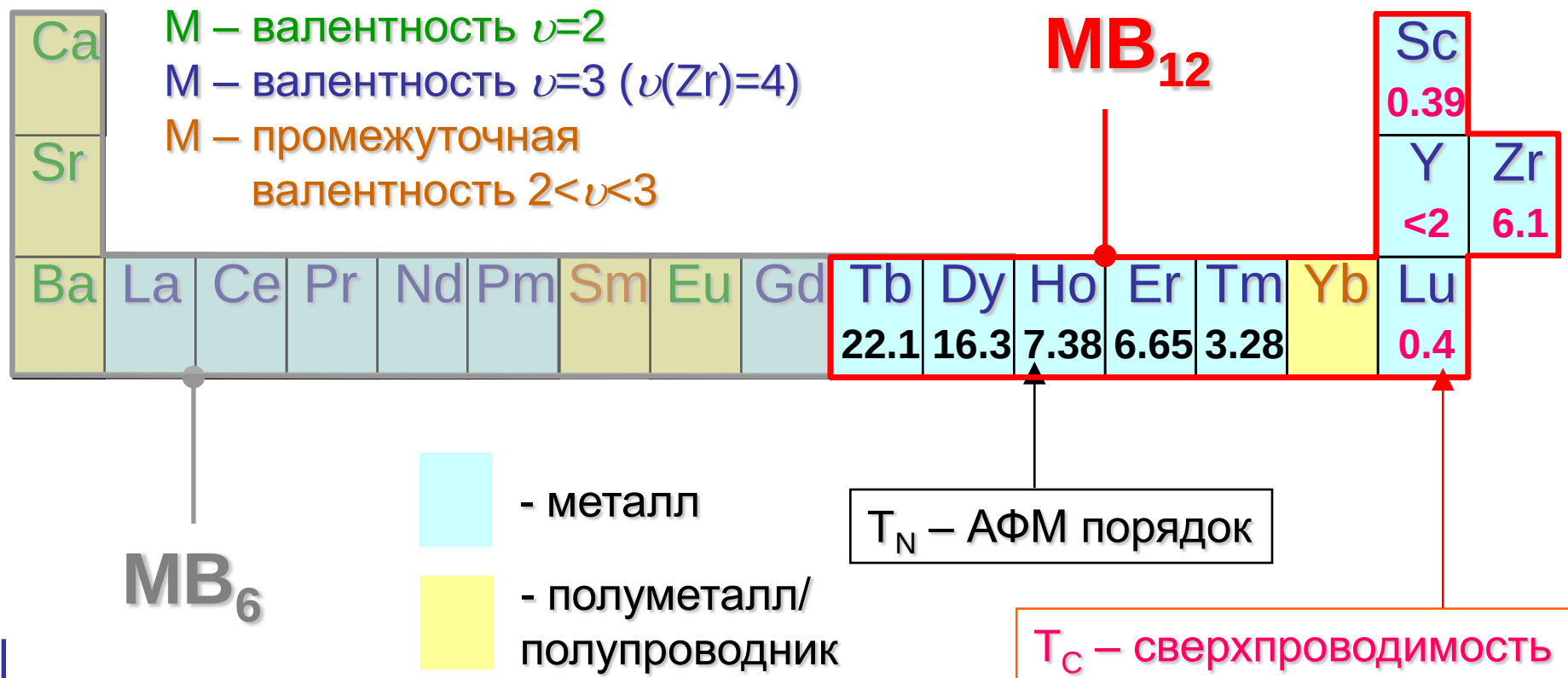


Исследование термоэлектрических эффектов в сверхпроводнике ZrB_{12} позволило установить, что **электрон-фононное взаимодействие и сверхпроводимость в этом соединении определяются эйнштейновской локальной модой.**



Додекабориды редкоземельных и переходных металлов

MB_6 и MB_{12} - соединения на основе каркасных структур из кластеров бора B_6 и B_{12}



Роль локальных мод (обусловленных нанокластерами) в RB_{12} ?



ЧТО ТАКОЕ НАНОФИЗИКА?



Физика
неупорядоченных
сред



Неравновесные
фазовые
превращения



Nanophysics = very small physics

НАНОФИЗИКА В ДОИСТОРИЧЕСКИЕ ВРЕМЕНА



Аморфные полупроводники

Февраль 1994 г.

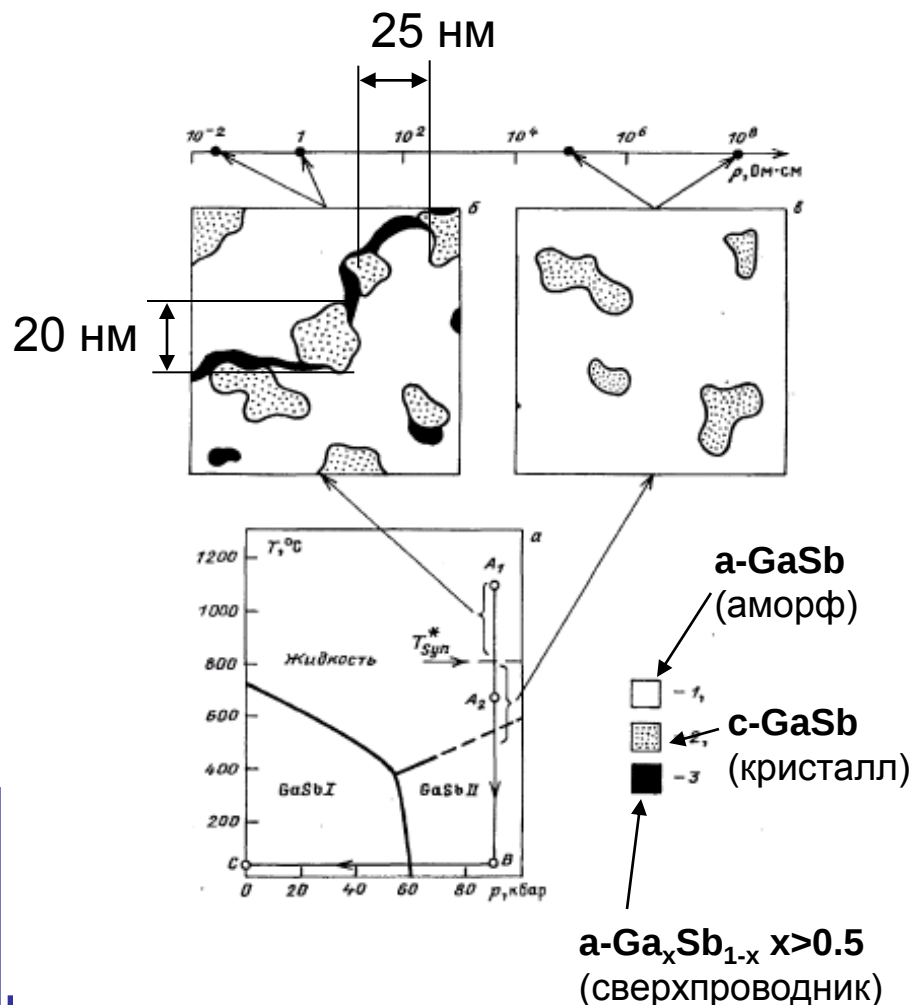
УСПЕХИ ФИЗИЧЕСКИХ НАУК

Том 164, № 2

ОБЗОРЫ АКТУАЛЬНЫХ ПРОБЛЕМ

Аморфные полупроводники, синтезированные закалкой под давлением

С.В. Демишев, Ю.В. Косичкин, Н.Е. Случанко, А.Г. Ляпин



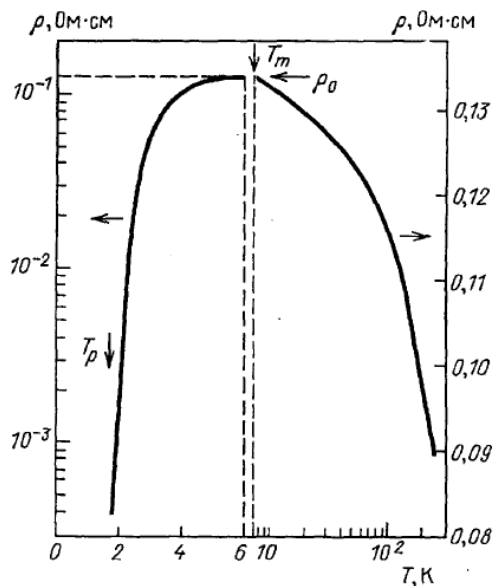
сложных многофазных систем. При этом включения субмикронного размера, образующиеся в процессе синтеза метастабильных фаз, как представляется, оказывают в ряде случаев определяющее воздействие не только на свойства аморфной матрицы, но также и кристаллических фаз двойных и тройных соединений.

В первом разделе обсуждаются существующие модификации схемы синтеза АПВД и используемые для описания ТФА феномено-

Поэтому на физически интересной нанометровой пространственной шкале в легированных полупроводниках будут доминировать квантовые эффекты [65—67], и в результате точка аномалии кинетических характеристик (порог подвижности) не будет связана с топологической особенностью при x_c [65, 66], а критический индекс для проводимости $\sigma \sim \tau'$ составит $t \approx 0,6$ [66—67].

В то же время в аморфных полупроводниках длина пробега существенно меньше $l_0 \sim L_{cor} \sim 10 \text{ \AA}$ [7, 6 рассмотренное выше ограничение снимается. Сле,

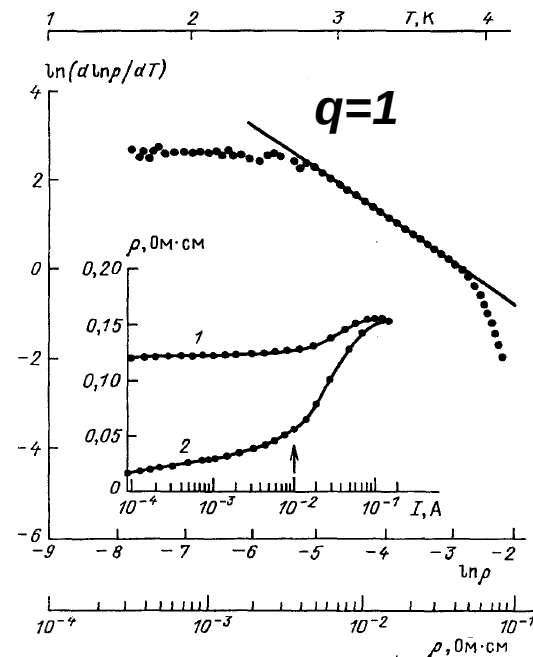




Сверхпроводимость кластеров нанометрового размера

$\text{Ga}_x\text{Sb}_{1-x} (x > 0.5)$

$$T_c = T_c(x)$$

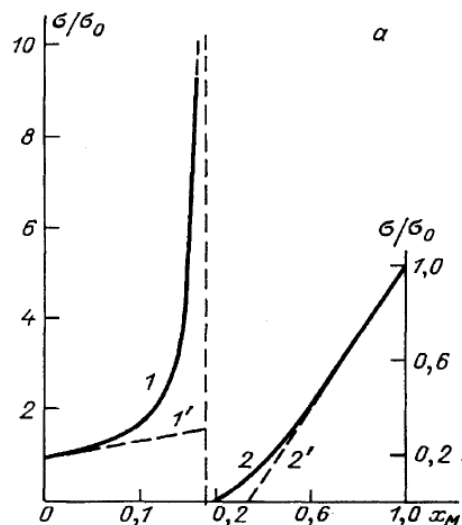
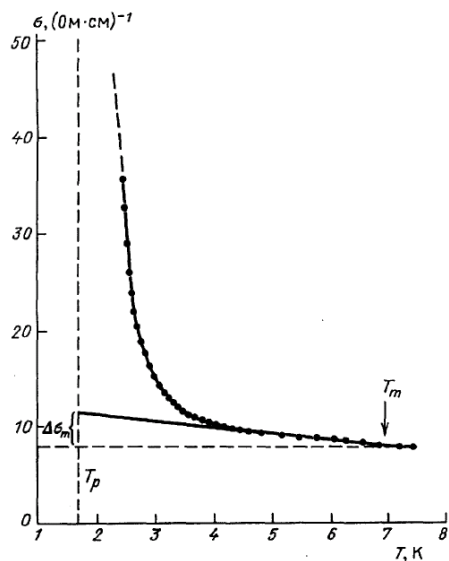


$$\sigma = \frac{\sigma_0}{[1 - (x_M/x_C)]^q} \equiv \sigma_0 \tau^{-q}$$

$$V_s(T) = \int_T^{\infty} \varphi(T_c) dT_c \quad \frac{1}{\rho} \frac{\partial \rho}{\partial T} = q \frac{\varphi(T)}{n_c} \left(\frac{\rho}{\rho_0} \right)^{-1/q}$$

$$\ln \left(\frac{1}{\rho} \frac{\partial \rho}{\partial T} \right) = f(\ln \rho) \quad \Rightarrow \quad q$$

Определение критического
поведения в системе со
сверхпроводящими
включениями



Physical Mechanisms of the Non-Equilibrium Phase Transitions in Amorphous Solids

T.V. Ischenko and S.V. Demishev

Low Temperatures Laboratory, General Physics Institute,
 Vavilov street 38, RU-117942 Moscow, Russia

The idea of the non-equilibrium process driven by the special metastable states means that the processes of the crystallisation and energy transfer at the phase boundary are synchronised [4,5]. Consequently the simple analysis of the energy transfer allows to predict the possible structure of the sample which undergo the non-equilibrium phase transition. In semiconductors the characteristic time of life of the metastable state is about $\tau \sim 10^{-9}$ s and the velocity of the EC front is $v_{ex} \sim 1$ m/s. These data taken together with the equilibrium values of the thermal diffusivity $D_T^0 = 10^{-5} \div 10^{-6}$ m²/s allow to define three characteristic spatial scales for an non-equilibrium process

$$L' = v_{ex} \cdot \tau \approx 1 \text{ nm} \quad (1)$$

$$L'' = (D_T^0 \tau)^{1/2} \approx 10 \div 100 \text{ nm} \quad (2)$$

$$L''' = D_T^0 / v \approx 1 \div 10 \text{ } \mu\text{m} \quad (3)$$

undergo EC is in agreement with the available experimental data [6]. Consequently we can conclude that for the non-equilibrium process a well-defined scales hierarchy is characteristic:

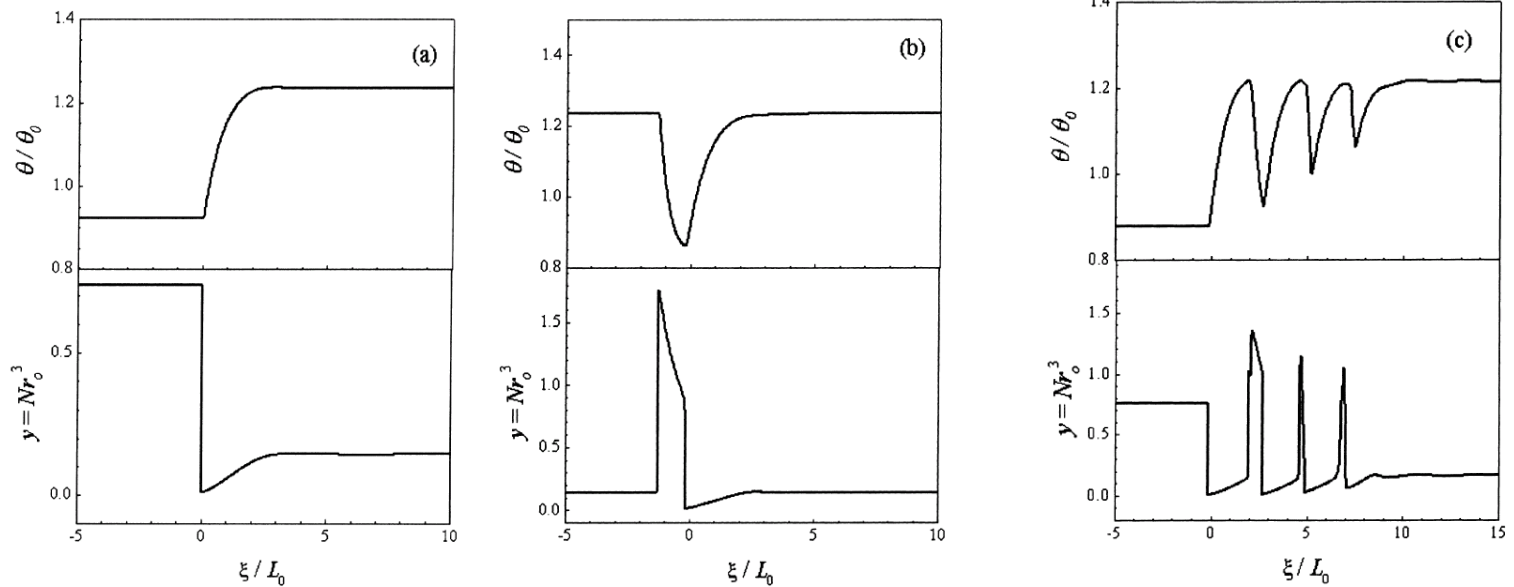
$$L' \approx L_{MRO} < L'' < L''', \quad (4)$$

that is in contrast with the equilibrium process. Indeed, in the equilibrium diffusion controlled process of phase transition the parameter L' is about atomic distance a ; the thermal field is almost homogeneous and $L'', L''' \rightarrow \infty$. As a result instead of relation (4) we get $L' \approx a \ll L'', L'''$ that is typical for standard process of nucleation and growth.

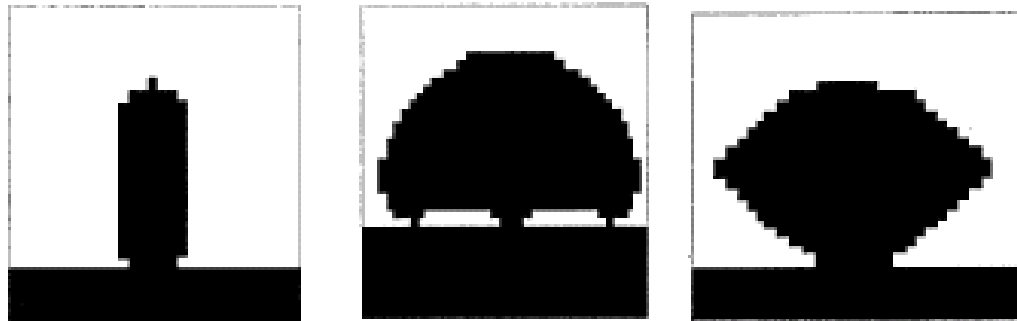


Simulated waves of non-equilibrium phase transformations

T.V. Ischenko et al. / Computational Materials Science 17 (2000) 331–335



The case of solid-state amorphization



The case of explosive crystallization



«Кантемировская нанотанковая дивизия принуждает к миру
кэш второго уровня процессора Pentium-IV»

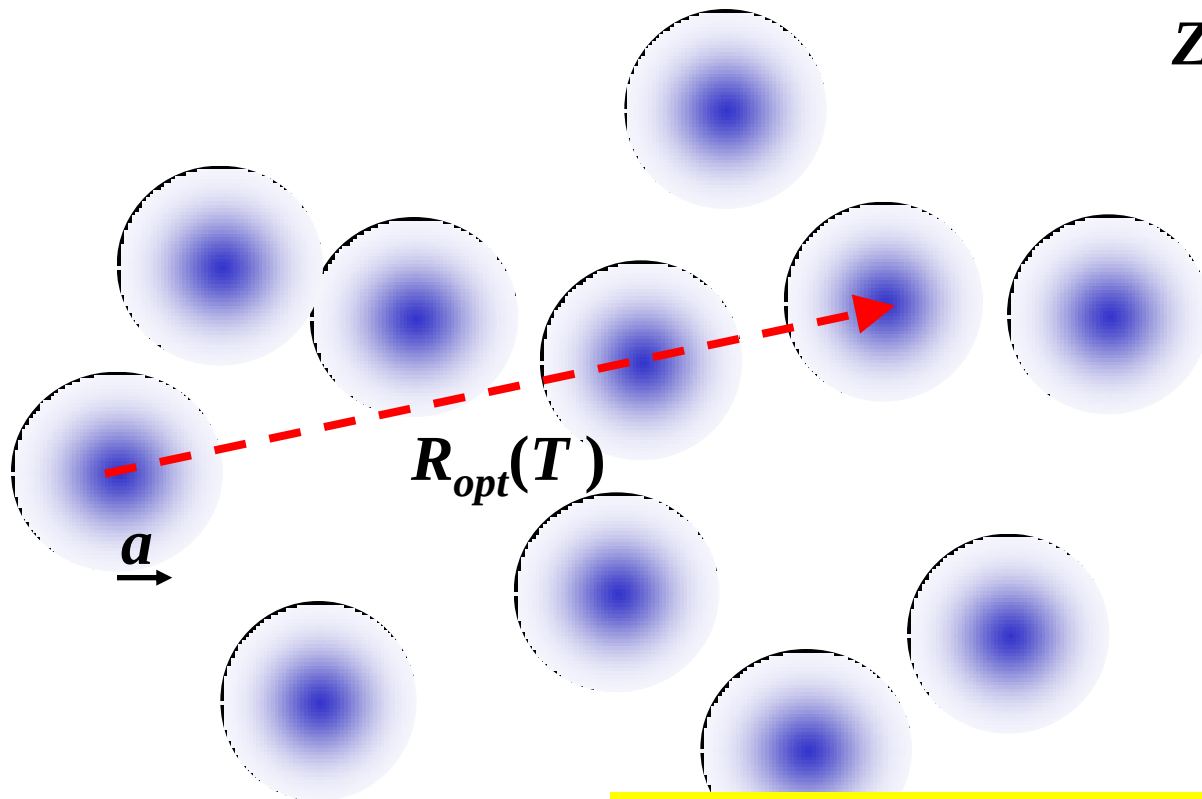
НАНО ТРАНСПОРТ



000051 25KV X980 2.45um

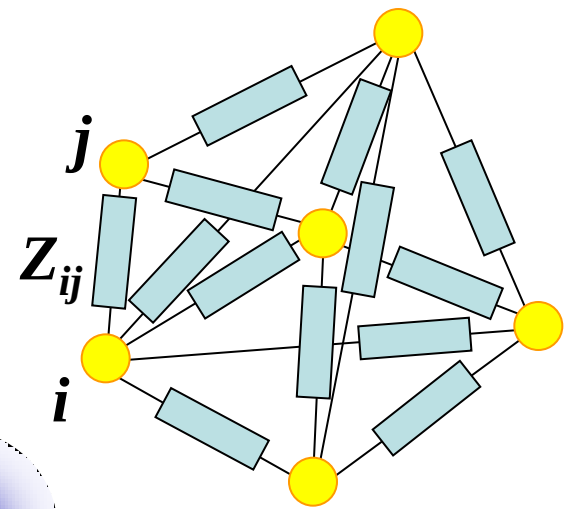


Hopping conductivity- transport on a nanometer scale



$$\frac{R_{opt}}{a} \sim 3-10 \quad \longrightarrow$$

In an amorphous material
the estimate $a \sim 1$ nm is
expected and therefore
should be $R_{opt} \sim 3-10$ nm.
**How about finding
localization length?**



$$Z_{ij} = Z_0 e^{\xi_{ij}}$$

$$\xi_{ij} = 2 \frac{R_{ij}}{a} + \frac{E_{ij}}{k_B T} \leq \xi_c$$

$$\rho = \rho_0 e^{\xi_c}$$

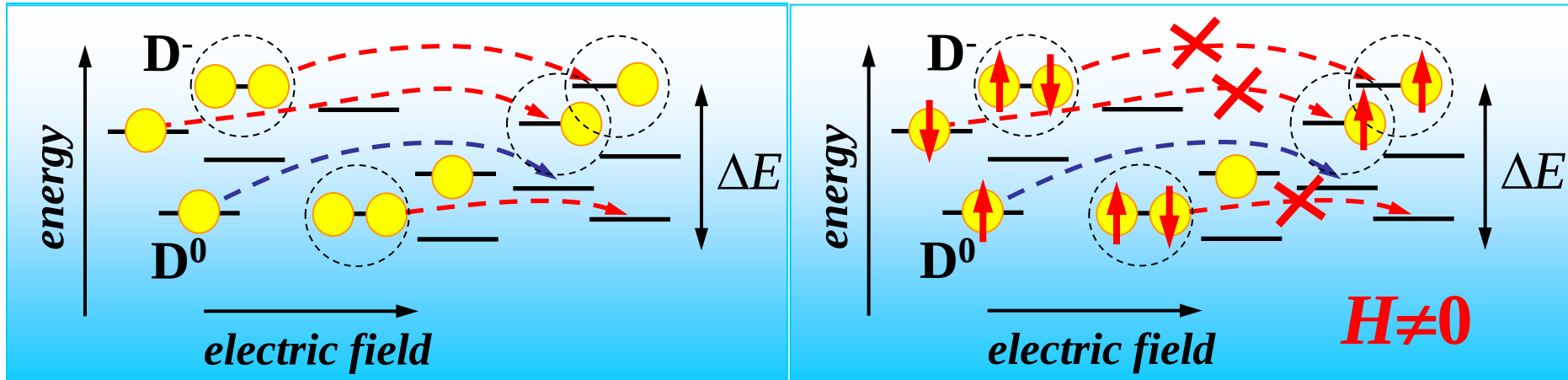
$$\xi_c = \left(\frac{T_0}{T} \right)^\alpha, \alpha = \frac{1}{d+1}$$

$$R_{opt} = \frac{a}{2} \xi_c, \Delta E = k_B T \xi_c$$



Spin effects in variable range hopping.

“Convenient” hopping Hopping with D^0 and D^- states



Magnetoresistance

Orbital effects (shrinkage of the wave function)

PMR

Spin effects:

Spin-polarization mechanism

Scaling

Quantum interference

NMR



Spin-polarization mechanism

D^0 and D^- centers exist in the vicinity of the Fermi level and form common MA network. Polarization of the spin part of the wave function “switch” different types of transitions.

Hopping system $\equiv$ paramagnet

Colored percolation

$$\sum n_i = \sum n_i(\xi, H) + n_{\uparrow\downarrow}(\xi, H) \approx$$

$$\approx a_1^d g_1 \xi^{d+1} k_B T \cdot [1 - w_{\uparrow\downarrow}(H)] + a_2^d g_2 \xi^{d+1} k_B T \cdot w_{\uparrow\downarrow}(H) = n_c$$

$$\xi_c = (T_0(H)/T)^\alpha; \alpha = \frac{1}{d+1}$$

$$\ln \left[\frac{\rho(H)}{\rho(0)} \right] = \xi_0 F(x) \equiv \left(\frac{T_0}{T} \right)^\alpha F(x) \quad F(x) = \left(1 - A \cdot \tanh^2(x) \right)^{-\alpha} - 1$$

$$x = \frac{\mu H}{k_B T}$$

$$A = \frac{g_2 a_2^d - g_1 a_1^d}{g_2 a_2^d + g_1 a_1^d}$$

$$x \ll 1$$

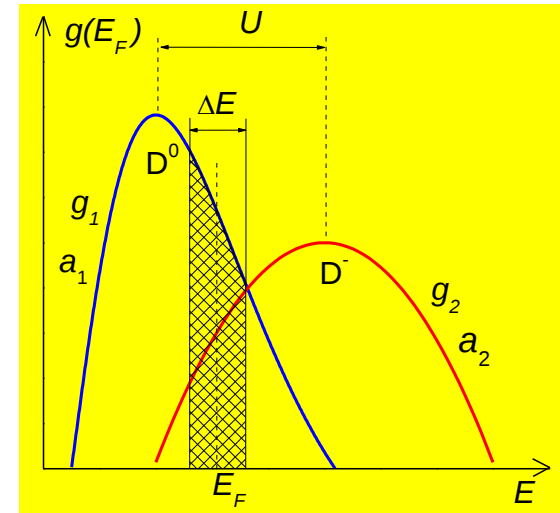
$$F(x) \approx \alpha \cdot A \cdot x^2$$

Easy accounting of both spin-polarization and shrinkage mechanisms :

$$\ln \left[\frac{\rho(H)}{\rho(0)} \right] = \left(\frac{T_0}{T} \right)^\alpha \alpha \cdot A_{\text{eff}}(T) \cdot \left(\frac{\mu H}{k_B T} \right)^2$$

$$A_{\text{eff}} = A + (t_d e^2 a_{\text{eff}}^4 k_B^2 T_0^{2\alpha} / c^2 \hbar^2 \mu^2 \alpha) \cdot T^{2-2\alpha}$$

$$a_{\text{eff}} \sim a_2$$



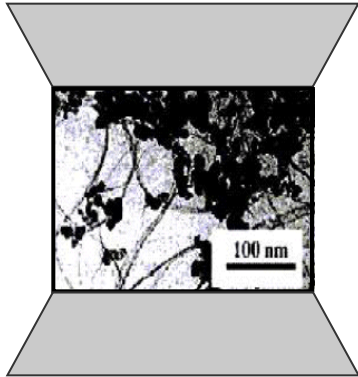
S.V.Demishev, A.A.Pronin,
Physics of the Solid State, 2006, No 7

Scaling



Conductivity and magnetoresistance data analysis.

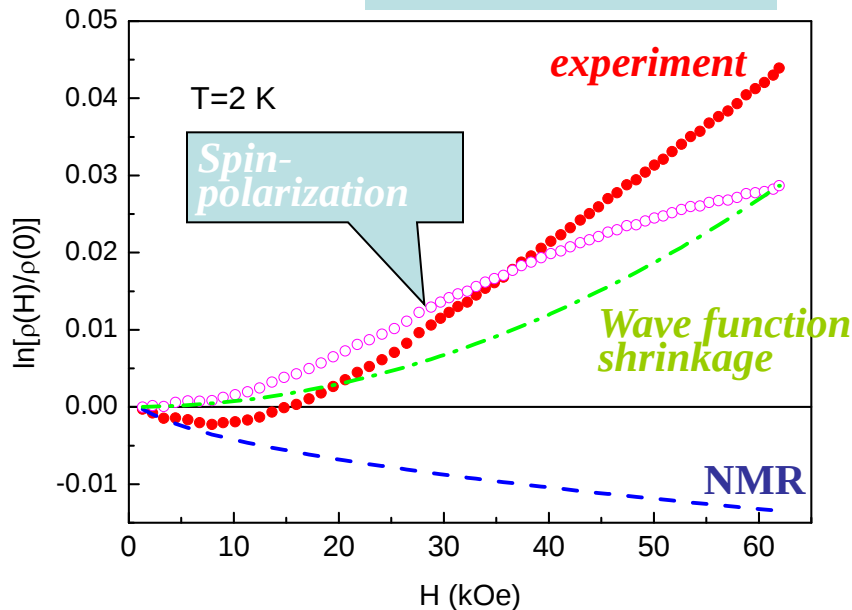
**7 GPa,
300-1000 °C**



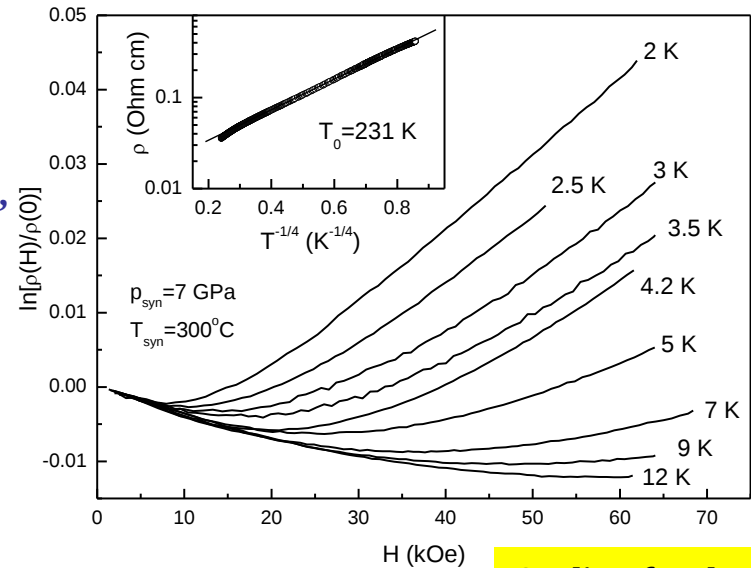
*Disordered nanomaterial
Obtained by modification
of SWNT under high pressure
and temperature.*

*Wide temperature range ($1.8 < T < 60$ K),
where Mott law with
 $\alpha=1/4$ and $T_0=231$ K is observed.*

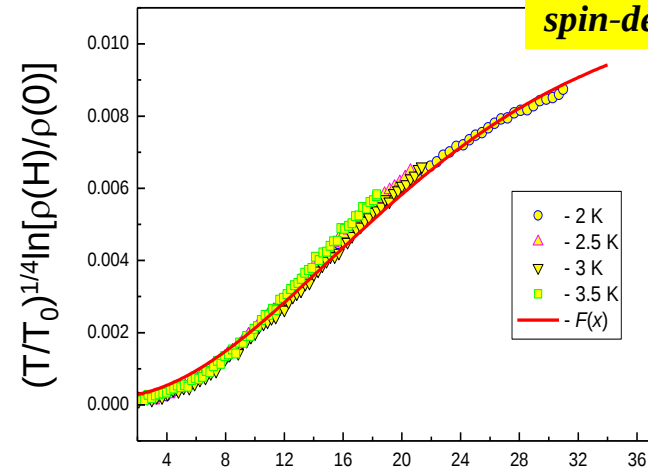
*Magnetoresistance
analysis*



Hopping conductivity & magnetoresistance



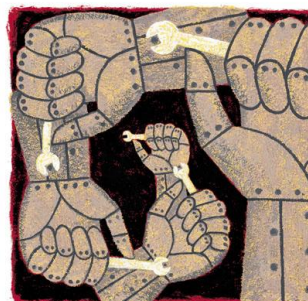
*Scaling for the
spin-dependent part*



Shrinkage is essential and gives: $a_2 \sim 6$ nm



«НАНО», магнетизм и квантовая критичность



Richard P. Feynman,
The Nano Prophet

...The magnetic properties on a very small scale are not the same as on a large scale; there is the ``domain" problem involved.

...In the year 2000, when they look back at this age, they will wonder...

“Plenty of Room at the Bottom”
1959



Real-space observation of a two-dimensional skyrmion crystal

X. Z. Yu^{1,2}, Y. Onose^{2,3}, N. Kanazawa³, J. H. Park⁴, J. H. Han⁴, Y. Matsui¹, N. Nagaosa^{3,5} & Y. Tokura^{2,3,5}

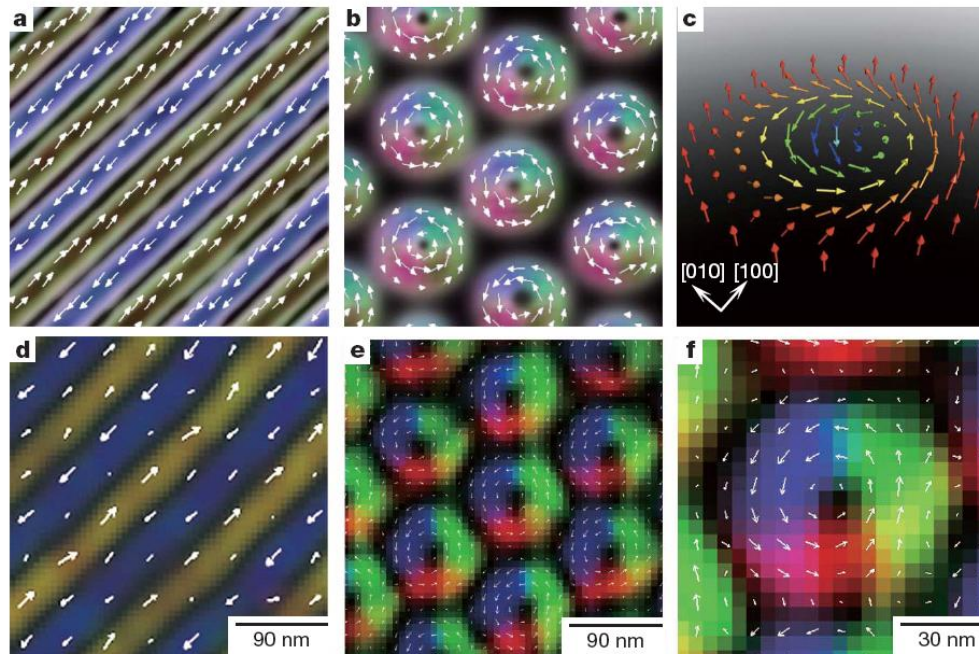
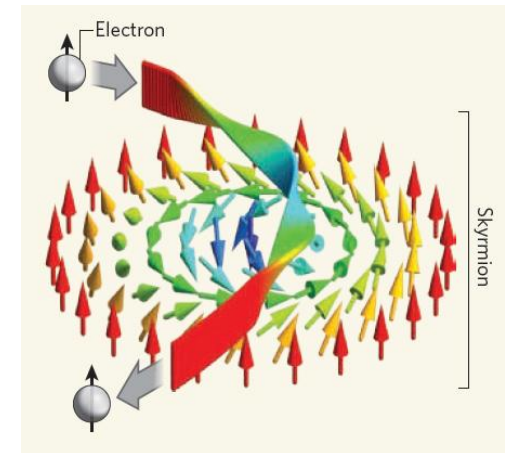


Figure 1 | Topological spin textures in the helical magnet $\text{Fe}_{0.5}\text{Co}_{0.5}\text{Si}$. **a, b**, Helical (**a**) and skyrmion (**b**) structures predicted by Monte Carlo simulation. **c**, Schematic of the spin configuration in a skyrmion. **d–f**, The experimentally observed real-space images of the spin texture, represented by the lateral magnetization distribution as obtained by TIE analysis of the

Lorentz TEM data: helical structure at zero magnetic field (**d**), the skyrmion crystal (SkX) structure for a weak magnetic field (50 mT) applied normal to the thin plate (**e**) and a magnified view of **e** (**f**). The colour map and white arrows represent the magnetization direction at each point.



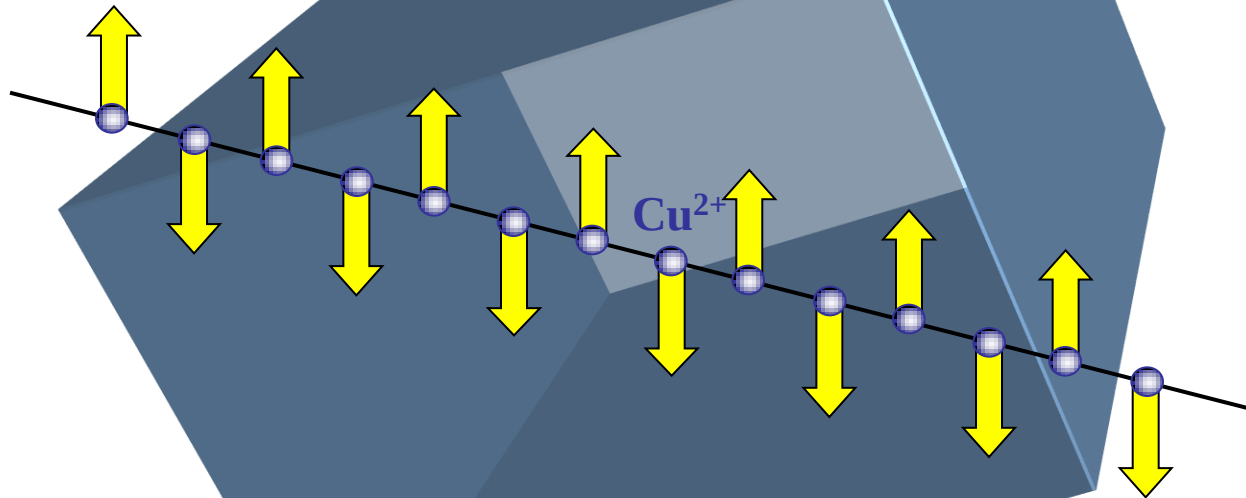
**Skyrmion =
Magnetic analog
of an Abrikosov
vortex in a type-II
superconductor**

Nanoscale magnetism can really provide new physics!



AFM $S=1/2$ спиновая цепочка- 1D модельный объект

Пример: купрат германия=германат меди



Макроскопическая квантовая система, сильные квантовые флуктуации.
Отсутствие магнитного упорядочения вплоть до $T=0$.

Эффекты беспорядка?

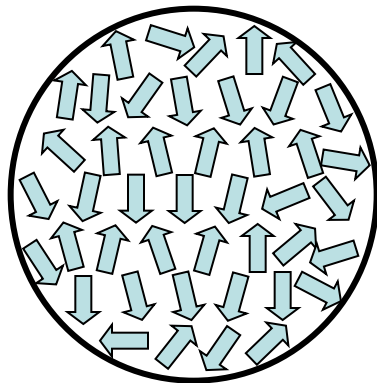
Квантовая критичность?

Пространственный масштаб ?



DISORDER DRIVEN QUANTUM CRITICAL PHENOMENA

In a disordered magnet dispersion of the exchange constants J exists

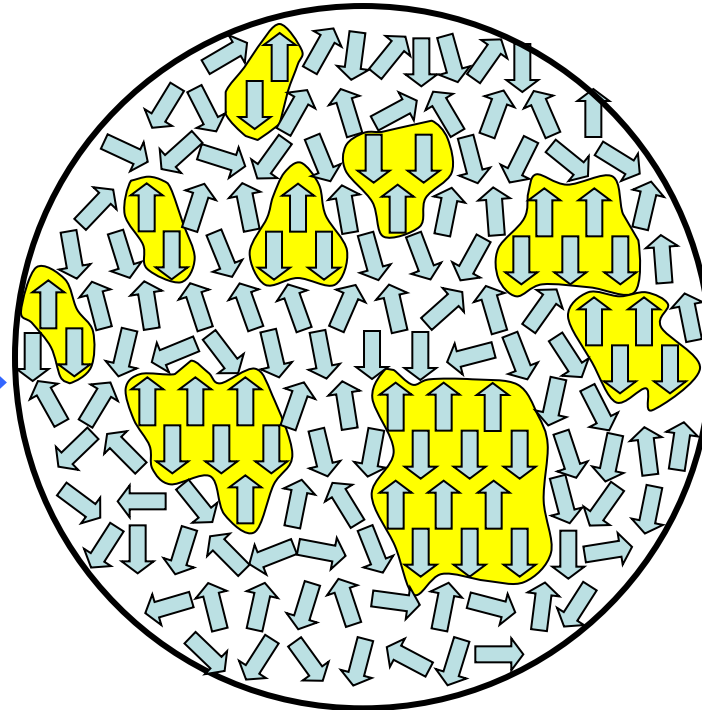


High temperatures

$$\chi = \frac{C}{T - \theta}$$

Uncorrelated spins.
Curie-Weiss law for susceptibility

Lowering temperature



Low temperatures

$$\chi \sim \frac{1}{T^\xi}$$
$$\xi < 1$$

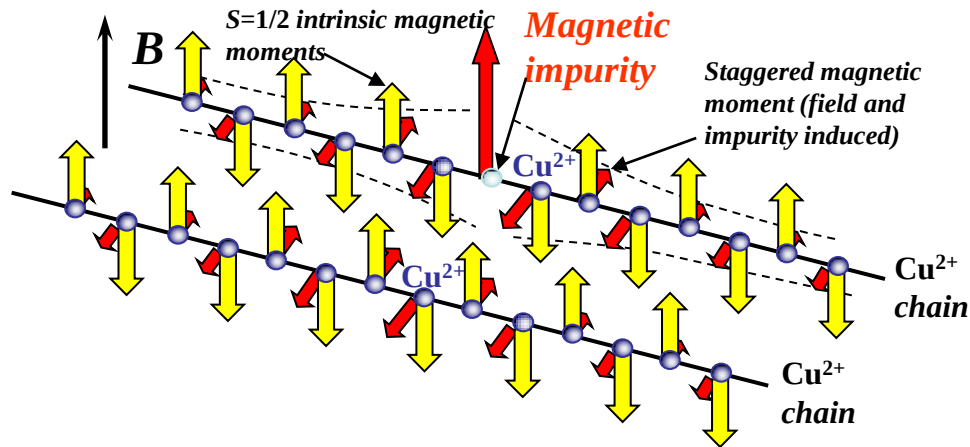
Correlated spin clusters.
Power law for susceptibility.

R.B.Griffiths. Phys. Rev. Lett., **23**, 17 (1969); A.J.Bray, Phys. Rev. Lett., **59**, 586 (1987)

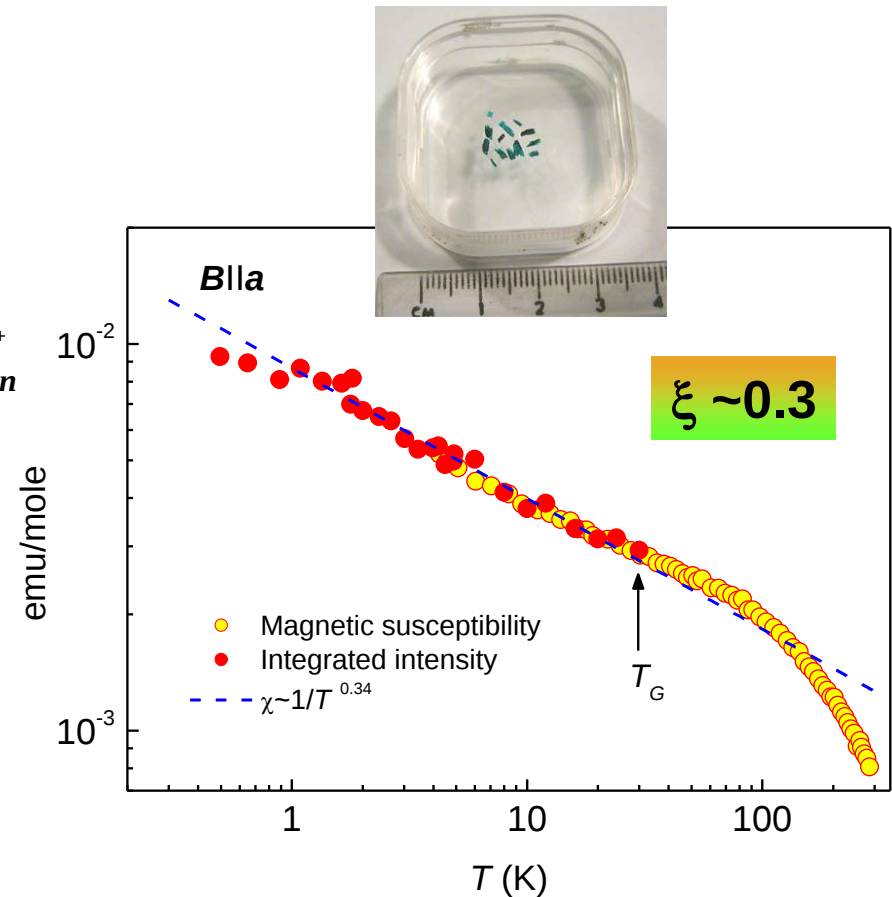
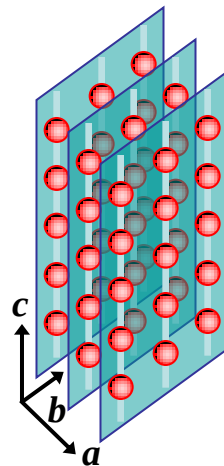
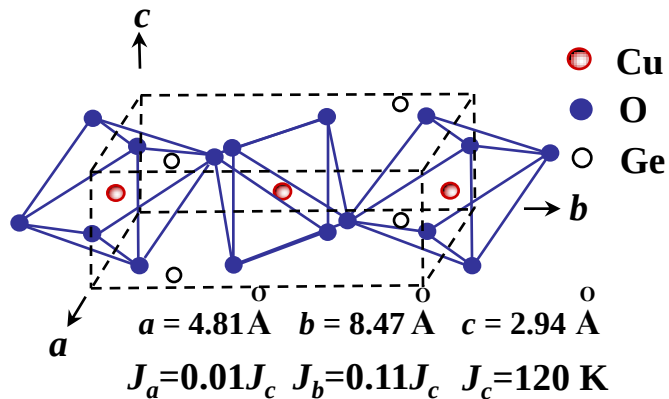


Practical realization: CuGeO_3 doped with magnetic impurities.
 $\text{Cu}_{1-x}\text{M}_x\text{GeO}_3$ ($x=0.02$ M=Co; $x=0.01$ M=Fe, $x=0.009$ M=Mn)

$S=1/2$ (Cu) AF chains



$S=3/2$ (Co) $S=2$ (Fe) $S=5/2$ (Mn)



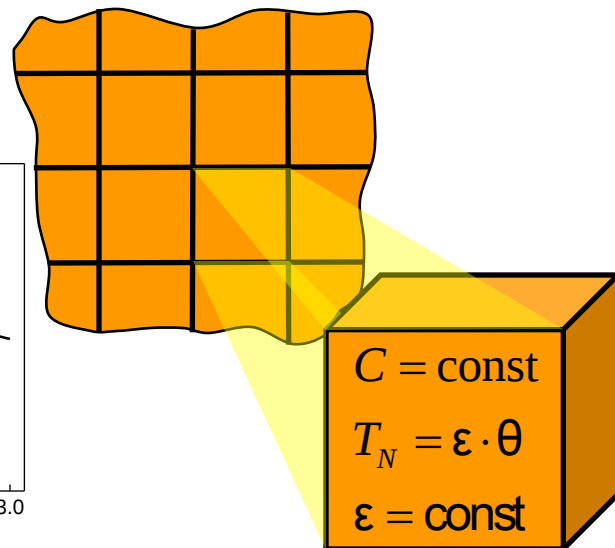
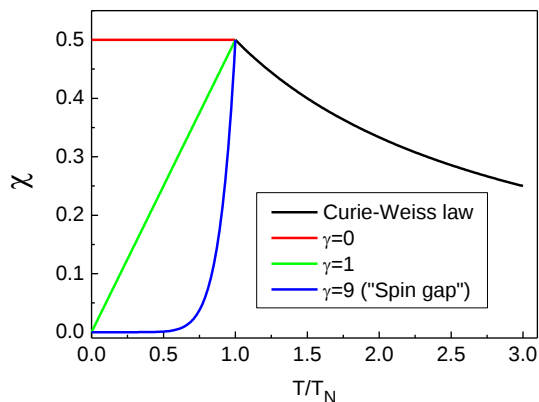
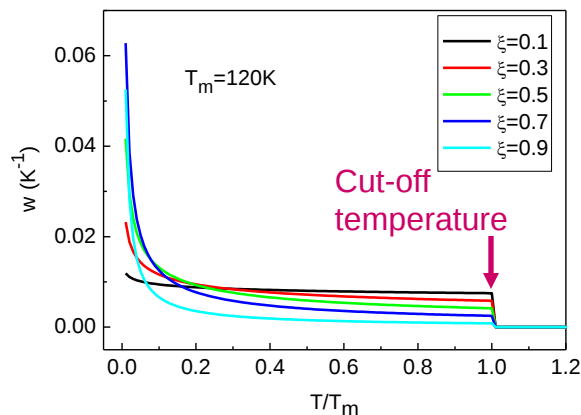
Quantum critical behavior in a wide temperature range (at least $1 < T < T_G \sim 30 \text{ K}$)!



The model:

S.V.Demishev, Phys.Sol.St., **51**(3), 514 (2009)

S.V.Demishev, Phys. Stat. Sol. B, **247**(3), 676 (2010)



Distribution of Neel temperatures in the sample:

$$w(T_N) = (1 - \xi)(T_m / T_N)^\xi / T_m$$

Susceptibility of the cluster with T_N :

$$\chi = C / (T + \varepsilon^{-1} T_N) \quad (T > T_N)$$

$$\chi = C(T / T_N)^\gamma / [T_N (1 + \varepsilon^{-1})] \quad (T < T_N)$$

Result (susceptibility at an arbitrary temperature):

$$\chi = C / (T + \theta^*) \quad (T > T_m)$$

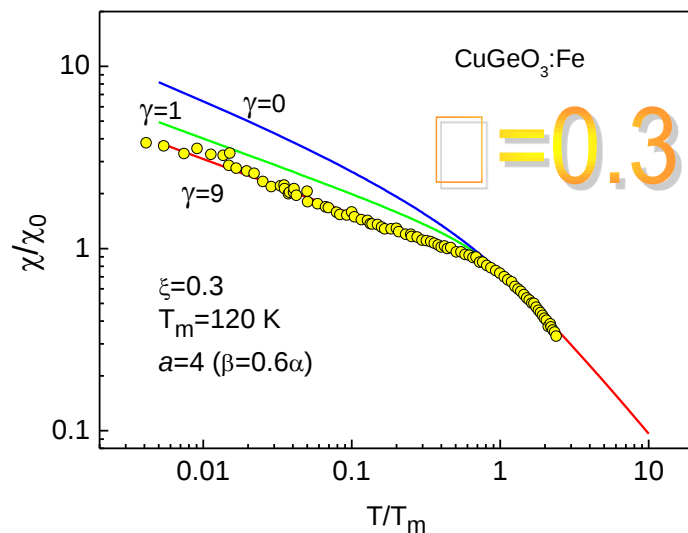
$$\chi = [C / (T_m + \theta^*)] (T / T_m)^{-\xi} \{1 + (1 - \xi)(1 + \theta^* / T_m)[1 - (T / T_m)^{\gamma + \xi}] / [(1 + \varepsilon^{-1})(\gamma + \xi)]\} \quad (T < T_m)$$

$$\theta^* = T_m [\varepsilon(1 - \xi) f(\varepsilon, \xi)]^{-1} - 1 \quad f(\varepsilon, \xi) = -\xi^{-1} - \sum_{r=1}^{\infty} (-1)^r \varepsilon^r / (r + \xi) + \pi \varepsilon^{-\xi} / \sin[\pi(1 - \xi)]$$



Modeling of the magnetic properties of a Griffiths phase.

S=2 (Fe)

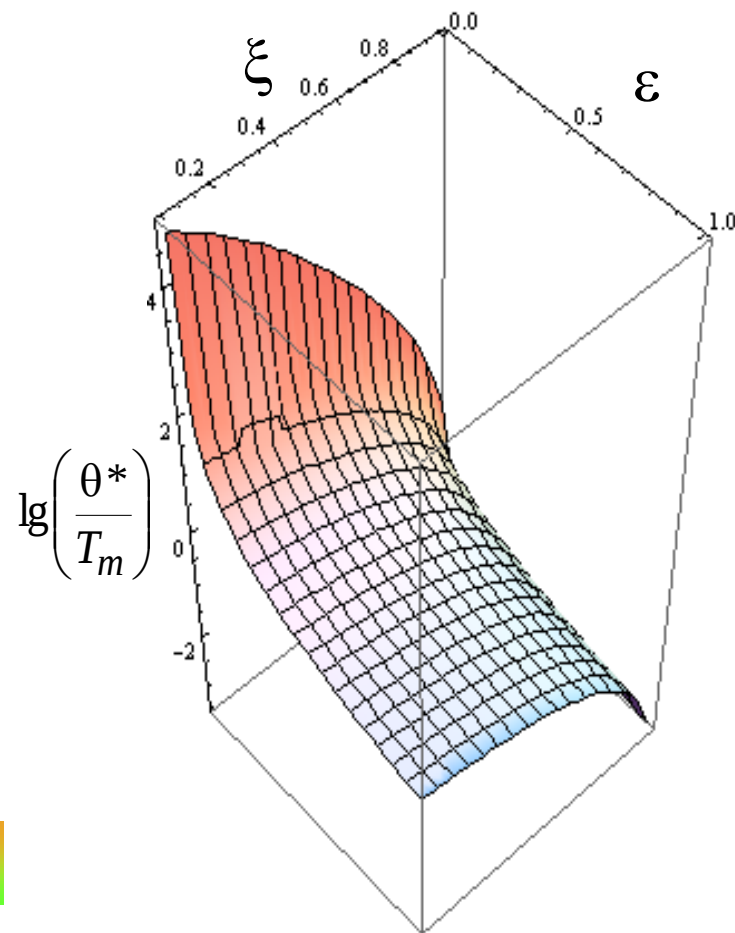


$$T_m \sim 120 \text{ K} \sim J_c$$

Temperature vary more than two orders of magnitude in the quantum critical region.

Doping reduces J in spin clusters

Paramagnetic temperature in Curie-Weiss law ($T > T_m$)



Estimate of the characteristic cluster size

Lowering temperature results in freezing of the magnetic contribution of the spin clusters for which condition $T_N > T$ holds.

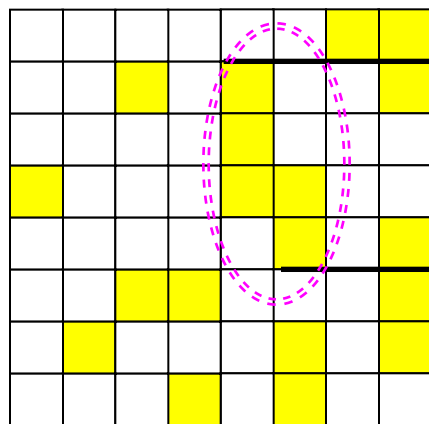
A two-phase model (“frozen” and “non-frozen clusters”) may be introduced. The probability $W(T_N)$ defines “frozen” part of the sample volume.

$$v_{AF} = 1 - \left(\frac{T}{T_m} \right)^{1-\xi}$$

$$R < R_m$$

$$r = R_m / l_0$$

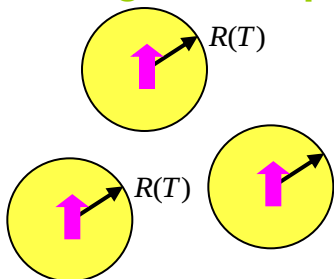
Percolation



$$r(T) \sim \frac{1}{|v_{AF}(T) - v_c|^\eta}$$

Correlation is missing

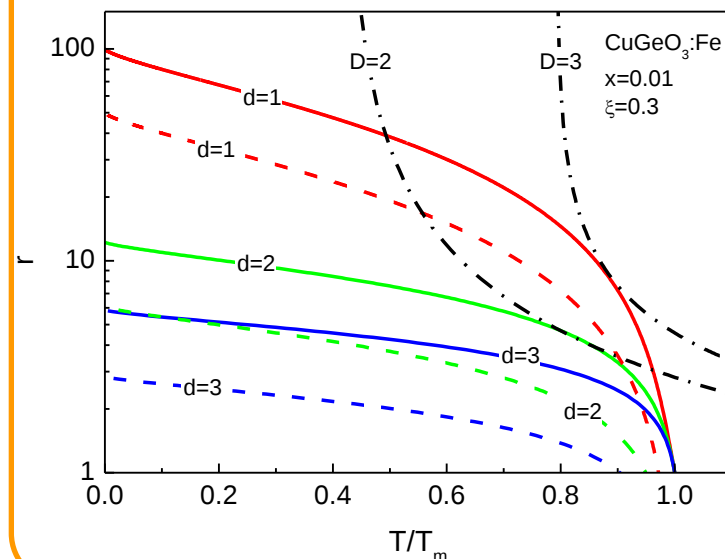
Cluster growth in vicinity of the magnetic impurity



$$\frac{T}{T_m} = \left[1 - \frac{2x}{d+1} \left(r^d - \frac{1}{r} \right) \right]^{\frac{1}{1-\xi}}$$

Correlation is essential

$\text{Cu}_{1-x}\text{M}_x\text{GeO}_3$ $l_0 \sim 1 \text{ nm}$



Griffiths phase is formed by nano spin clusters!?



КВАНТОВАЯ КРИТИЧНОСТЬ И НАНОМАСШТАБ

Что будет, если рассмотреть этот вопрос в
«противоположном» направлении:
от «нано» к квантовой критичности ??





Electron spin resonance and quantum critical phenomena in VO_x multiwall nanotubes

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ФМ-АФМ кроссовер в наноматериалах на основе оксида ванадия

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Н. А. Самарин, А. В. Семено

Институт общей физики им. А.М. Прохорова РАН, 119991 Москва, Россия

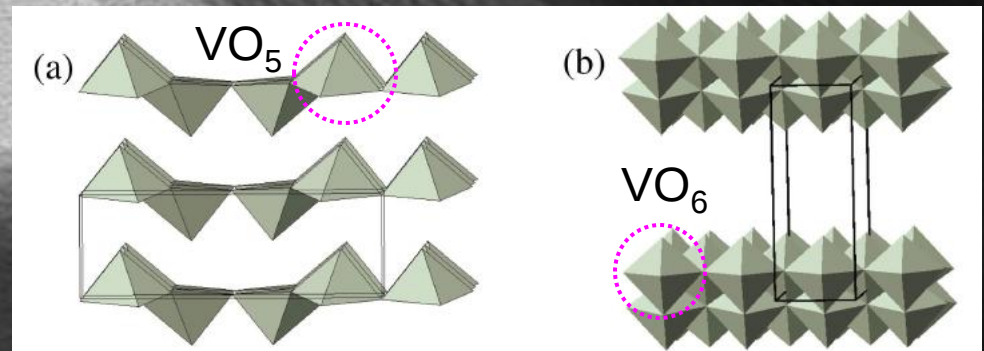
* Факультет наук о материалах, Московский государственный университет им. М.В. Ломоносова, 199991 Москва, Россия

Поступила в редакцию 5 ноября 2009 г.



Applications:

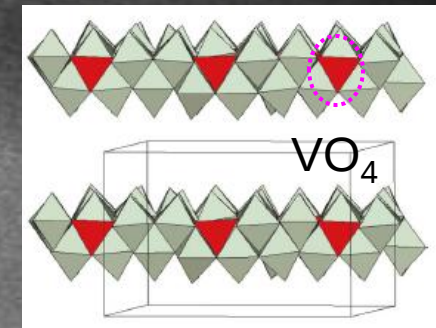
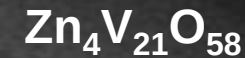
- Solid-state batteries
- Chemical sensors
- Catalysts
- Non-linear optics



Different V charge states...

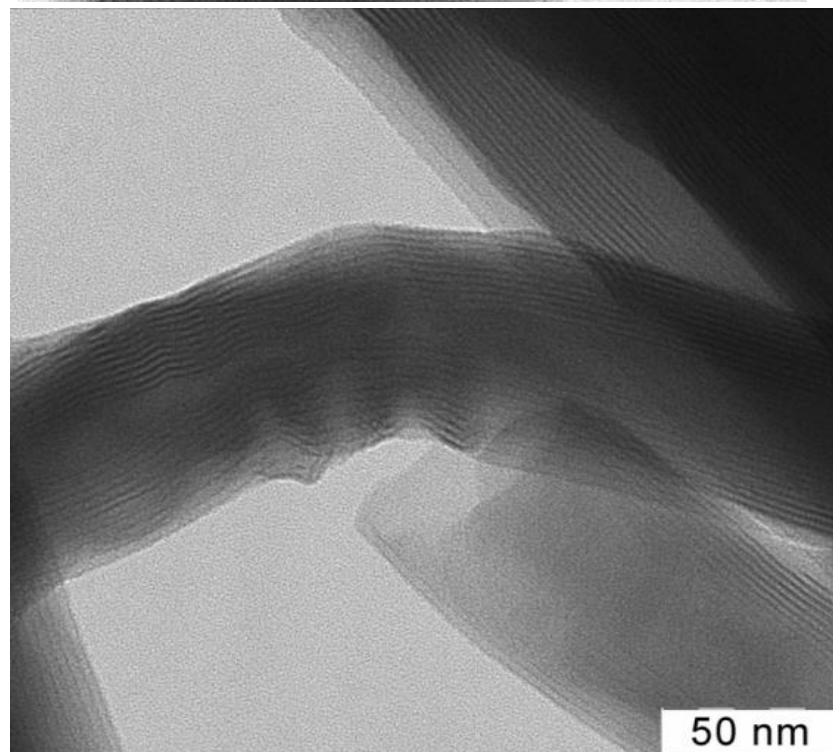
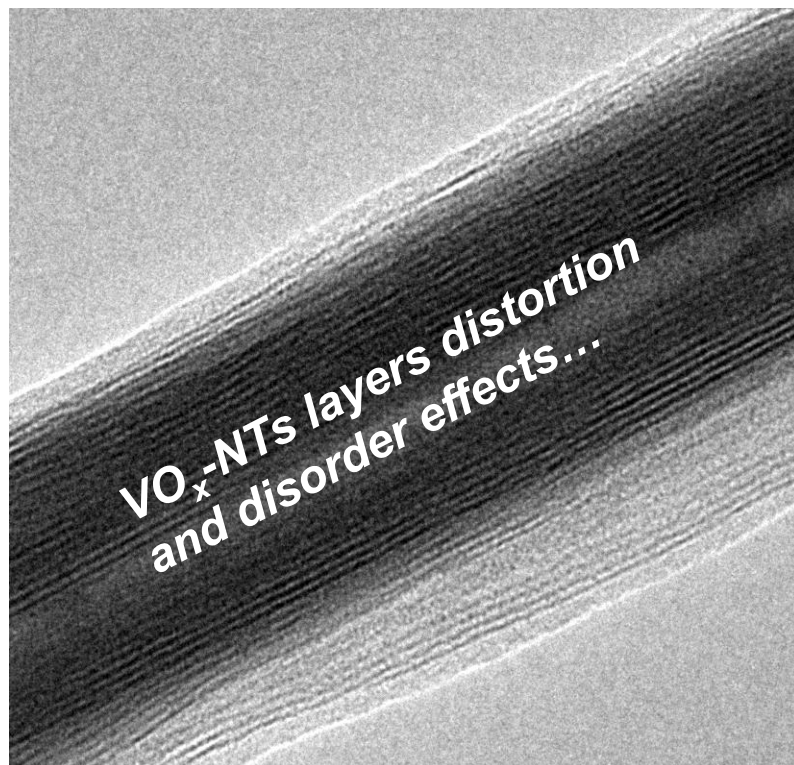
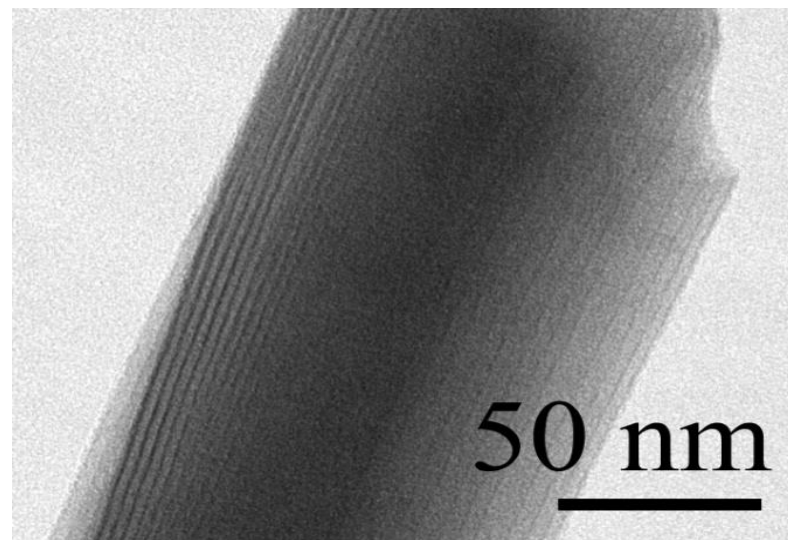
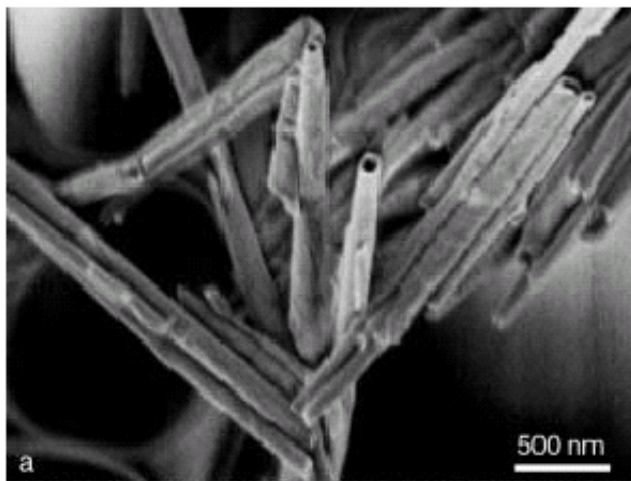
Fundamental interest:

- Structural studies
- Magnetic properties (nanoscale magnets etc.)



50 nm

VO_x multiwall nanotubes: TEM images



VO_x multiwall nanotubes: Structure

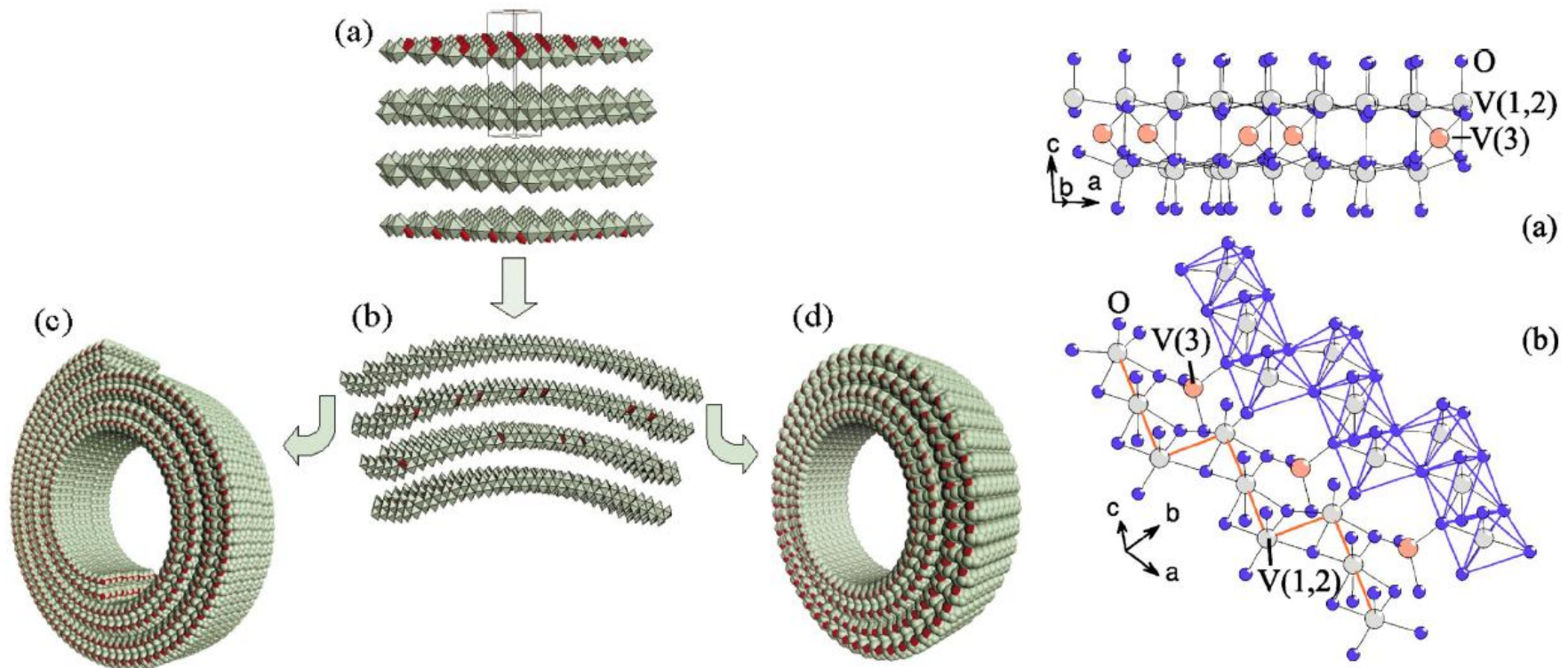
Precursor	Outer diameter, D (nm)	Inner diameter (nm)	Number of layers	Length, L (μm)
VO(PrO ⁱ) ₃	15 – 150	5 – 50	2 – 30	1 – 15
VOCl ₃	50 - 100	15 - 35	10 – 20	1,5 – 5
	75 - 100	20 – 35	11 – 14	0,8 – 1,5
V ₂ O ₅ crystal	70 - 140	20 – 35	9 – 13	2 – 12
	50 – 90	15 – 35	7 – 13	1 – 3
	70 – 100	20 – 45	6 – 11	1 – 2
	30 – 100	~ 45	3 – 10	1 – 10
	60 – 90	20 – 45	6 – 10	1 – 3
V ₂ O ₅ gel	50 – 130	30 – 40	5 – 25	1 – 10

$L/D \sim 10^2$

50 nm



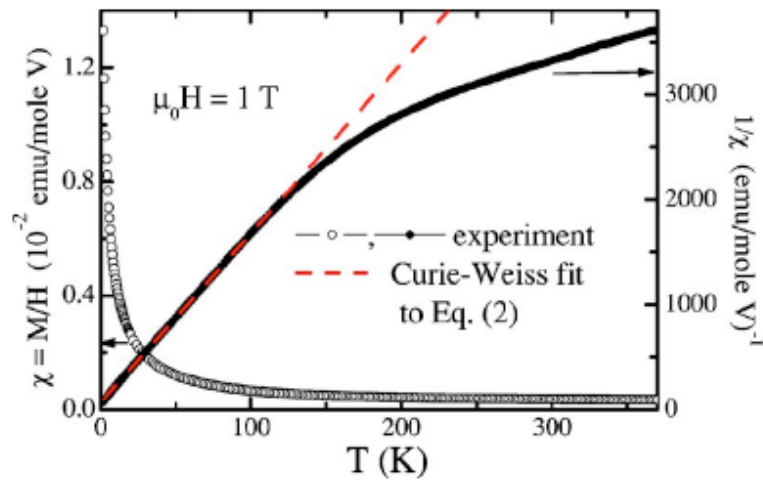
1. **Scrolling of one or two VO_x layers (“spiral”)** (Nesper et al., Advanced Materials – 2000)
2. **Scrolling of the stack of VO_x layers (“concentric”)** (Serdiri et al., Materials letters – 2007)
3. **1D motive (zigzag chain...). Anisotropy in the VO_x layer, several non-equivalent V sites** (Vavilova et al., Phys.Rev. B, 73, 144417 (2006))



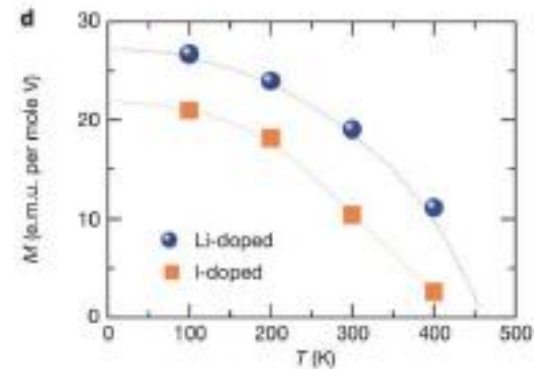
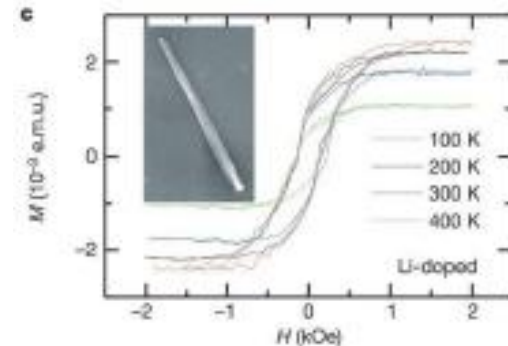
V.Petkov et al., PRB, **69**, 085410 (2004)



UNDOPED VO_x -NTs ARE ANTIFERROMAGNETS

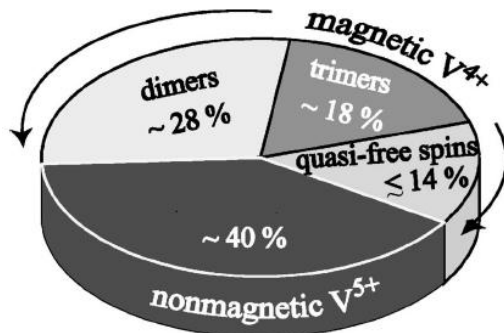


DOPED VO_x -NTs ARE FERROMAGNETS



Magnetism=Free spins(AF) + AF dimers

V^{5+} $S=0$ – non-magnetic ion
 V^{4+} $S=1/2$ – magnetic ion



**Ferromagnetism at room temperature
 In Li and I doped samples**
 L.Krushin-Elbaum et al.
 Nature, **431**, 672 (2004)

E.Vavilova, I.Hellmann et al., Phys.Rev. B, **73**, 144417 (2006)



Problems with various spin species
(E.Vavilova, I.Hellmann et al.,
Phys.Rev. B, **73**, 144417 (2006))

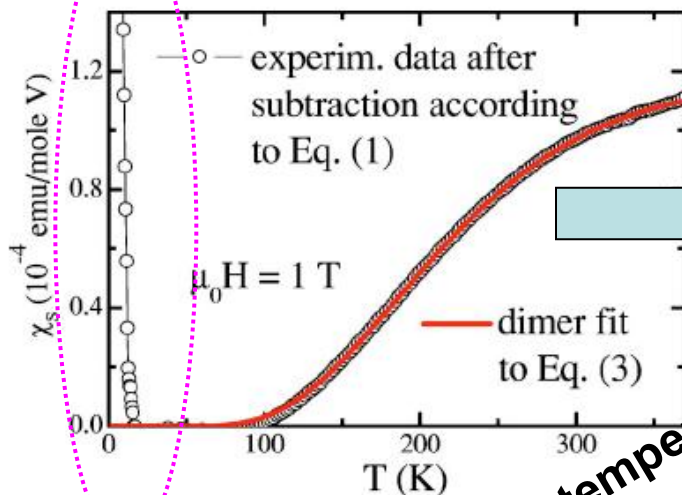
Free spins + AF dimers model

$$\chi = \chi_{CW} + \chi_D + \chi_0$$

$$\chi_{CW} = C / (T + \theta)$$

$$\chi_D = C_D / (T[3 + \exp(\Delta / k_B T)])$$

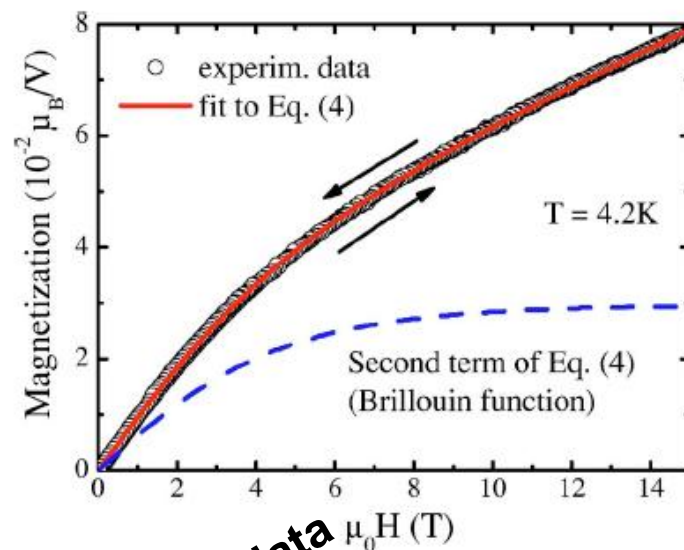
$$\chi_0 = \text{const}$$



$$\Delta = 710 \text{ K}$$

High-temperature data

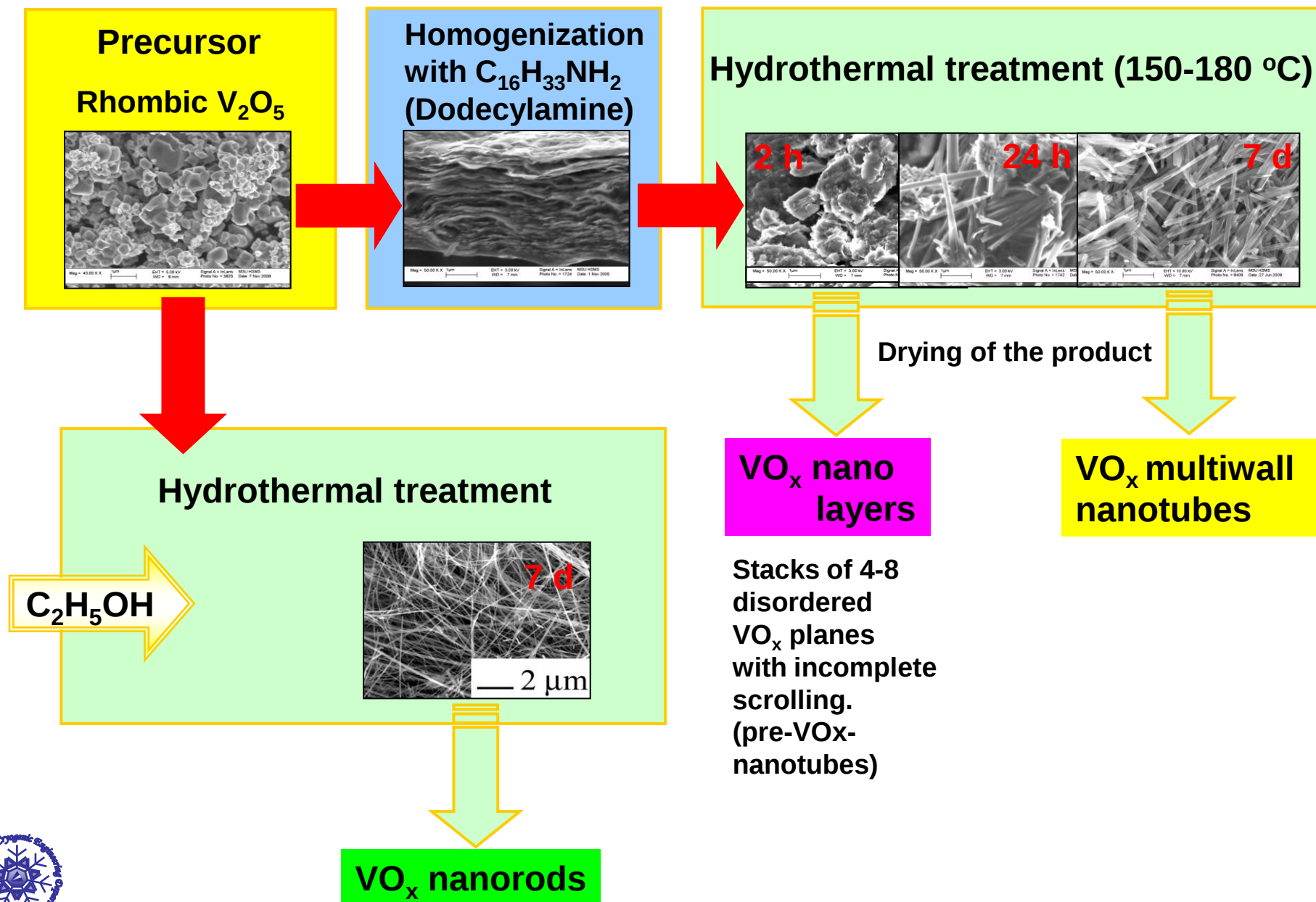
17% of V sites possess
the quasi-free spins



Low-temperature data

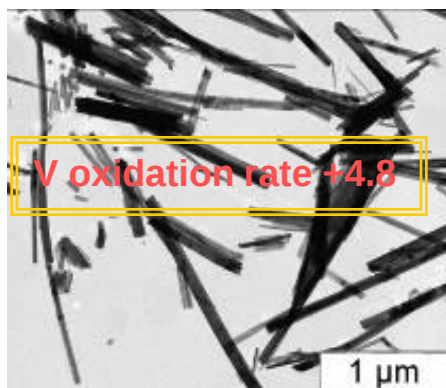
3% of V sites possess
the quasi-free spins





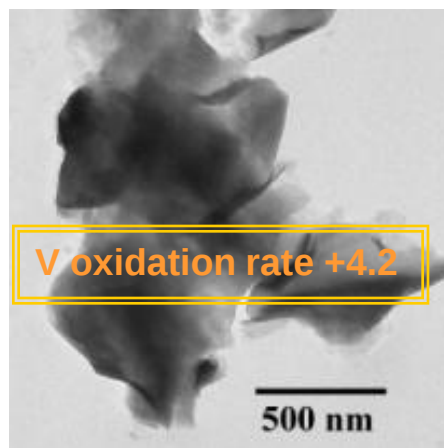
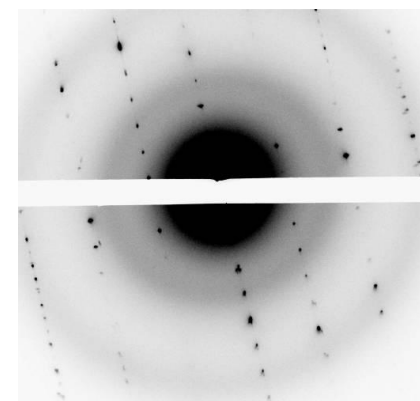
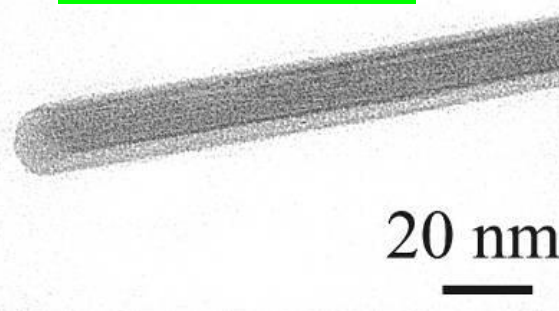
VO_x nanomaterials: different morphological forms.

Hydrothermal treatment allows obtaining different forms of VO_x nanomaterials

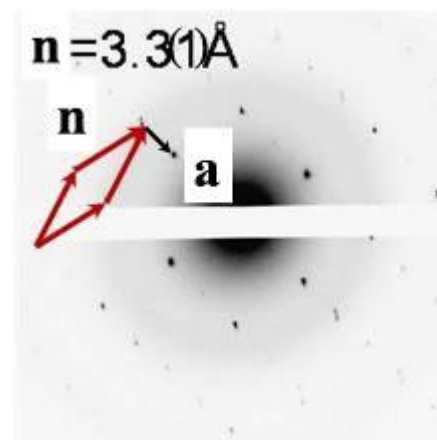


V oxidation rate +4.8

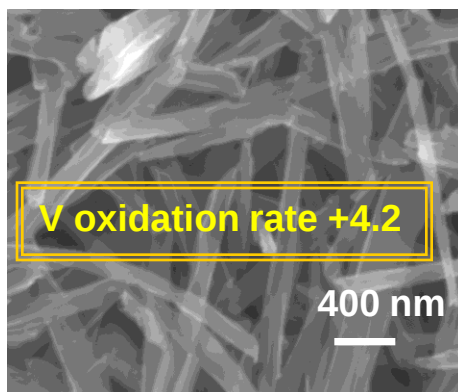
VO_x nanorods



V oxidation rate +4.2

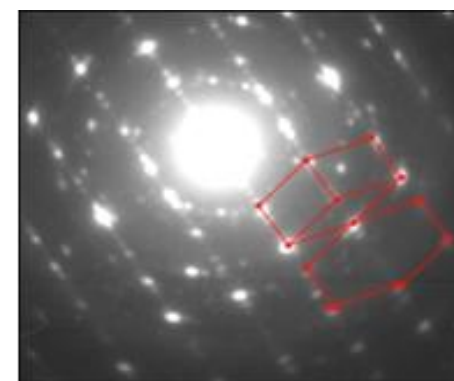
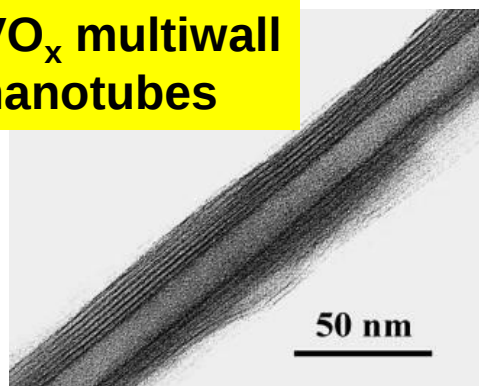


VO_x nanolayers
(pre- VO_x -nanotubes)



V oxidation rate +4.2

VO_x multiwall
nanotubes



IDEA: Understanding of the magnetism of VO_x-NTs in wider context of different morphological forms of VO_x nanomaterials as long as synthesis schema is essentially the same.

Questions remaining from the previous research of VO_x-NTs:

*Is not
studied
up to
now*

Indirect evidence for AF dimers

Concentration estimates

What happens at low temperatures?

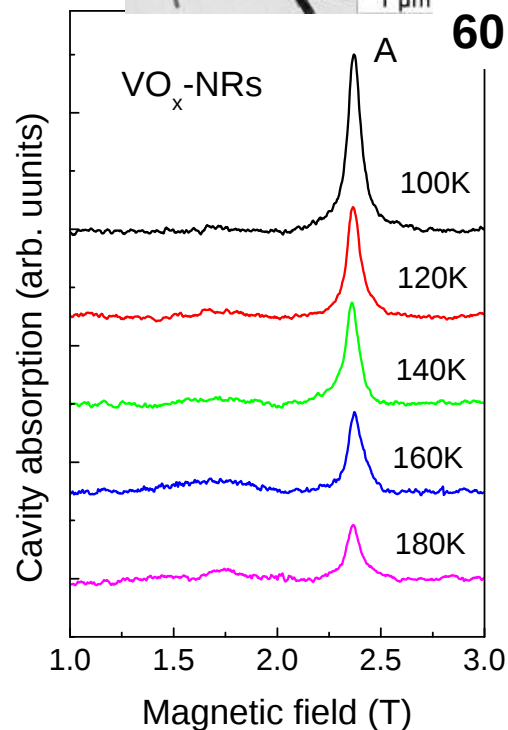
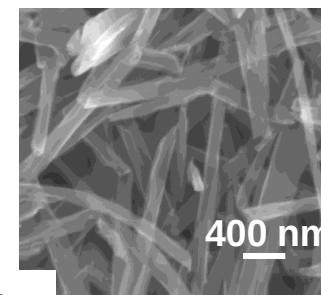
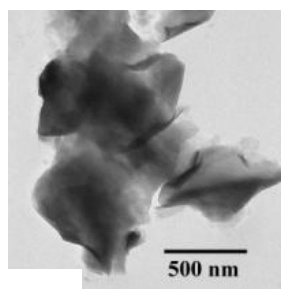
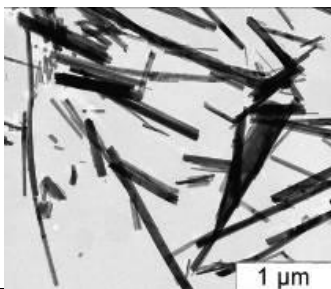


Several contributions to susceptibility,
thus the ESR is an adequate tool
(+ comparison with the static susceptibility data).

Available ESR data for VO_x-NTs:
X-band 77-300 K

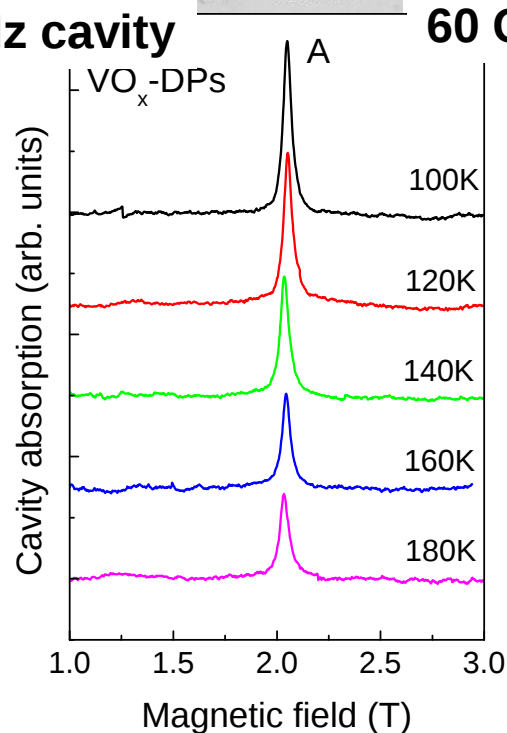
High frequency low temperature ESR
experiment is required

ESR in VO_x nanomaterials: spectra.

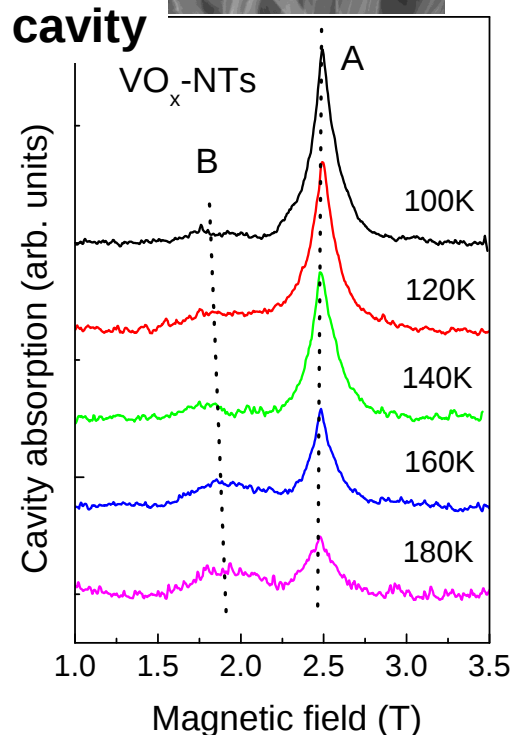


VO_x nanorods

Single ESR line



VO_x nano layers



VO_x nanotubes

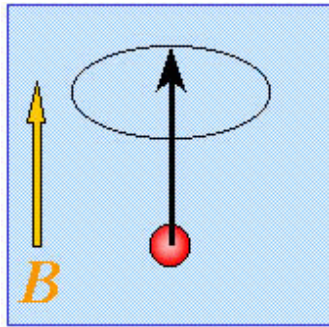
Two ESR lines

V^{5+} $S=0$ – non-magnetic ion

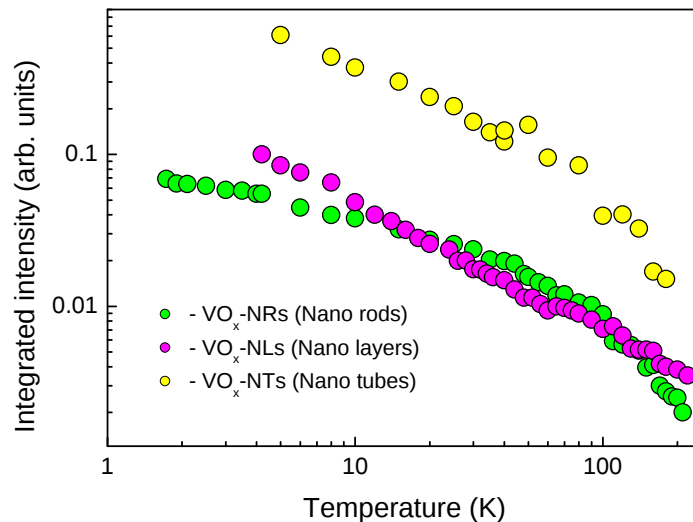
V^{4+} $S=1/2$ – magnetic ion



ESR in VO_x nano: Precession of the V^{4+} Magnetic moment in magnetic field

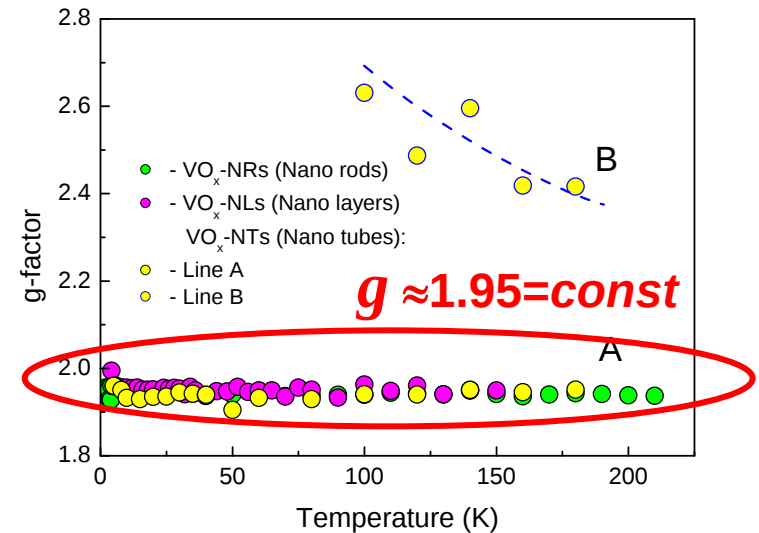


Hyromagnetic ratio, g-factor, magnitude of the oscillating magnetic dipole
 $g \sim \mu$

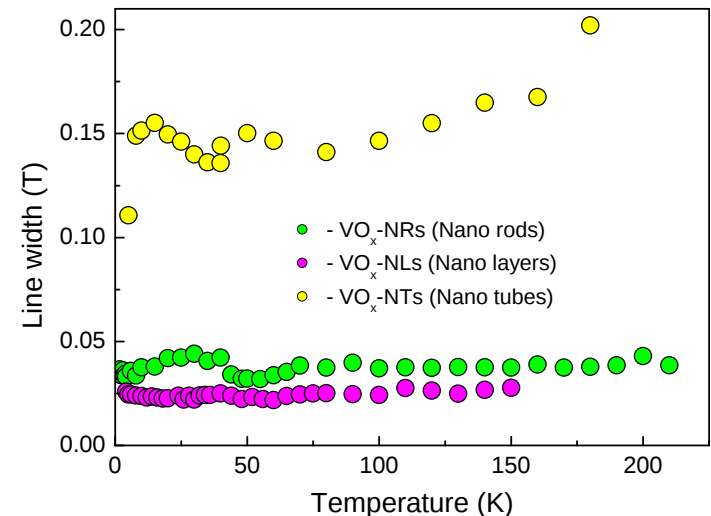


Integrated intensity, oscillating part of spin susceptibility (V^{4+} for VO_x nano)

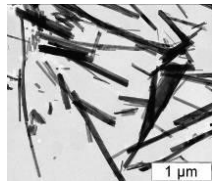
$$I(T) \sim \chi_s(T)$$



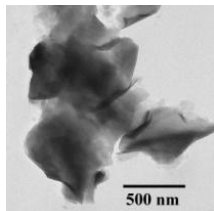
Line width, relaxation time T_2



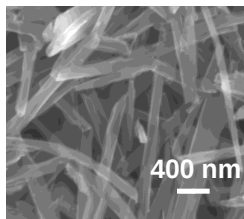
FM-AFM crossover in the VO_x nanomaterials.



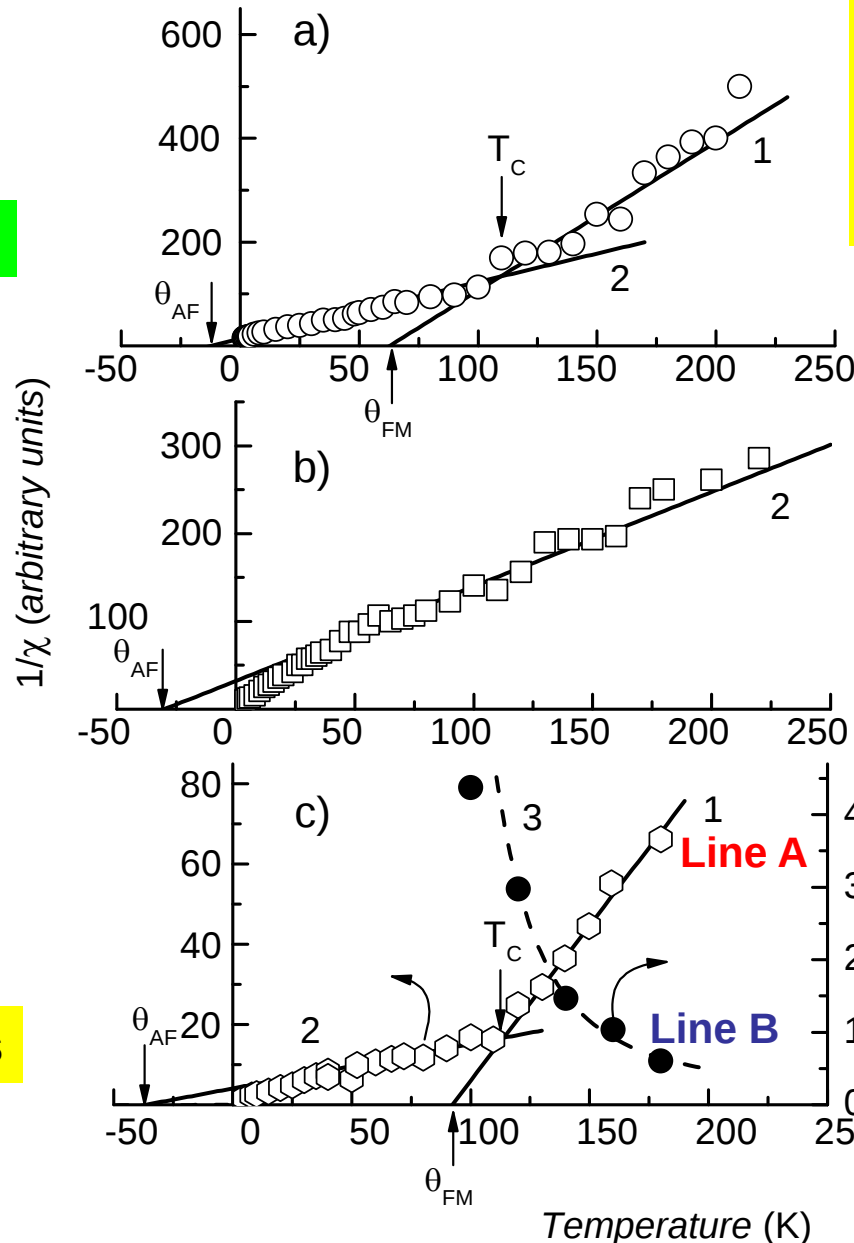
VO_x nanorods



VO_x nano layers



VO_x nanotubes



Crossover from the ferromagnetic interactions ($\theta_{FM} > 0$) to the antiferromagnetic interactions ($\theta_{AF} < 0$) at $T_c \sim 100$ K in nanorods and nanotubes. No crossover in nanolayers

Crossover is accompanied by increase of the Curie-Weiss constant in the AF region ($T < T_c$) by 3-7 times.

As long as $g = \text{const}$, this suggests the increase of the concentration of the oscillating magnetic moments at T_c .

Line B: description within AF dimers model

$$\chi_D = \frac{C_D}{T[3 + \exp(\Delta / k_B T)]}$$

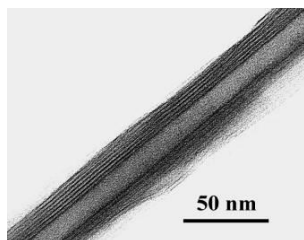
with the spin gap $\Delta = 716$ K.



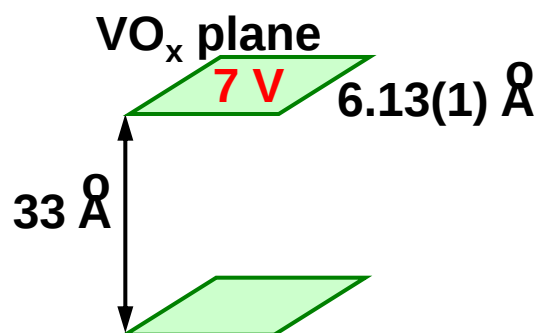
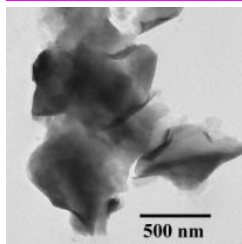
The nature of FM-AFM crossover.

Concentrations from X-ray structural analysis and oxidation rate.

VO_x nanotubes



VO_x nanolayers



V oxidation rate +4.2

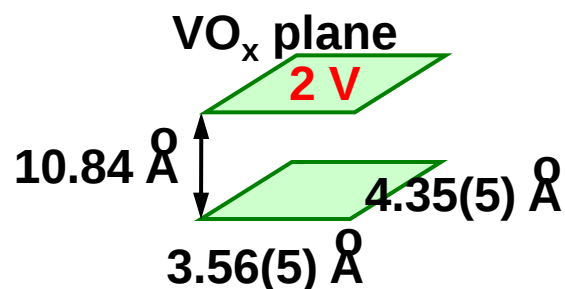
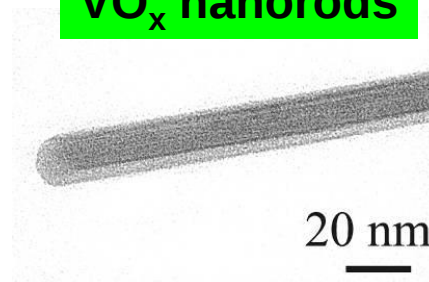
80% V⁴⁺
20% V⁵⁺

VO_x plane: N(V⁴⁺)=1.49·10¹⁵ cm⁻²

Sample volume:

N(V⁴⁺)=4.52·10²¹ cm⁻³

VO_x nanorods



V oxidation rate +4.8

20% V⁴⁺
80% V⁵⁺

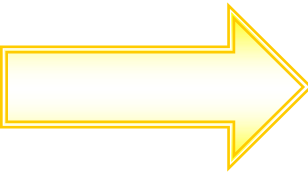
VO_x plane: N(V⁴⁺)=2.58·10¹⁴ cm⁻²

Sample volume:

N(V⁴⁺)=2.27·10²¹ cm⁻³



The nature of FM-AFM crossover.


$$\frac{N(V^{4+})_{nanolayers}}{N(V^{4+})_{nanorods}} \sim \begin{cases} 2, \text{ sample volume} \\ 6, \text{ VO}_x \text{ plane} \end{cases}$$



Magnetic subsystem in VO_x nanorods is diluted with respect to magnetic subsystem in VO_x nanolayers.

FM interaction for diluted system and AFM interaction for concentrated system (agrees with the susceptibility temperature dependence for VO_x nanorods).

How about nanotubes? The V^{4+} concentration is the same as in nanolayers...

But there are dimers, which are missing in nanolayers. This make magnetic subsystem of VO_x nanotubes diluted.

Curie-Weiss constants and g-factors give

- $T > 100$ K: $\sim 1.3\%$ V^{4+} FM spins and $\sim 98.7\%$ V^{4+} AF dimers
- $T < 100$ K: $\sim 8.6\%$ V^{4+} AF spins and $\sim 91.4\%$ V^{4+} AF dimers

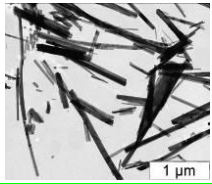
**AF dimers
dominate !**

Suggested idea works!

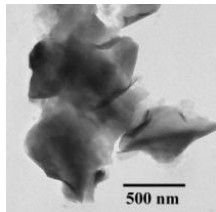
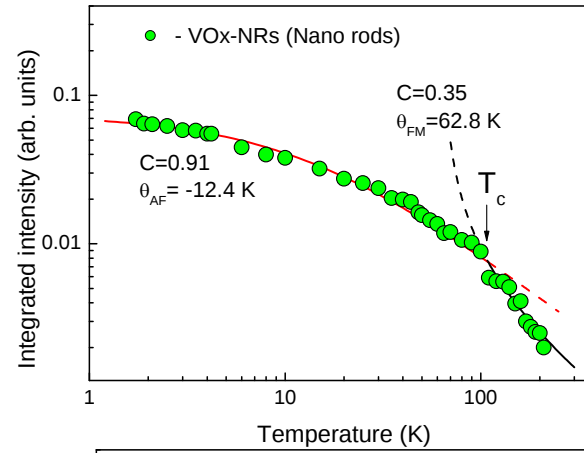
FM-AFM crossover : $e + V^{5+} \rightarrow V^{4+}$ at T_c
A kind of electron localization effect?



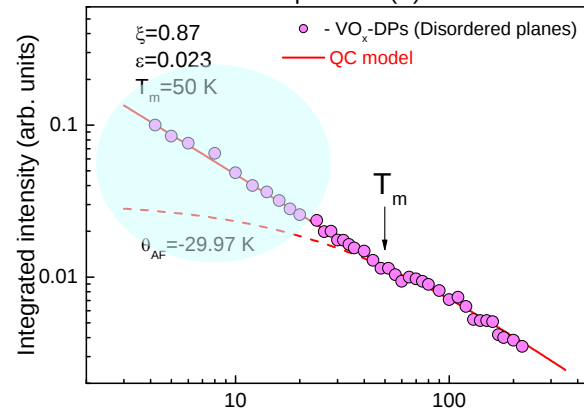
FM-AFM crossover in the VO_x nanomaterials.



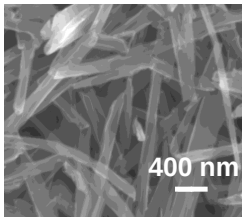
VO_x nanorods



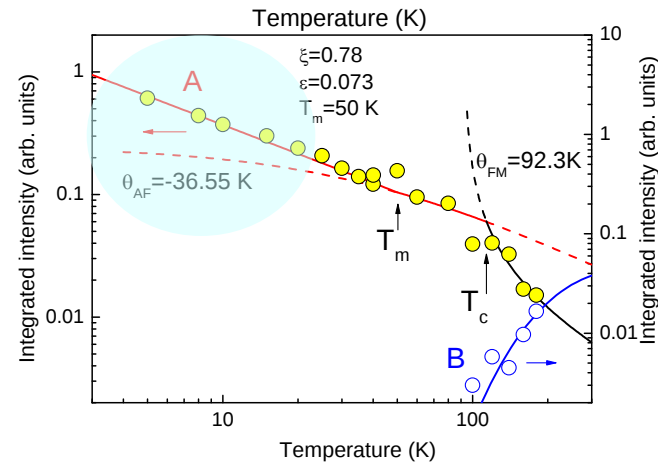
VO_x nano layers



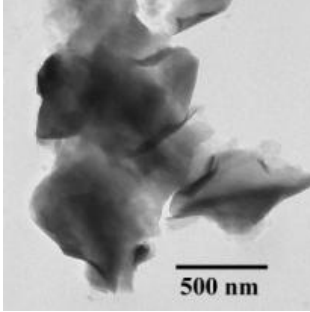
Low temperature anomaly (departures from Curie- Weiss law) at $T_m \sim 50 \text{ K}$



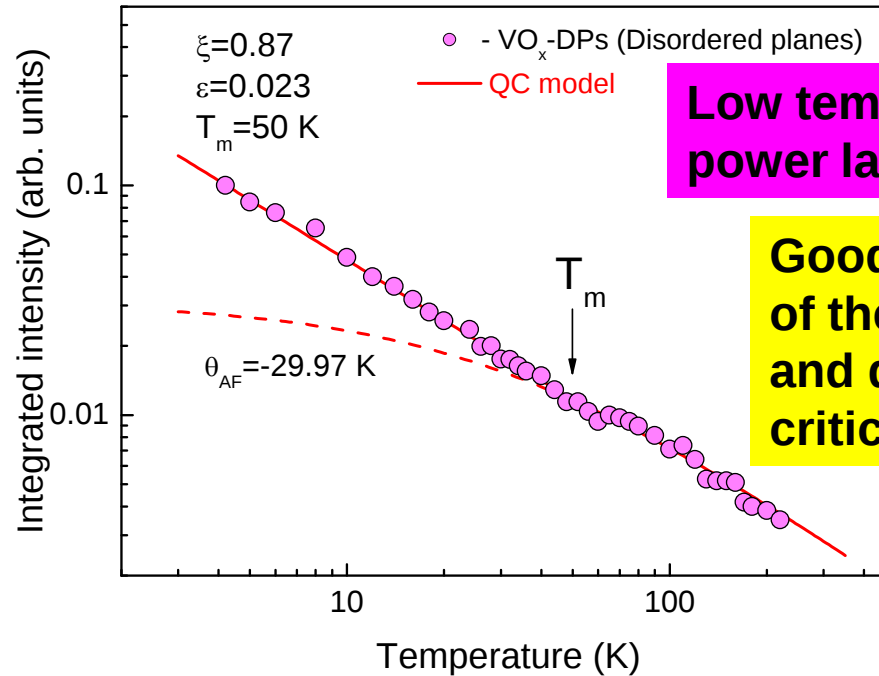
VO_x nanotubes



Low temperature anomaly



VO_x nanolayers



Low temperature power law with $\xi=0.87$

Good agreement of the experiment and quantum critical model.

The model:

Distribution of Neel temperatures in the sample:

$$w(T_N) = (1 - \xi)(T_m / T_N)^\xi / T_m$$

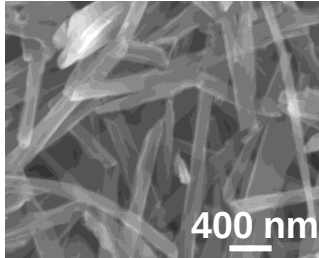
Result (susceptibility at arbitrary temperature):

$$\chi = C / (T + \theta^*) \quad (T > T_m)$$

$$\chi = [C / (T_m + \theta^*)] (T / T_m)^{-\xi} \{1 + (1 - \xi)(1 + \theta^* / T_m)[1 - (T / T_m)^{\gamma + \xi}] / [(1 + \varepsilon^{-1})(\gamma + \xi)]\} \quad (T < T_m)$$

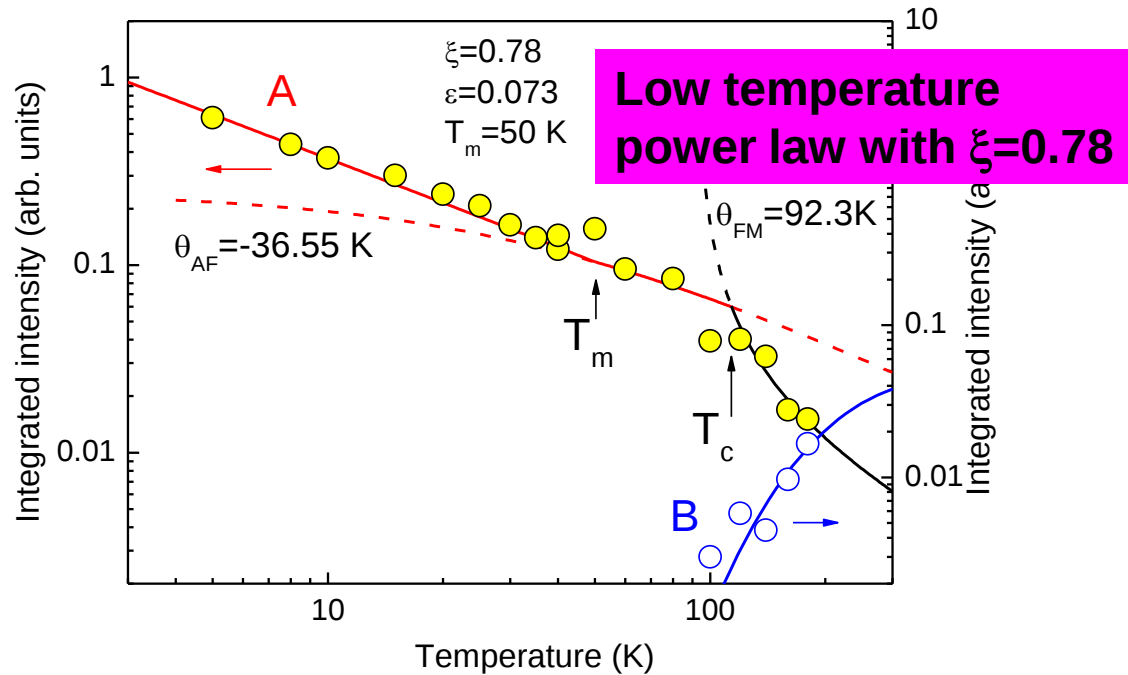
$$\theta^* = T_m [\varepsilon(1 - \xi) f(\varepsilon, \xi)]^{-1} - 1 \quad f(\varepsilon, \xi) = -\xi^{-1} - \sum_{r=1}^{\infty} (-1)^r \varepsilon^r / (r + \xi) + \pi \varepsilon^{-\xi} / \sin[\pi(1 - \xi)]$$

Low temperature anomaly



VO_x nanotubes

The model:



Distribution of Neel temperatures in the sample:

$$w(T_N) = (1 - \xi)(T_m / T_N)^\xi / T_m$$

Result (susceptibility at arbitrary temperature):

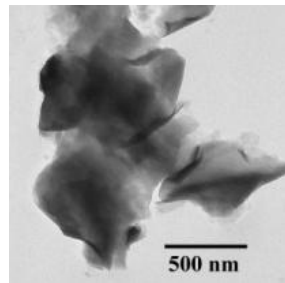
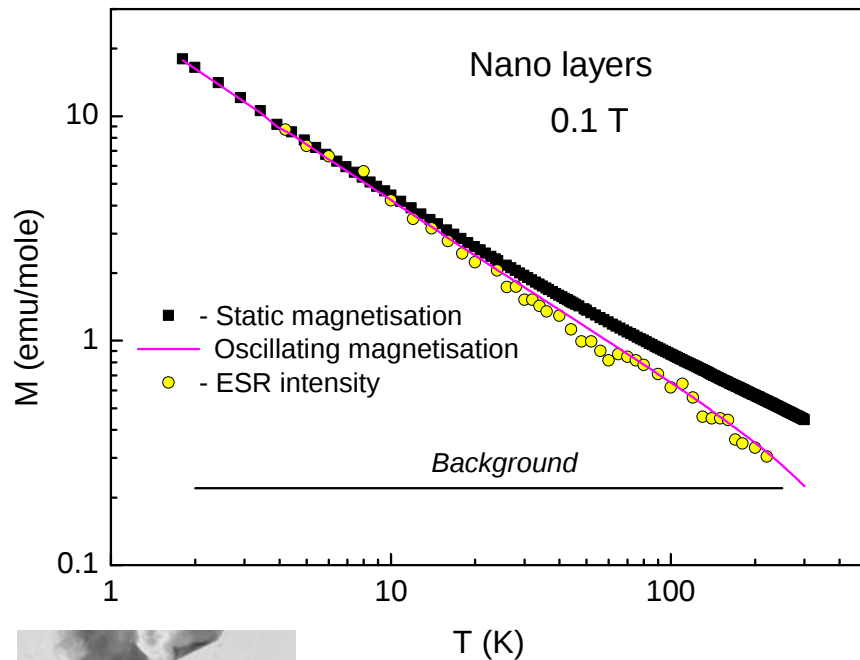
$$\chi = C / (T + \theta^*) \quad (T > T_m)$$

$$\chi = [C / (T_m + \theta^*)] (T / T_m)^{-\xi} \{1 + (1 - \xi)(1 + \theta^* / T_m)[1 - (T / T_m)^{\gamma + \xi}] / [(1 + \varepsilon^{-1})(\gamma + \xi)]\} \quad (T < T_m)$$

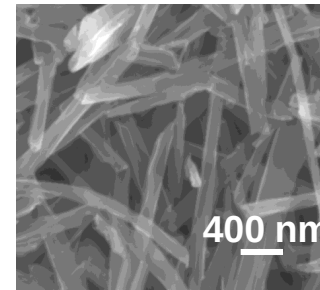
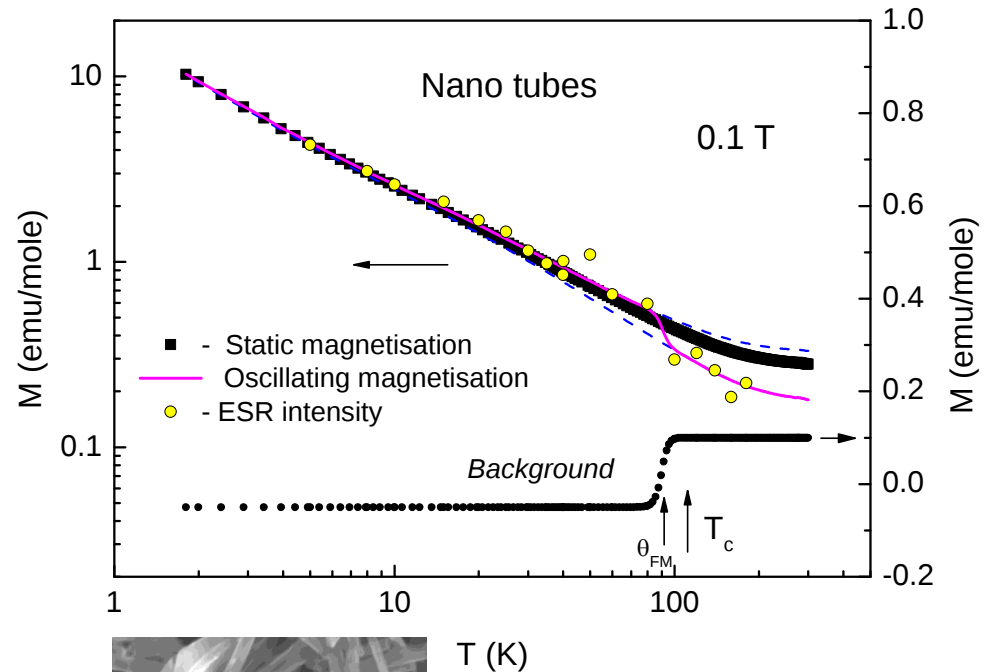
$$\theta^* = T_m [\varepsilon(1 - \xi) f(\varepsilon, \xi)]^{-1} - 1 \quad f(\varepsilon, \xi) = -\xi^{-1} - \sum_{r=1}^{\infty} (-1)^r \varepsilon^r / (r + \xi) + \pi \varepsilon^{-\xi} / \sin[\pi(1 - \xi)]$$



VO_x nanomaterials: static and dynamic magnetic properties.



VO_x nano layers



VO_x nanotubes

$$M = M_{osc} + M_b$$

SQUID
(static)

ESR
(dynamic)

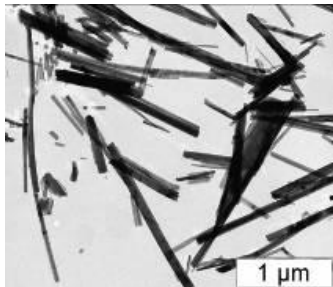
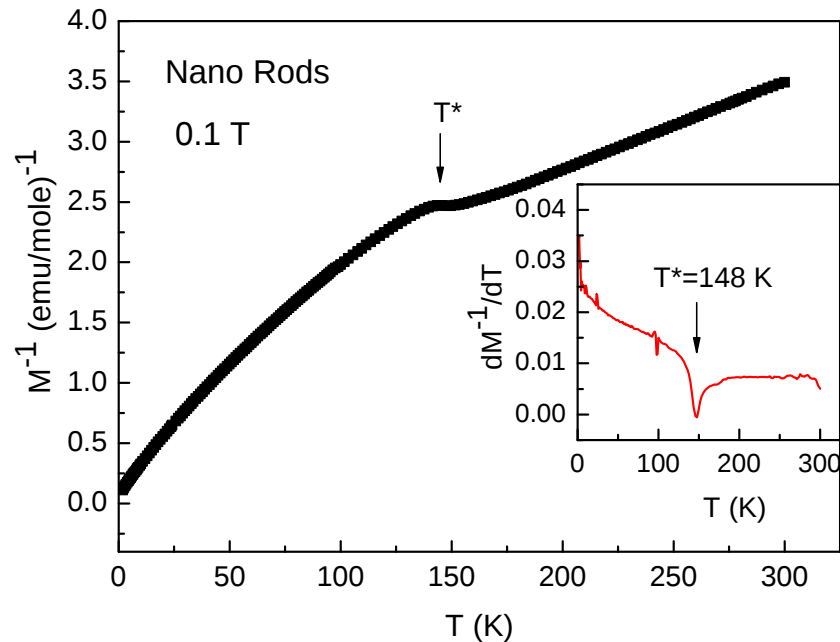
Background

Simple Van Vleck type background structure.

Change of the background in the FM-AFM crossover region.



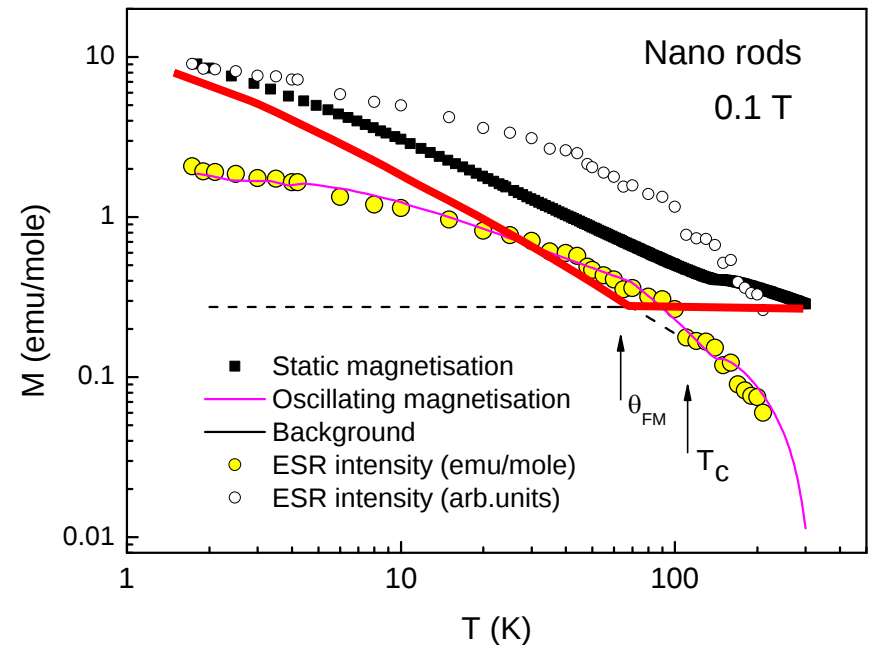
Mystery of the VO_x nanorods: static vs. dynamic magnetisation.



VO_x nanorods

Two types of V^{4+} with “high” and “low” spin fluctuation rate ?

Is this related with ferromagnetism ?



Magnetic transition in static magnetisation at $T^* \sim 148 \text{ K} > T_c$ (not pronounced in ESR).

**$M_b = \text{const}$ only for $T > \theta_{\text{FM}}$!
Strong increase of the non-oscillating part of magnetisation in the range $T > \theta_{\text{FM}}$.**

Results:

Ferromagnetic – antiferromagnetic crossover in various VO_x nano-materials.

Type of magnetic interactions may be controlled by concentration of V^{4+} ions. FM interactions correspond to diluted case and AFM interactions correspond to concentrated case.

Observation of the disorder driven quantum critical phenomena in VO_x nano-materials, including VO_x multiwall nanotubes.

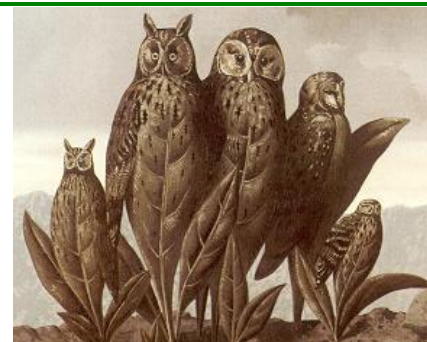
Probably the first observation of the QC behavior in nanomagnets.

Direct ESR evidence of the presence of the V^{4+} $S=1/2$ AF dimers in VO_x multiwall nanotubes.

Strange behavior of static magnetisation in VO_x nanorods. Effects of spin fluctuations ?

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СПАСИБО ЗА ВНИМАНИЕ!

