



Escolas de Inverno do IFGW

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24/07/2015

Elusive superconductors

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University of Campinas (UNICAMP), Brazil

OUTLINE

- Long standing problem of possible high-temperature superconductivity in a variety of systems.
- Fröhlich (super)conductivity ?
- **Charge ordering and low-resistance state: a new experimental evidence**
- **New high-temperature USO:**
“Unidentified Superconducting Objects”
+ conclusions



Shedding some light...



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Physica C

journal homepage: www.elsevier.com/locate/physc



Unstable and elusive superconductors



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One of the pioneers of the field of superconducting materials.

Ted Geballe



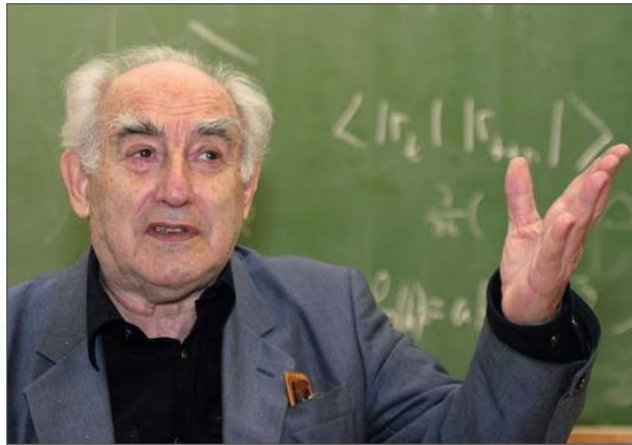
Special Issue

Superconducting Materials: Conventional,
Unconventional and Undetermined
Dedicated to Theodore H. Geballe on the year
of his 95th birthday

Edited by

J.E. Hirsch
M.B. Maple
F. Marsiglio

Before a “cuprate era” (< 1986)

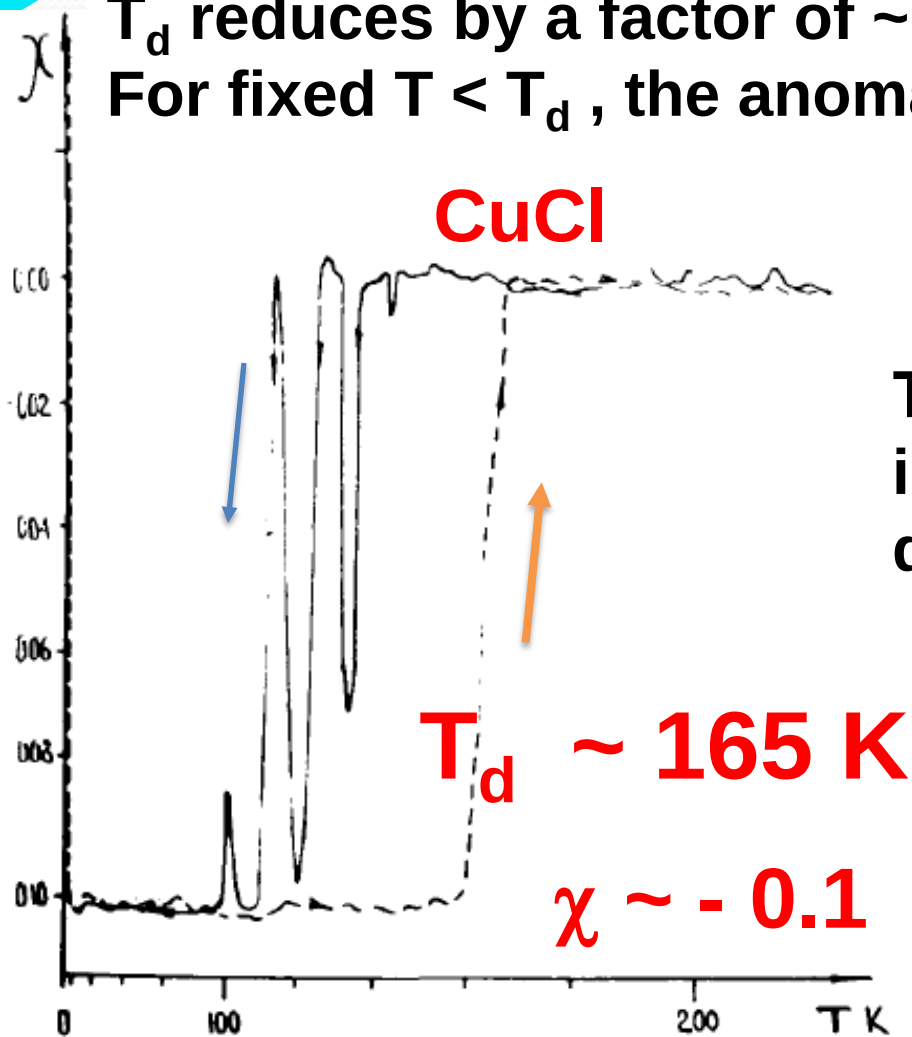


V. L. Ginzburg: If dia-

magnetic anomalies in CuCl and CdS are real (i.e. are not explained by some mistakes in experiments, etc.), they could, in principle, be connected not only with superdiamagnetism (in our sense), but also with volume or surface type superconductivity

High-Temperature Superconductivity (Edited by V.L. Ginzburg & D.A. Kirzhnits), Consultance Bureau, New York, London (1982)

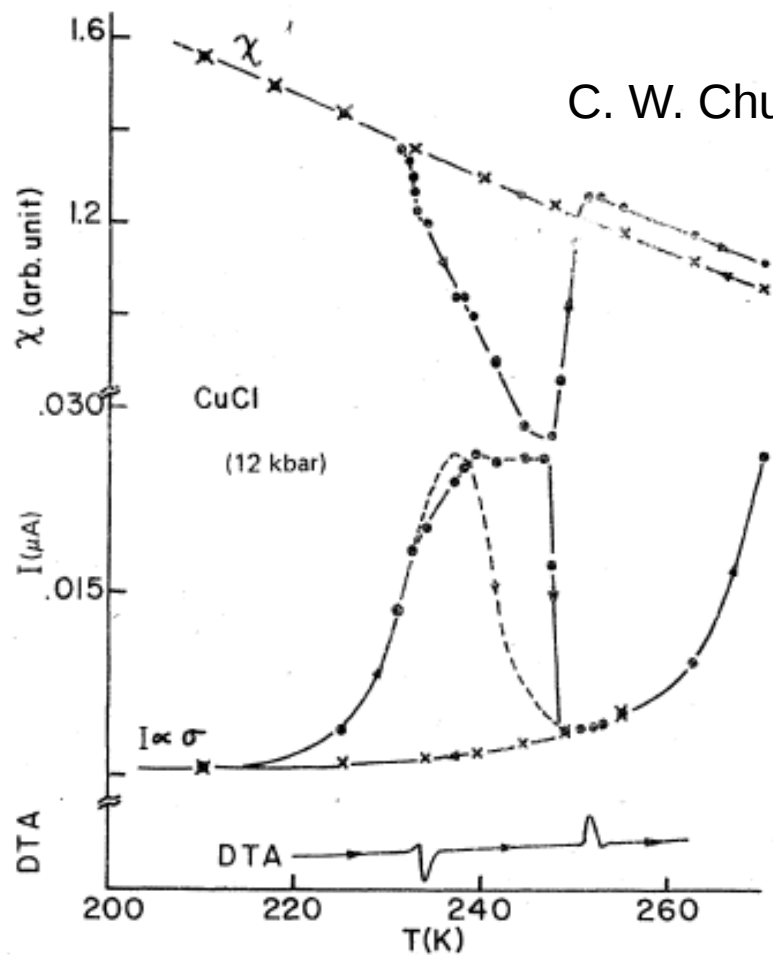
Hydrostatic pressure $P \sim 5$ kbar, cooling/heating rate ~ 20 K/min. After several thermal cycles $4.2 \text{ K} < T < 350 \text{ K}$, T_d reduces by a factor of ~ 3 . For fixed $T < T_d$, the anomalous state is stable for hours.



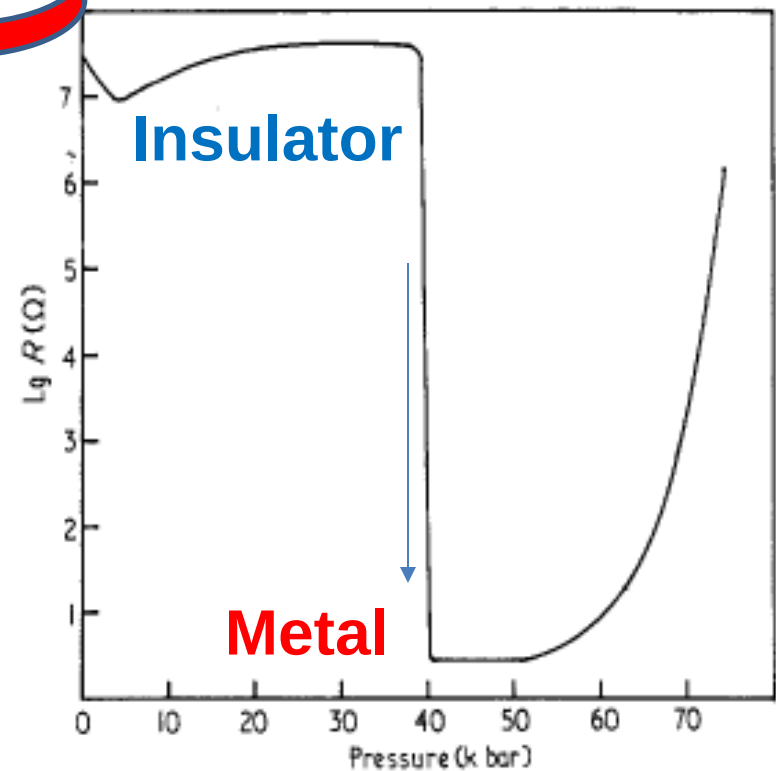
The “diamagnetic transition” is accompanied by a resistance drop by 4-6 orders of magnitude

High-temperature superconductor ?

$2\text{CuCl} \rightarrow 2\text{Cu} + \text{CuCl}_2 \Rightarrow$ formation of Cu-CuCl metal-insulator interfaces responsible for the transient high-temperature superconductivity.

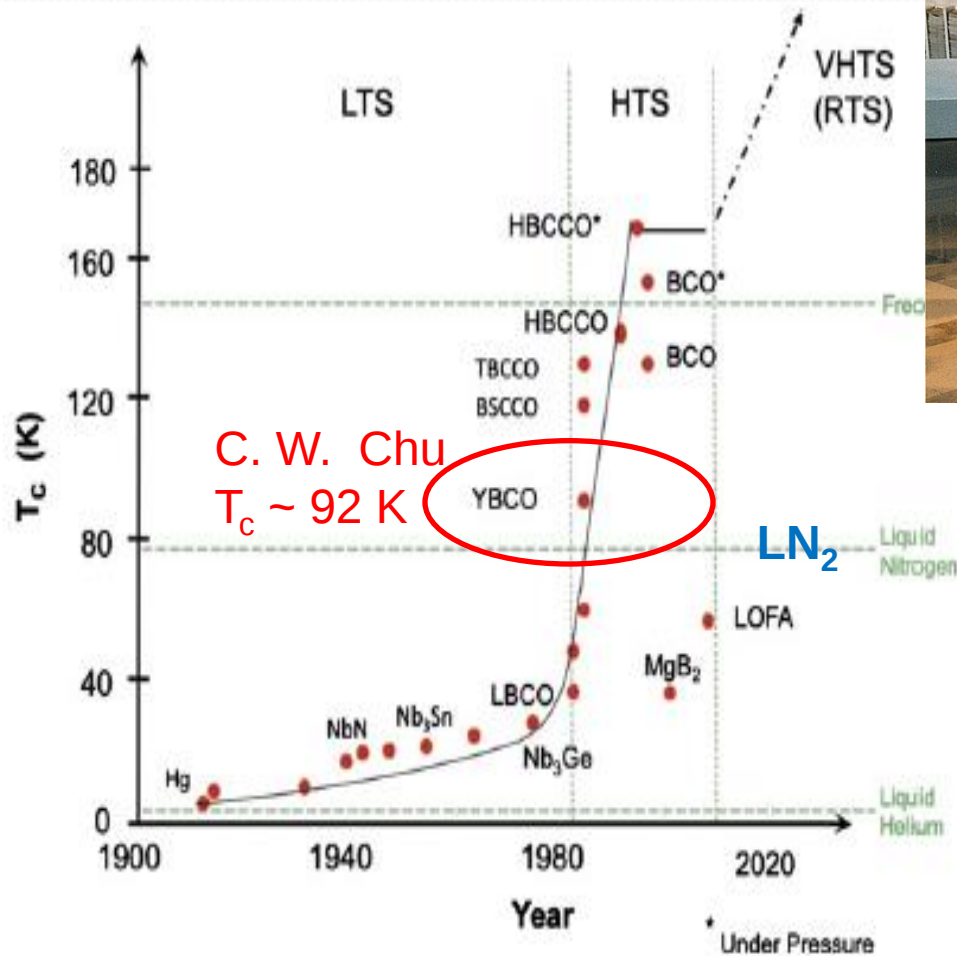


Phys. Rev. B 18 (1978) 2116.



J. Phys. C: Solid State Phys., Vol. 8, 1975

By passing...



YBCO was included in the White House Millennium Time Capsule Closing Ceremony -December 6, 2000 in the National Archives, Washington DC

Electric-field-induced insulator-metal transition in CuCl

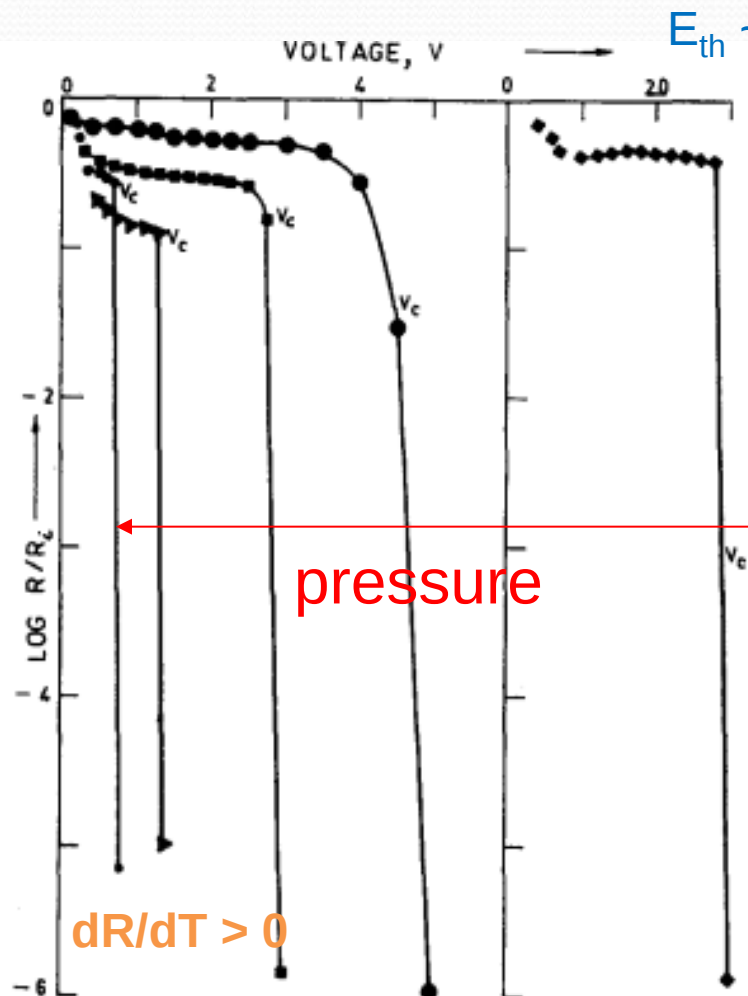


Fig. 1. Curve showing the variation of $\log(R/R_i)$ with applied voltage at different pressures. $\blacklozenge$, 1, bar; $\bullet$, 1.3; $\blacksquare$, 2.6; $\blacktriangledown$, 3.9; $\bullet$, 4.4 GPa.

C. Divakar et al., Solid State Commun. 34 (1980) 385.

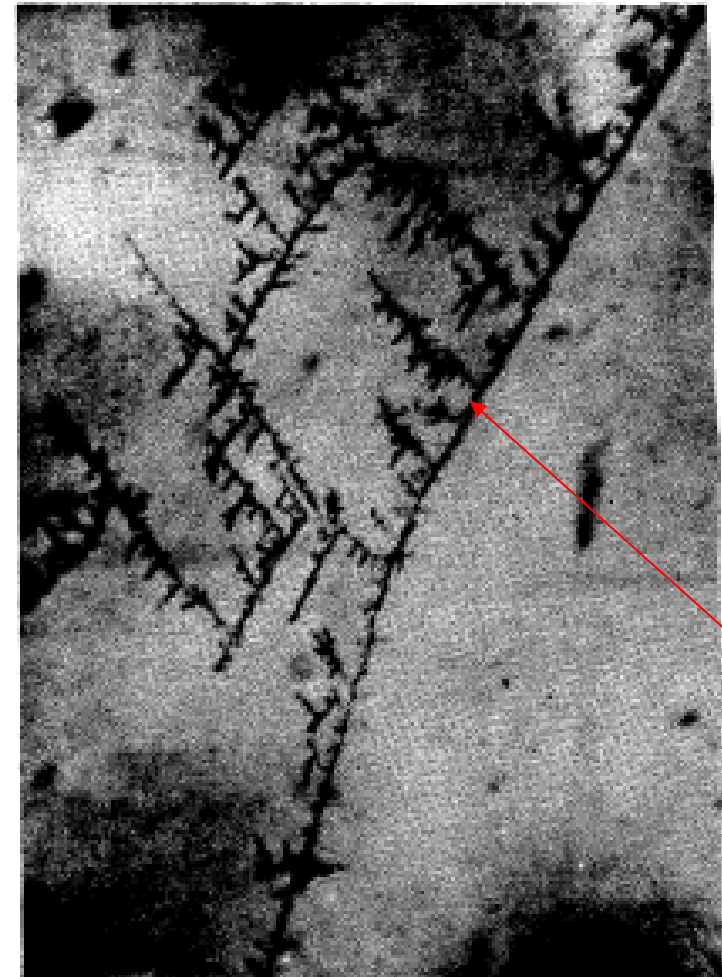


Fig. 1. Copper filament with dendrite branches in CuCl.

A. L. Gentile, Appl. Phys. Lett. 9 (1966) 237.

Electric-field-induced insulator-metal transition in CuCl

C. Divakar et al. :

Insulating state re-appears removing the applied voltage.

The recovery time depends on various factors, and it could be as long as 3 days when the conducting state kept for 48 hours.

Flux Exclusion in CdS at 77 K: Superconductivity at High Temperatures?E. Brown^(a) and C. G. Homan*U. S. Army Armament Research and Development Command, Large Caliber Weapons Systems,
Benet Weapons Laboratory, Watervliet, New York 12189*

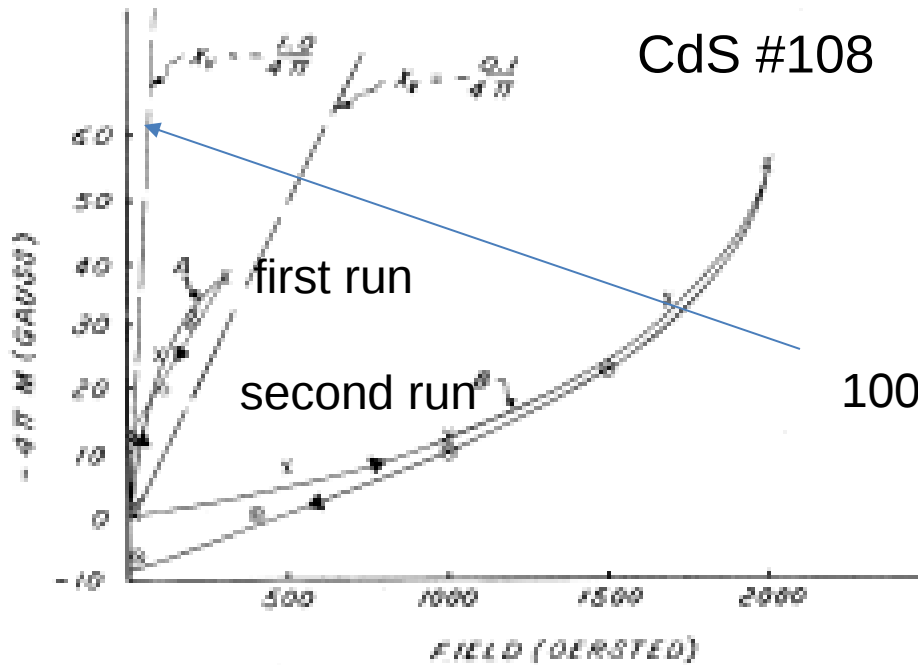
and

R. K. MacCrone

*Department of Materials Science, Rensselaer Polytechnic Institute, Troy, New York 12180
(Received 31 March 1980)*

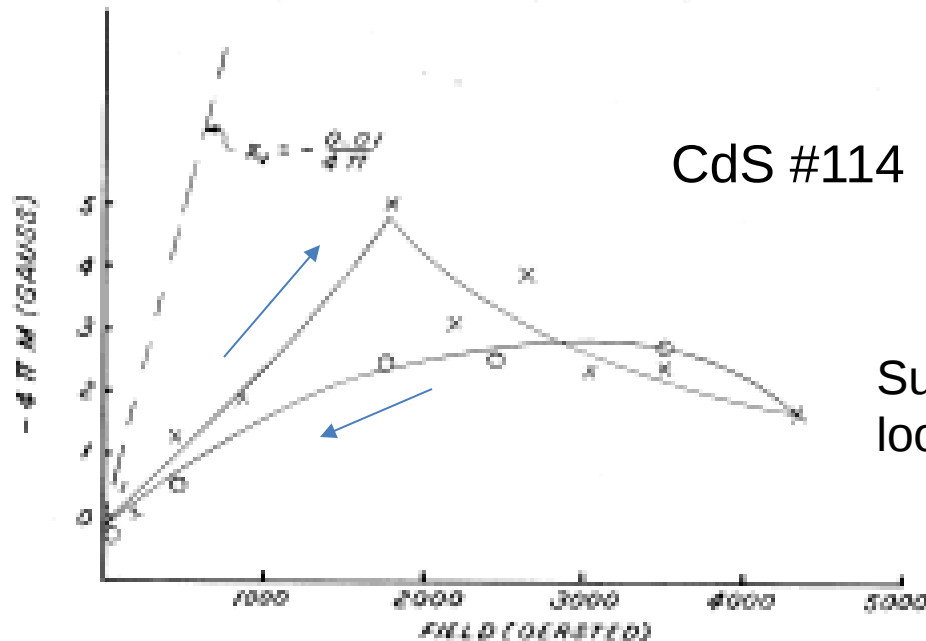
**applied pressure $P > 40$ kbar $\rightarrow$ pressure
release: 10^6 bar/sec $\rightarrow$ Resistance drops by
 ~ 5 orders of magnitude (wurtzite - to -
NaCl-type structure transition) $\rightarrow$ large
diamagnetism and superconducting-type
 $M(H)$**

CdS #108



T = 77 K

CdS #114



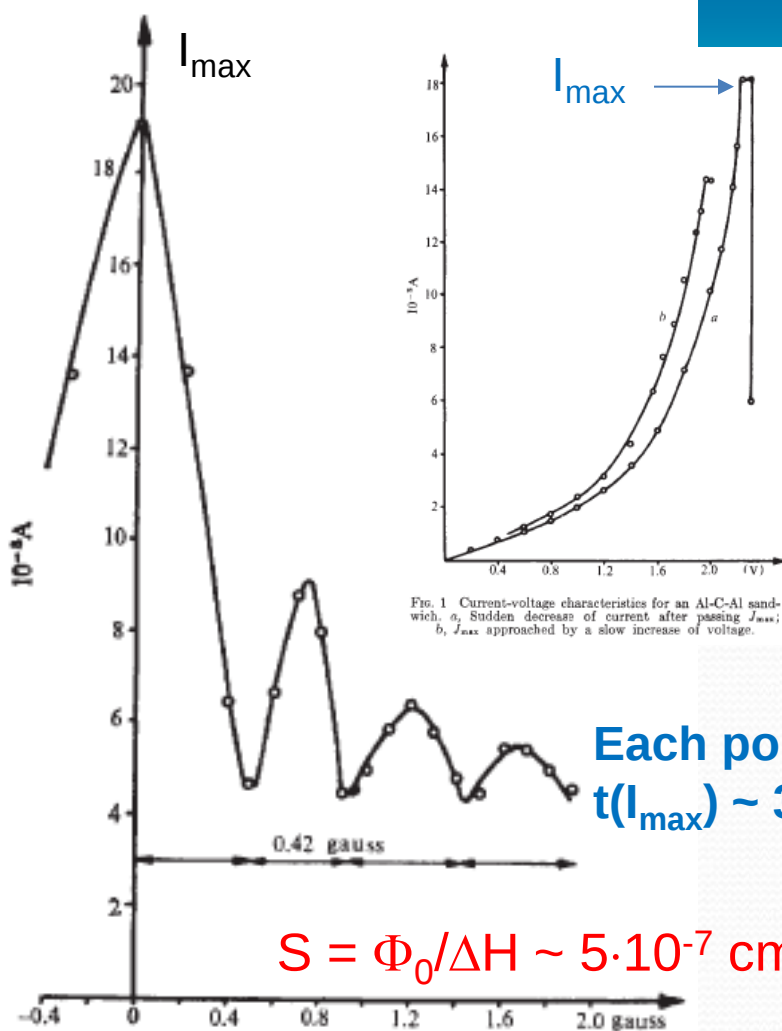
Superconducting-like M(H) hysteresis loop

Possible superconductivity at room temperature

K. ANTONOWICZ

Al – amorphous carbon – Al sandwiches

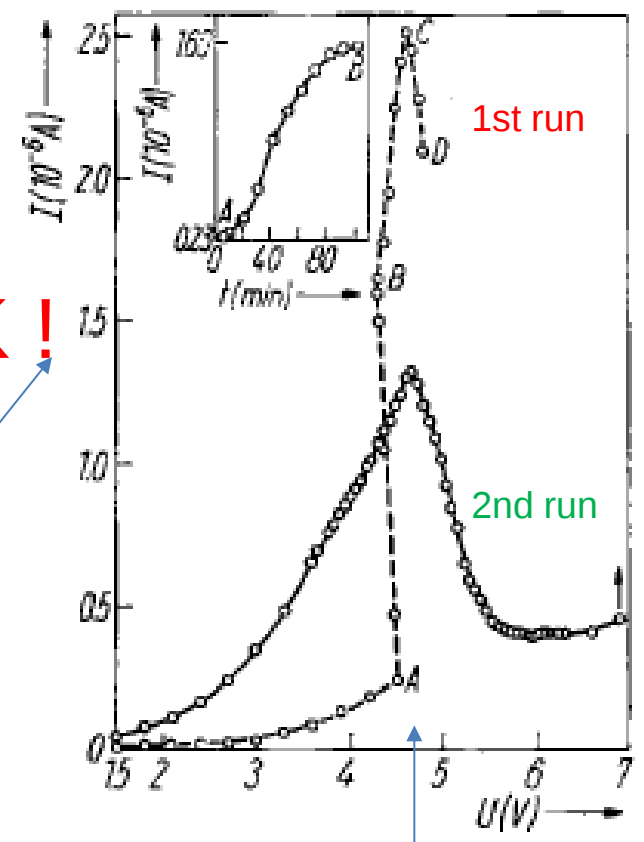
- Electric-field- induced resistance drop by a factor of ~ 100 ($\rho \sim 10^{10} \Omega\text{cm}$; diamond-like AC films: $10^2 - 10^{16} \Omega\text{cm}$);
- “Low-resistance” state decays with time : several days
- Josephson-type oscillations in magnetic field;
- Shapiro-like steps.



$T = 300 \text{ K} !$

Each point is taken after $t(I_{max}) \sim 30\text{-}100 \text{ min}$

$$S = \Phi_0 / \Delta H \sim 5 \cdot 10^{-7} \text{ cm}^2 (?)$$



$$E_{th} \sim 100 \text{ kV/cm}$$

K. Antonowicz, phys. stat. sol.(a) 28, 497 (1975)

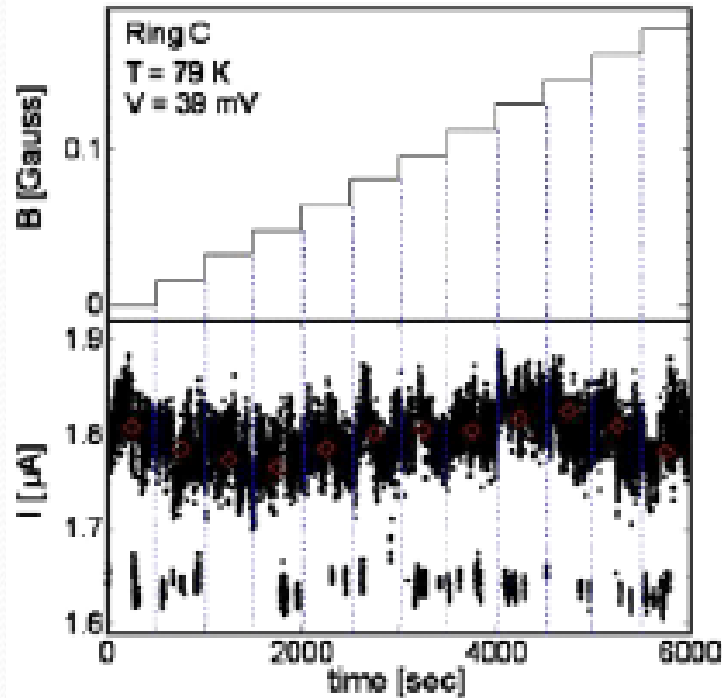
K. Antonowicz,
Nature ' 1974

$$\Phi_0 = h/e^*$$

$$e^* = ?$$

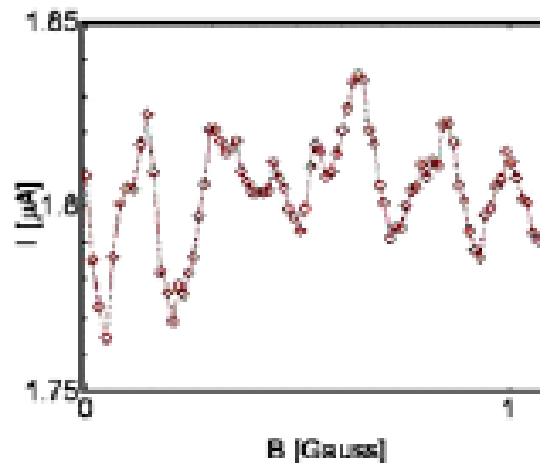
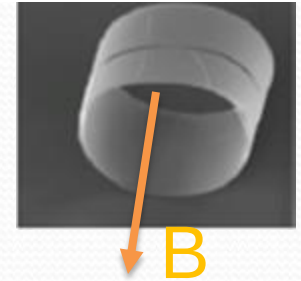
The results indicate that in the low resistance state carriers are concentrated on the conducting paths and remain there for days.

Abstract – We report evidence for Aharonov-Bohm (AB) oscillations with temporal current switching at 5.1 and 79 K by using charge-density wave (CDW) loops in TaS₃ ring crystals. The periodicity of the AB oscillations is $\hbar/2e$, and this is confirmed by employing four samples with different diameters. This means that sliding CDWs carry $2e$ charge quanta. We observe current switching between the two states, namely the high and low current states.



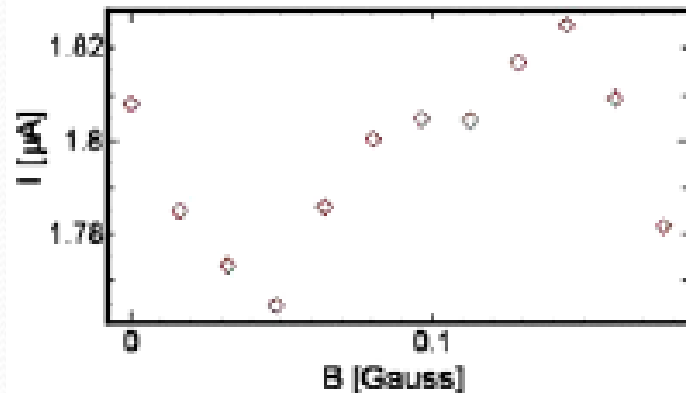
M. Tsubota et al., EPL (2012)

“Aharonov-Bohm effect in CDW loops...”



$$\Delta B = \frac{\Phi_0}{S} = \frac{h}{e^*} \cdot \frac{1}{\pi r^2}$$

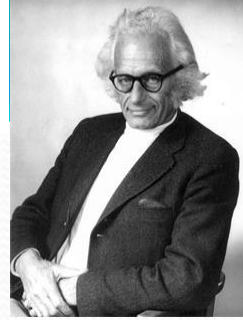
$$e^* = 2e$$



the whole system at 79 K. With our sample, the possibility of the Al'tshuler-Aronov-Spivak (AAS) effect [6], namely the $\hbar/2e$ oscillation of a quasi-particle, is ruled out.

Fröhlich “superconductivity” ?

Herbert Fröhlich
(1905-1991)



Ions uniformly spaced



uniform electron density

$T > T_p$ (Peierls transition temperature)

In, e. g., transition metal-chalcogenides (NbSe_2 , NbSe_3 , TaS_2 , TaS_3 , ...), or “blue bronze” $\text{K}_{0.3}\text{MoO}_3$, **the electron gas and the ion lattice spontaneously develop a periodic modulation**

Ions develop static periodic distortion



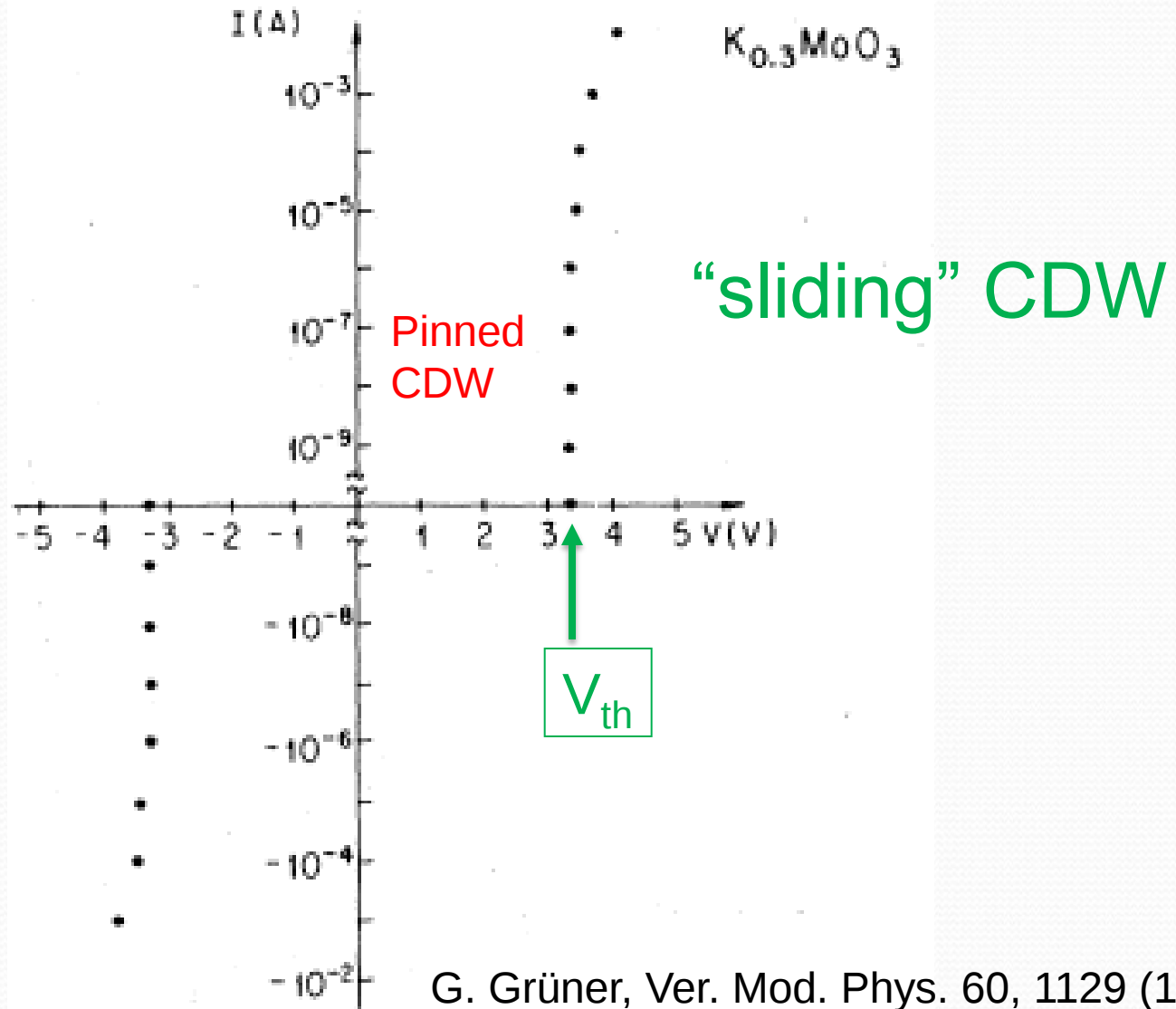
electron density modulated (charge density wave)

$T < T_p$

The charge density wave (CDW) is an example of a cooperative state in which the ionic lattice and electron gas both develop a distortion to lower the total free energy of the sample.

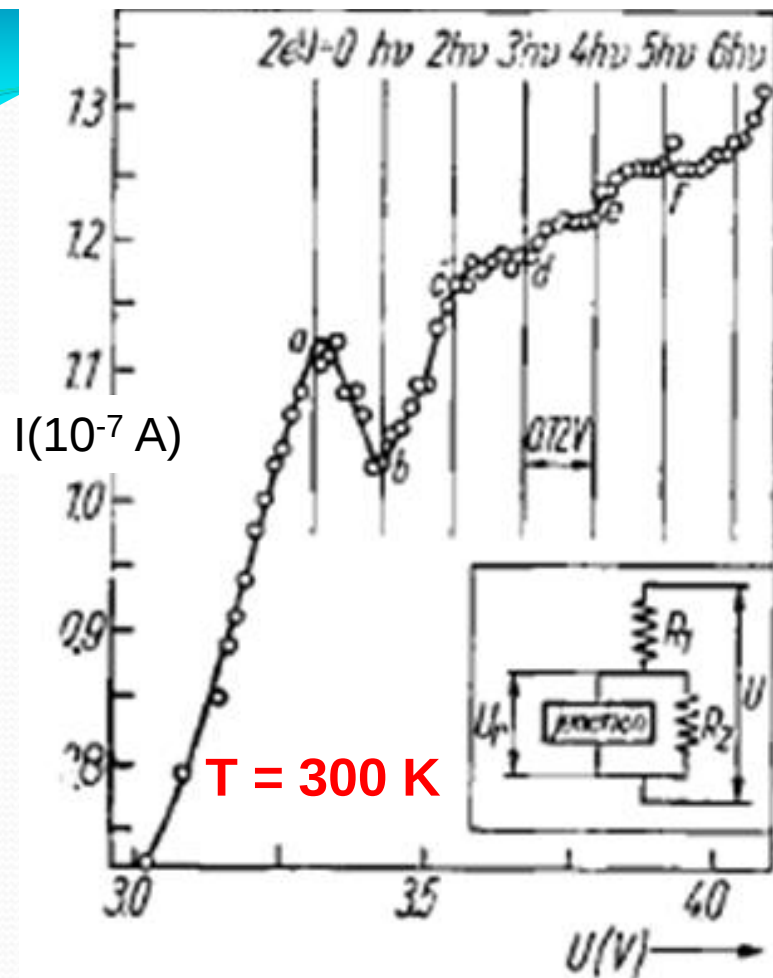
In an applied electric field, CDW could conduct an electric current, and possibly superconduct !

CDW depinning



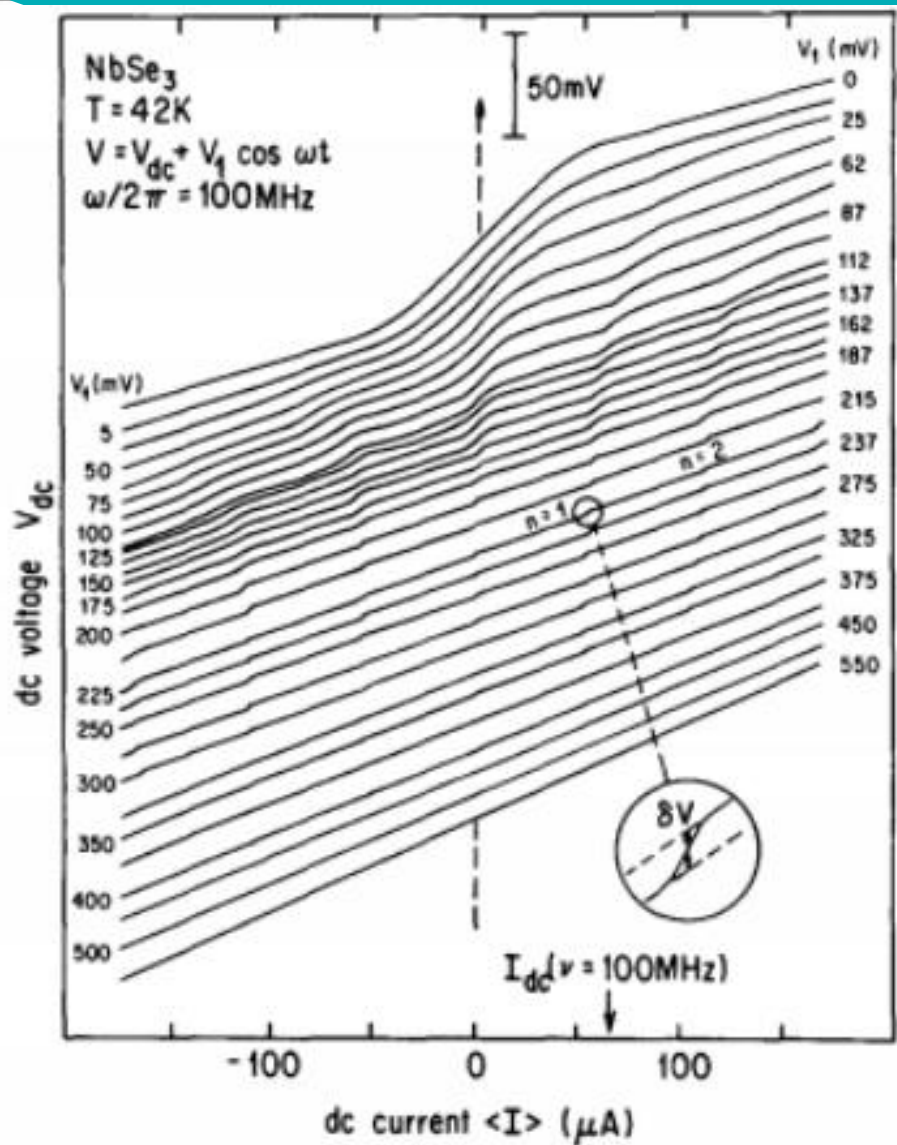
G. Grüner, Ver. Mod. Phys. 60, 1129 (1988)

“Shapiro steps” in amorphous carbon



Sample is mounted in a 3 cm wave guide

K. Antonowicz, phys. stat. sol.(a) 28, 497 (1975)



Shapiro steps: **moving CDW** in NbSe_3
A. Zettli & G. Grüner ´ SSC 1983

Metal(M)-Ammonia (M-NH₃) solutions (M = Li, Na)

In 1946 Ogg[10] reported the production of a persistent current in a ring of sodium-ammonia solution which had been rapidly cooled from -33°C to liquid-air temperature in the presence of a magnetic field.



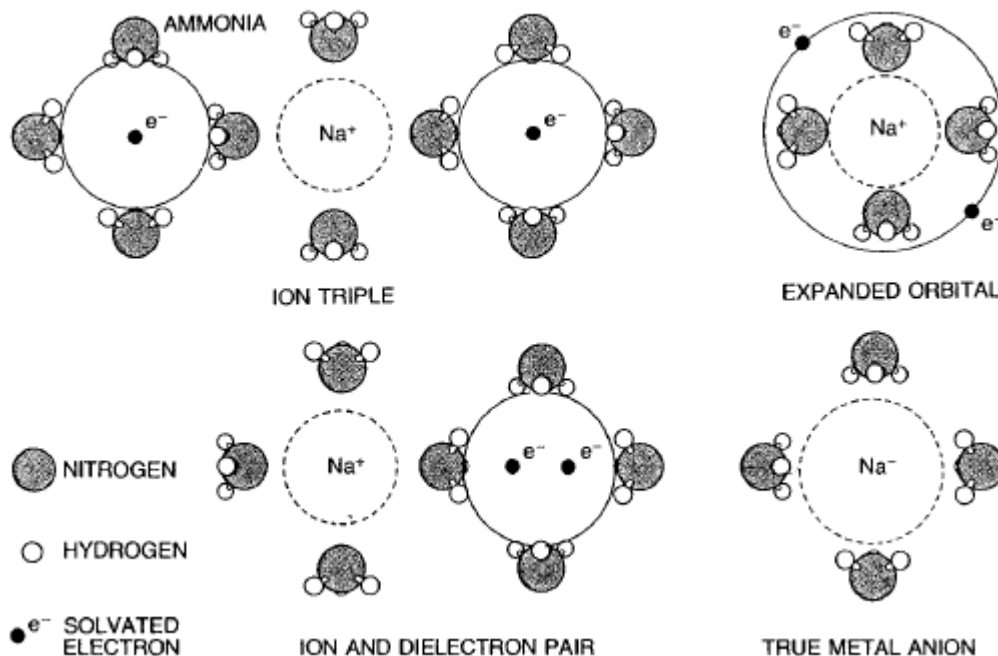
Bose-Einstein Condensation of Trapped Electron Pairs. Phase Separation and Superconductivity of Metal-Ammonia Solutions
 RICHARD A. OGG, JR.
 Department of Chemistry, Stanford University, California
 March 2, 1946

BEC, e. g. F. London, Phys. Rev. 1938

$$T_c = \frac{3.31 h^2 n^{2/3}}{m^* k_B} = 2.9 \times 10^{-11} \left(\frac{m_e}{m^*} \right) n^{2/3} K$$

$$N \sim 10^{21} \text{ cm}^{-3}, m^* \sim 2m_e \Rightarrow$$

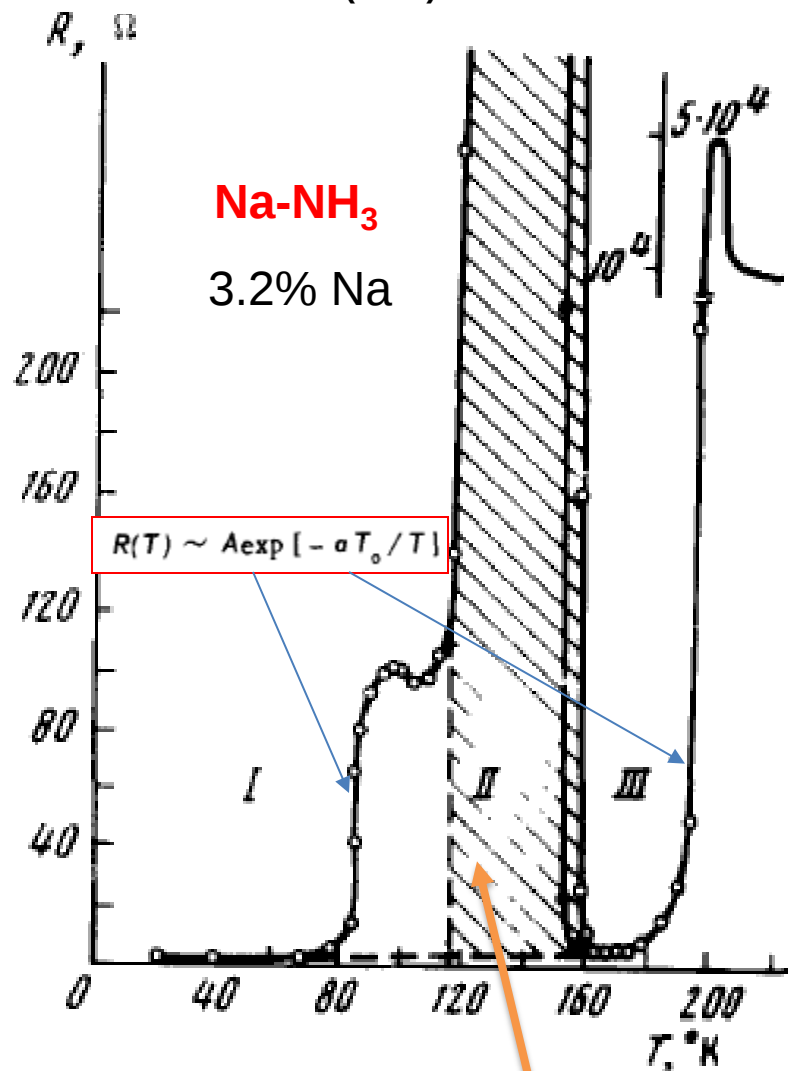
$$T_c \sim 10^3 \text{ K}$$



Oggs results were difficult to reproduce, and his work was ridiculed and largely disregarded ...

G. Gamow:

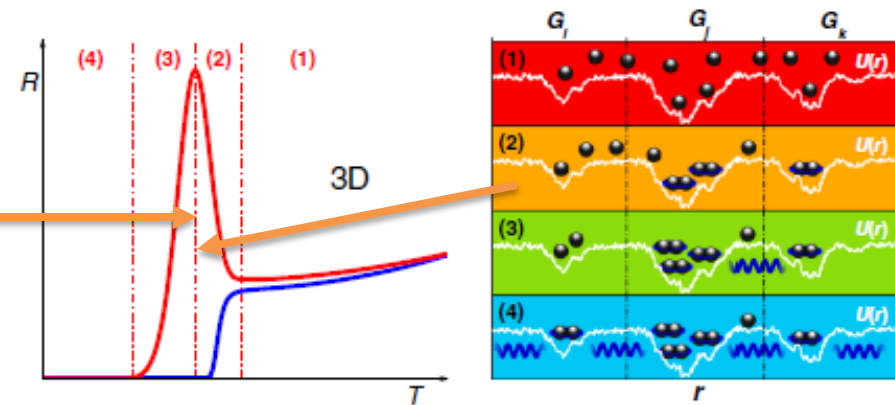
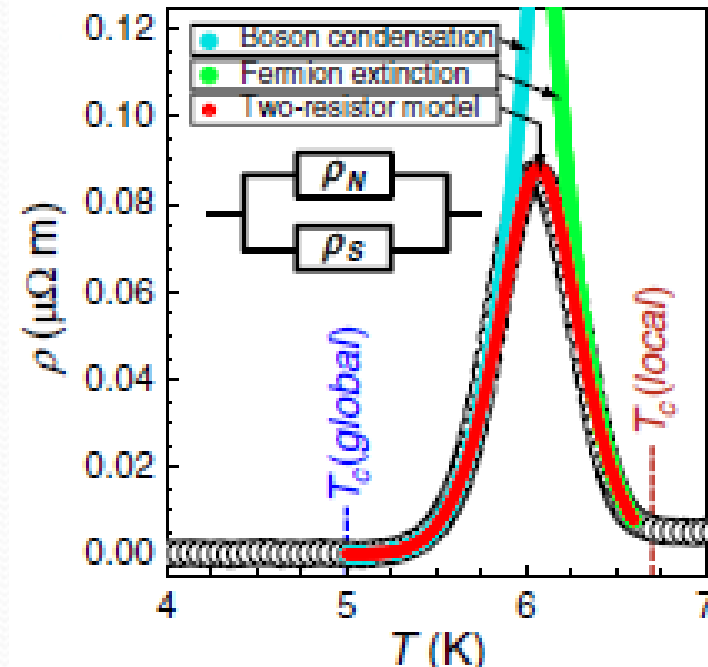
In Ogg's theory it was his intent
That the current keep flowing, once sent;
So to save himself trouble,
He put them in double,
And instead of stopping, it went.



Insulating phases
Bosonic insulator ?

Metal-Bosonic Insulator-Superconductor Transition in Boron-Doped Granular Diamond

Gufei Zhang,^{1,*} Monika Zeleznik,² Johan Vanacken,¹ Paul W. May,² and Victor V. Moshchalkov^{1,†}



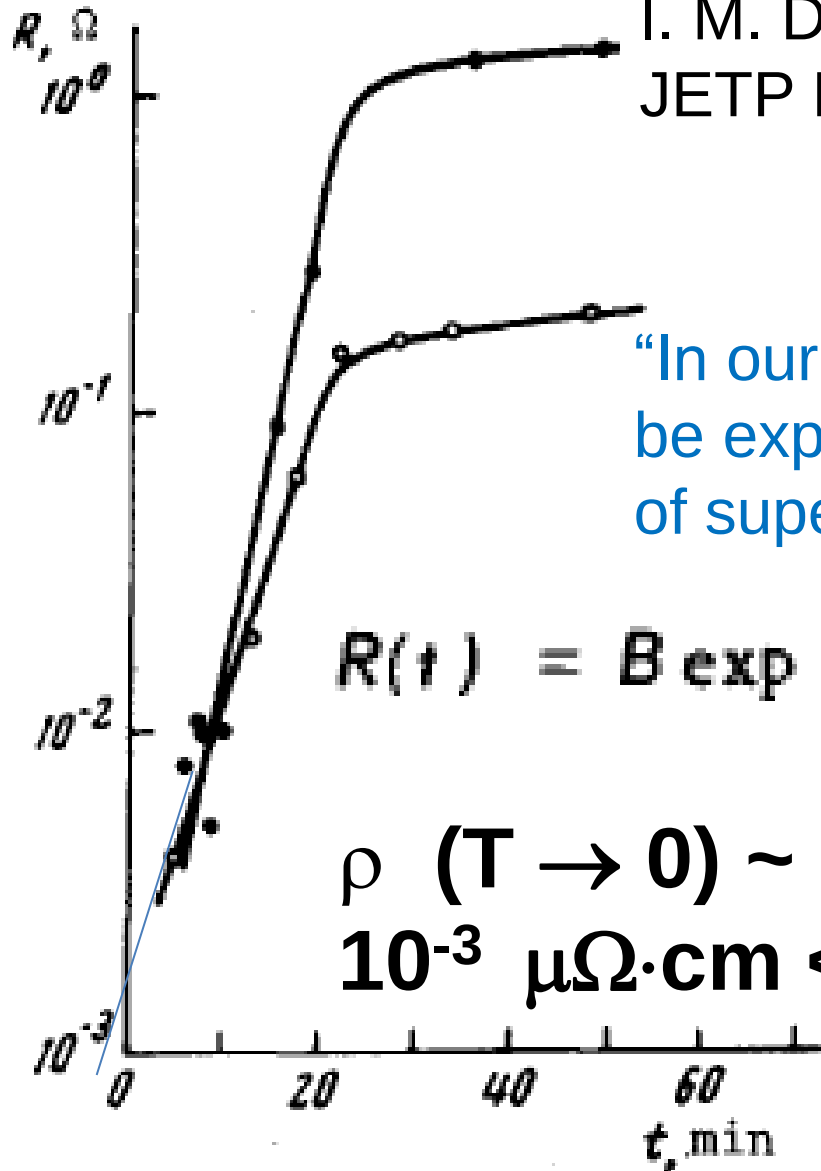
T = 77 K

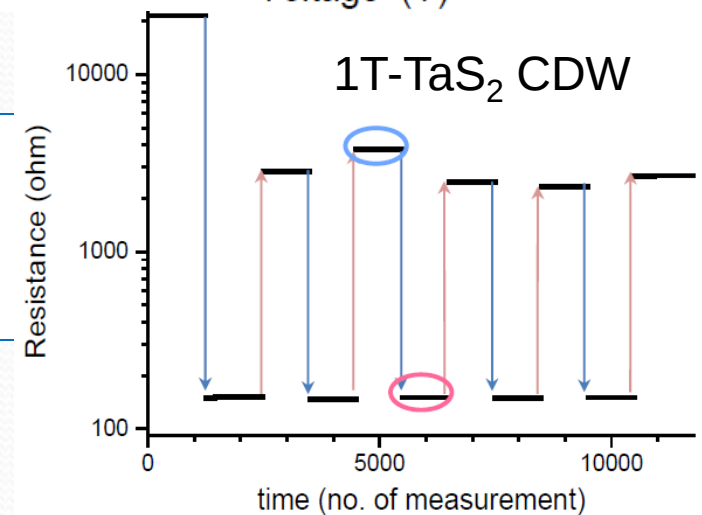
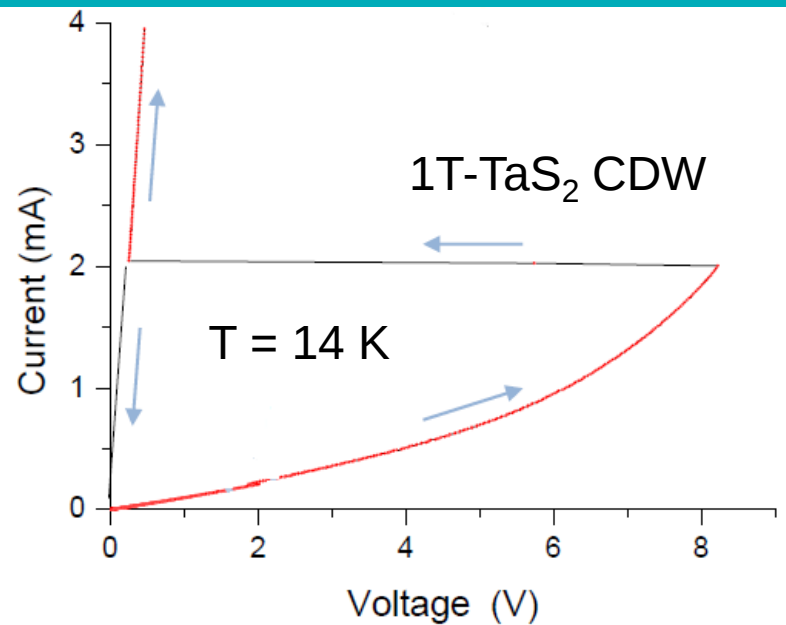
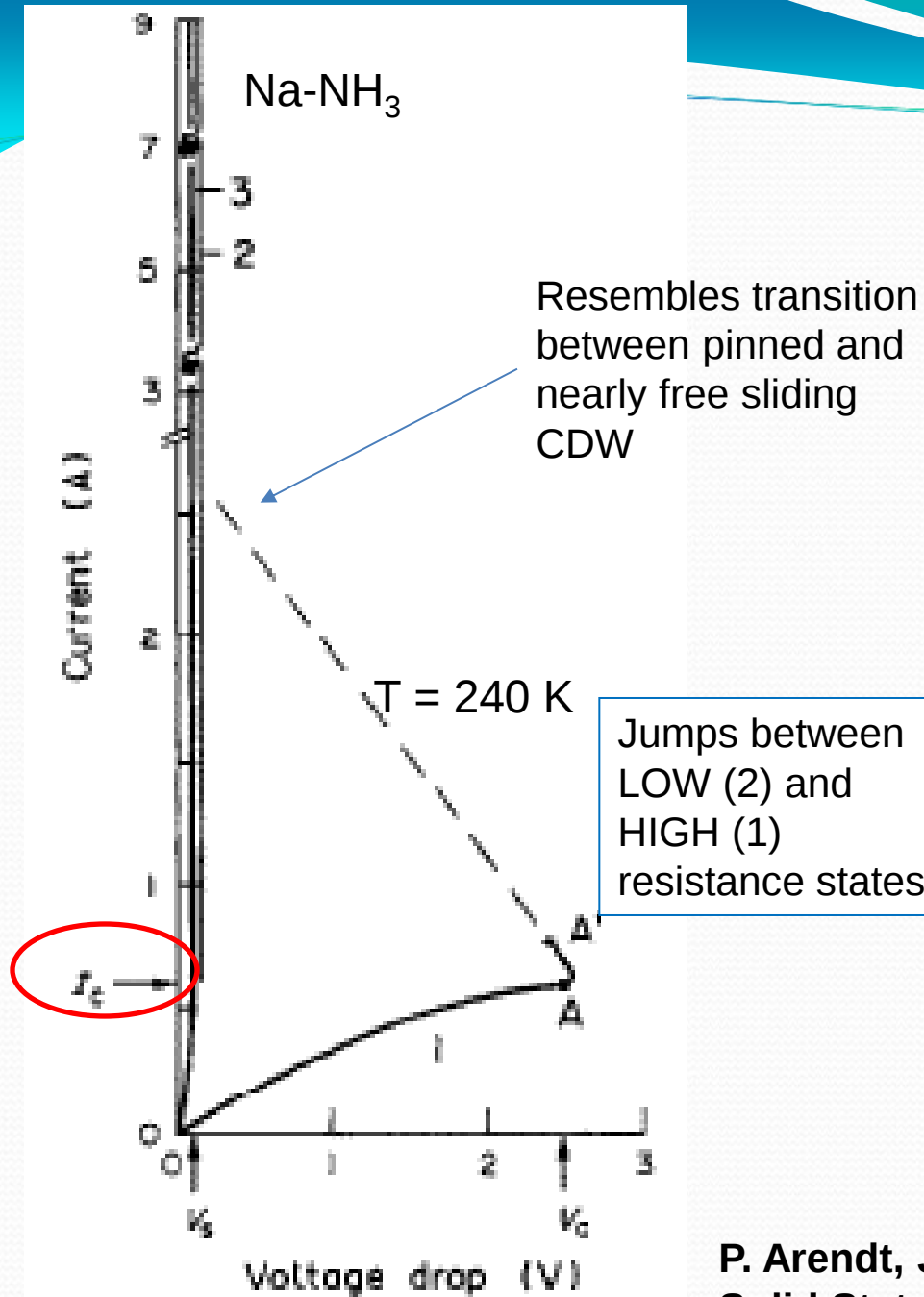
I. M. Dmitrenko and I. S. Shchetkin,
JETP Lett. 18 (1973) 292.

“In our opinion, such low resistivity can
be explained by assuming the existence
of superconductivity in the Na-NH₃ “

$$R(t) = B \exp [-b t_0 / t] \quad B \sim 100, b \sim 1$$

$$\rho (T \rightarrow 0) \sim 10^{-9} \Omega \cdot \text{cm} =$$
$$10^{-3} \mu\Omega \cdot \text{cm} \ll \rho_{\text{Cu}}$$





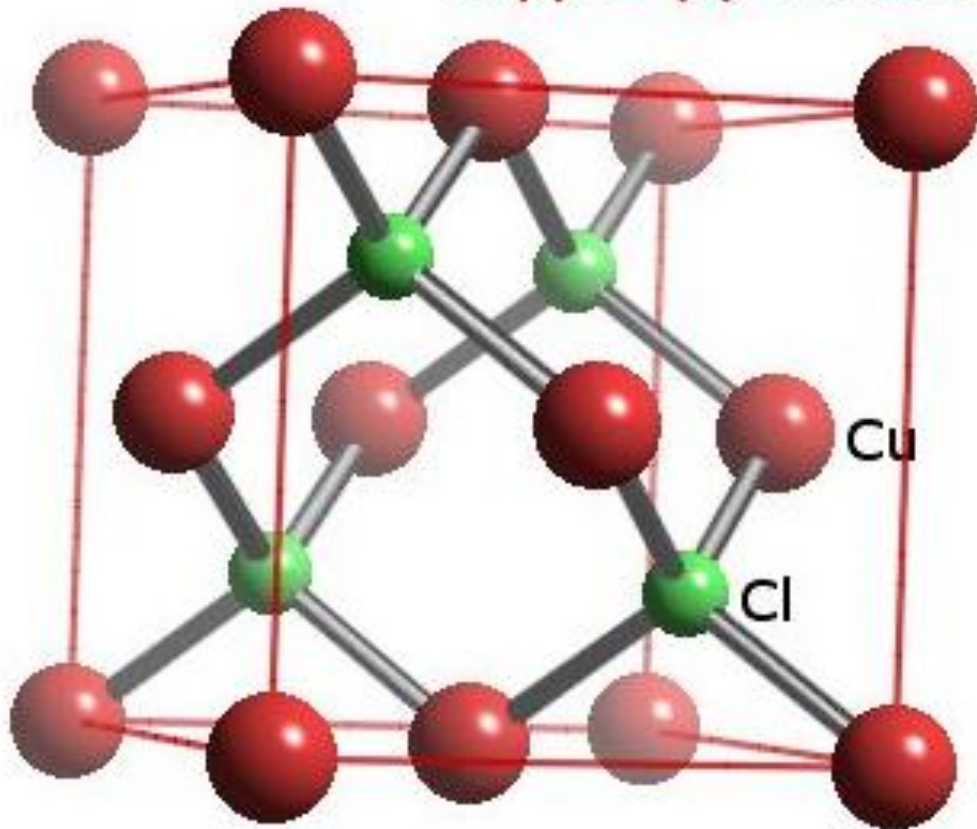
I. Vaskivskyi et al, arXiv:1409.3794

P. Arendt, J. Phys. Chem. Solids 49 (1988) 511;
Solid State Commun. 67 (1988) 1167.

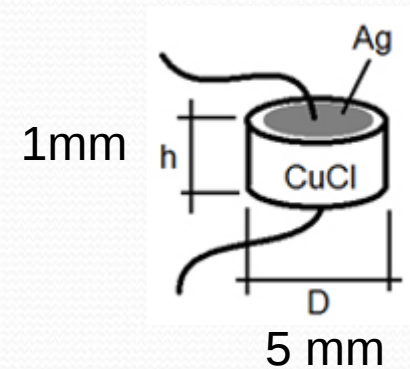
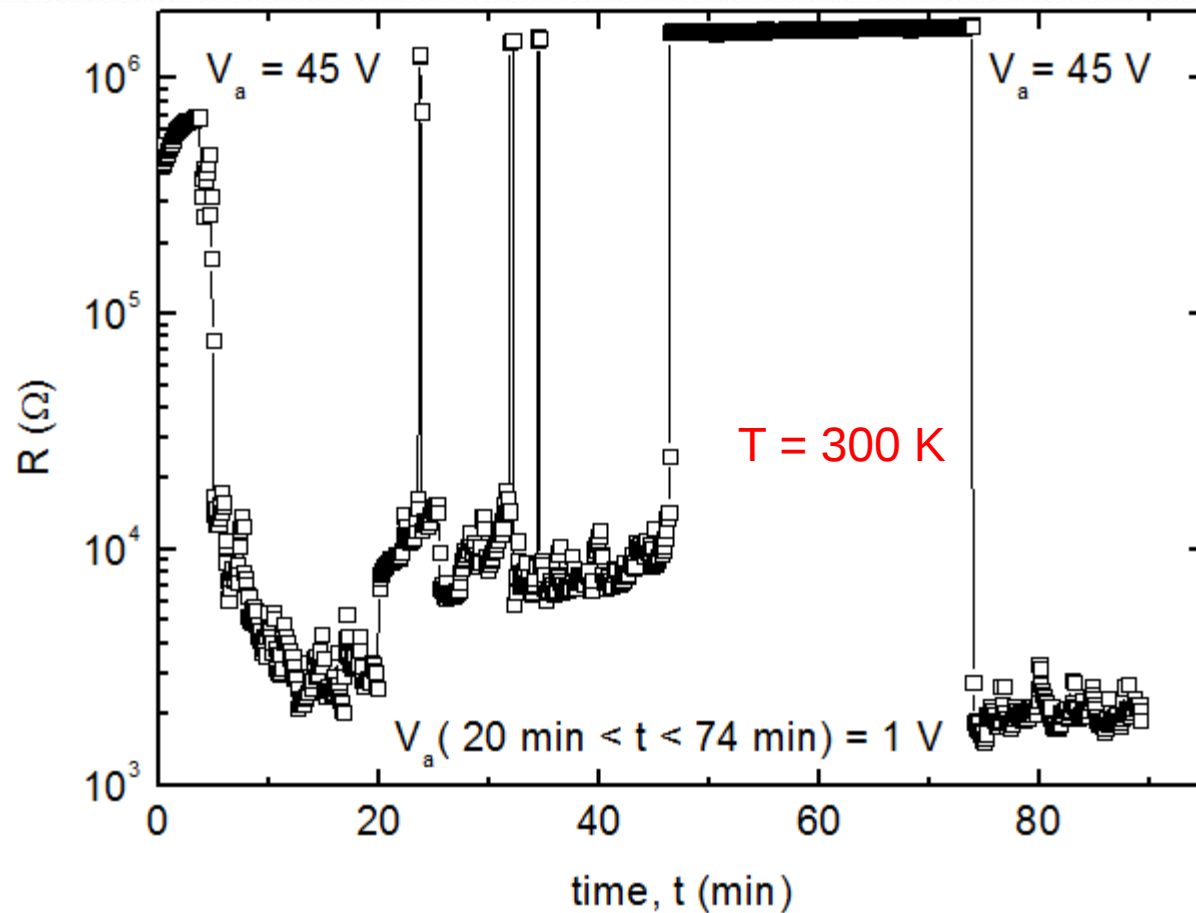
Back to CuCl: We try to shed some light on the problem

Prototypical structure: ZnS (sphalerite, zinc blende)

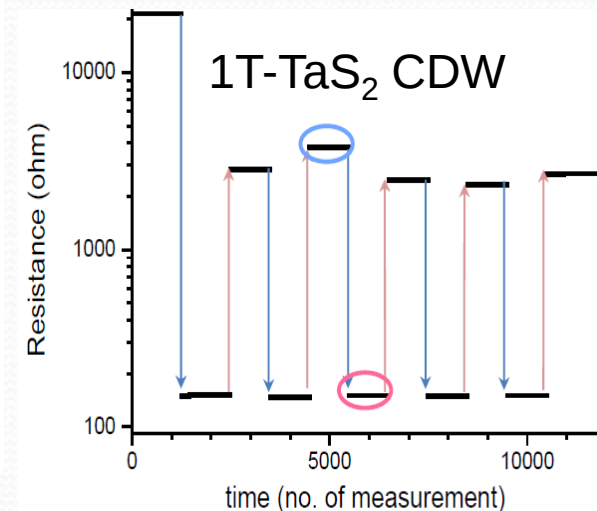
copper (I) chloride



Object: compressed ($P = 1$ GPa) cylindrical pellets of white CuCl powder (Sigma Aldrich; 99.995%); grain size $\sim 40 - 400 \mu\text{m}$

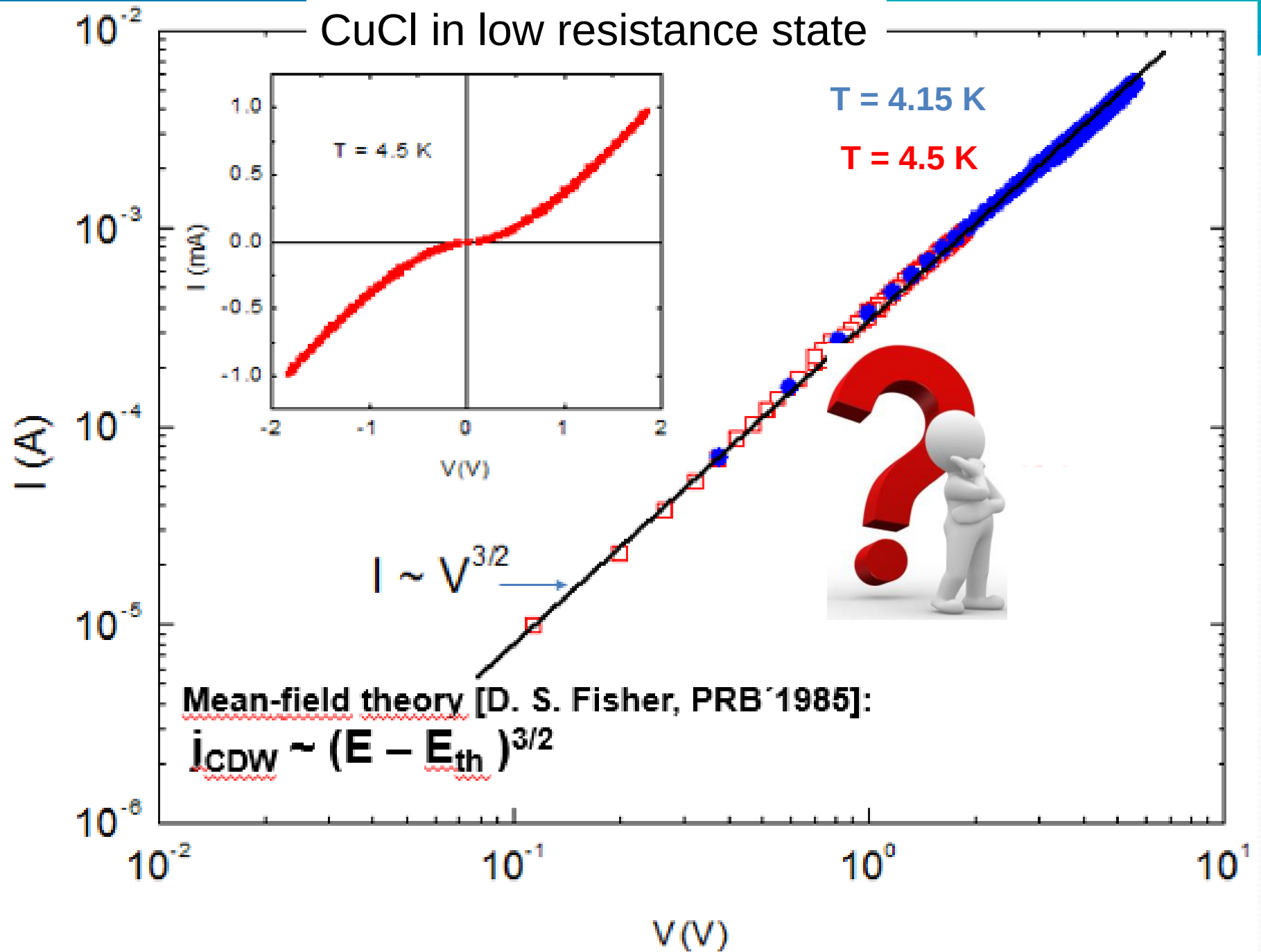


Compare:



Electric-field-driven transition between high- and low-resistance states in CuCl and its intermittent time dependence.

CuCl in low resistance state



PHYSICAL REVIEW B 75, 205428 (2007)

Scaling theory of the Peierls charge density wave in metal nanowires

D. F. Urban,¹ C. A. Stafford,² and Hermann Grabert¹

¹*Physikalisches Institut, Albert-Ludwigs-Universität, D-79104 Freiburg, Germany*

²*Department of Physics, University of Arizona, Tucson, Arizona 85721, USA*

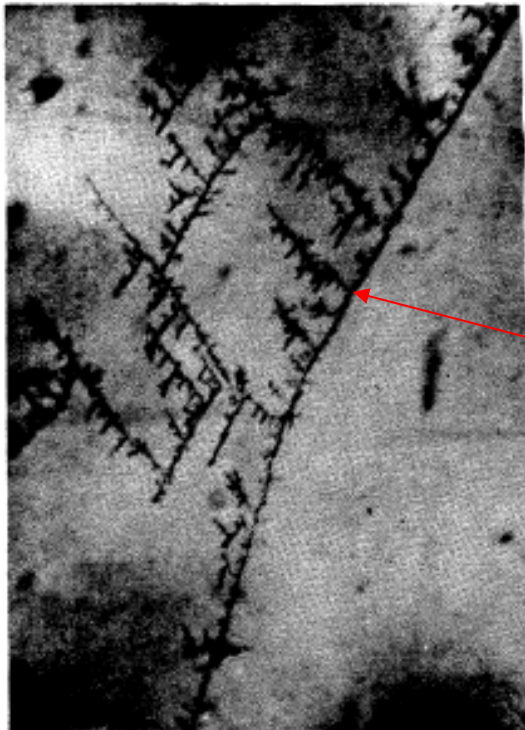
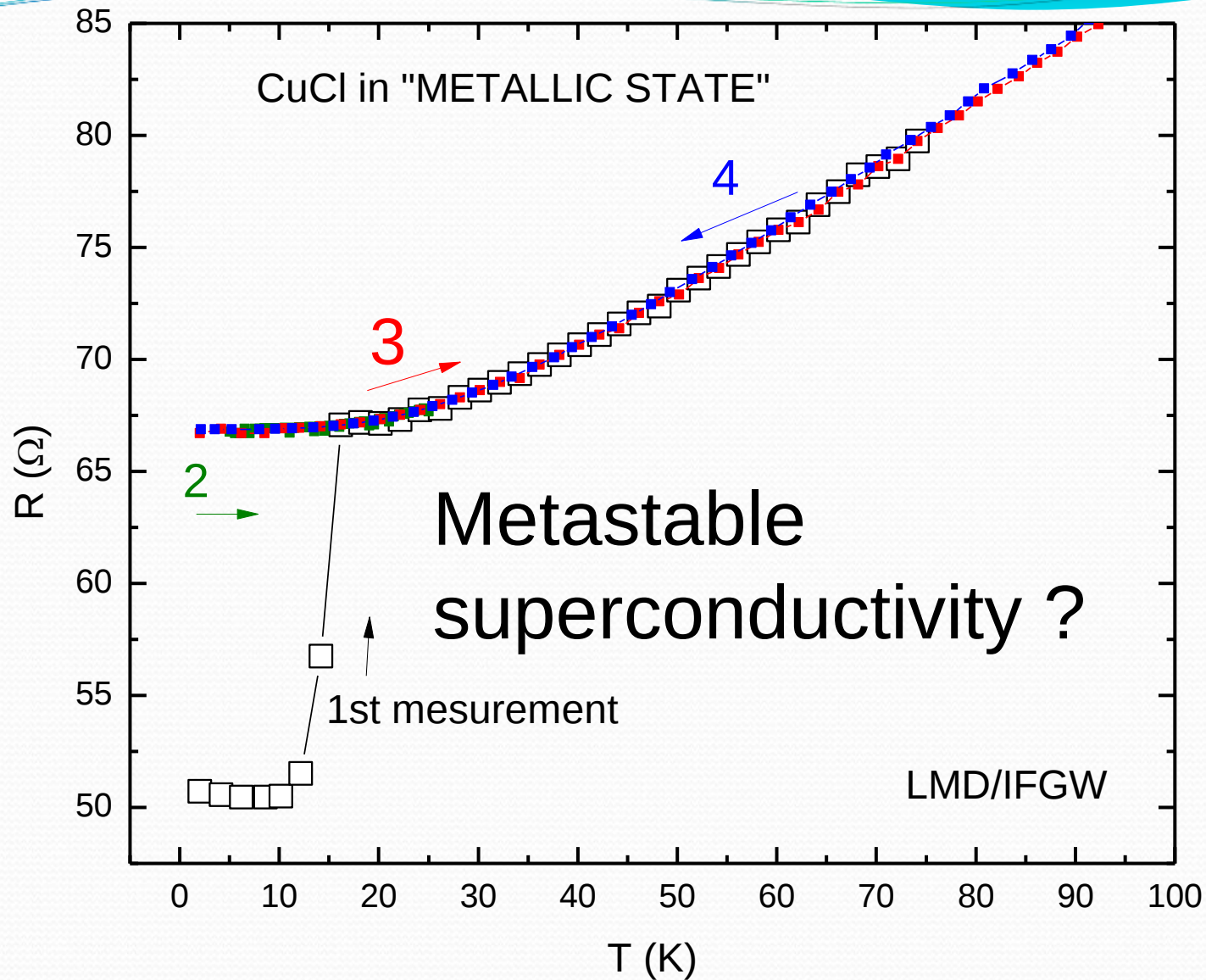


Fig. 1. Copper filament with dendrite branches in CuCl.

Cu filaments

CDW ?

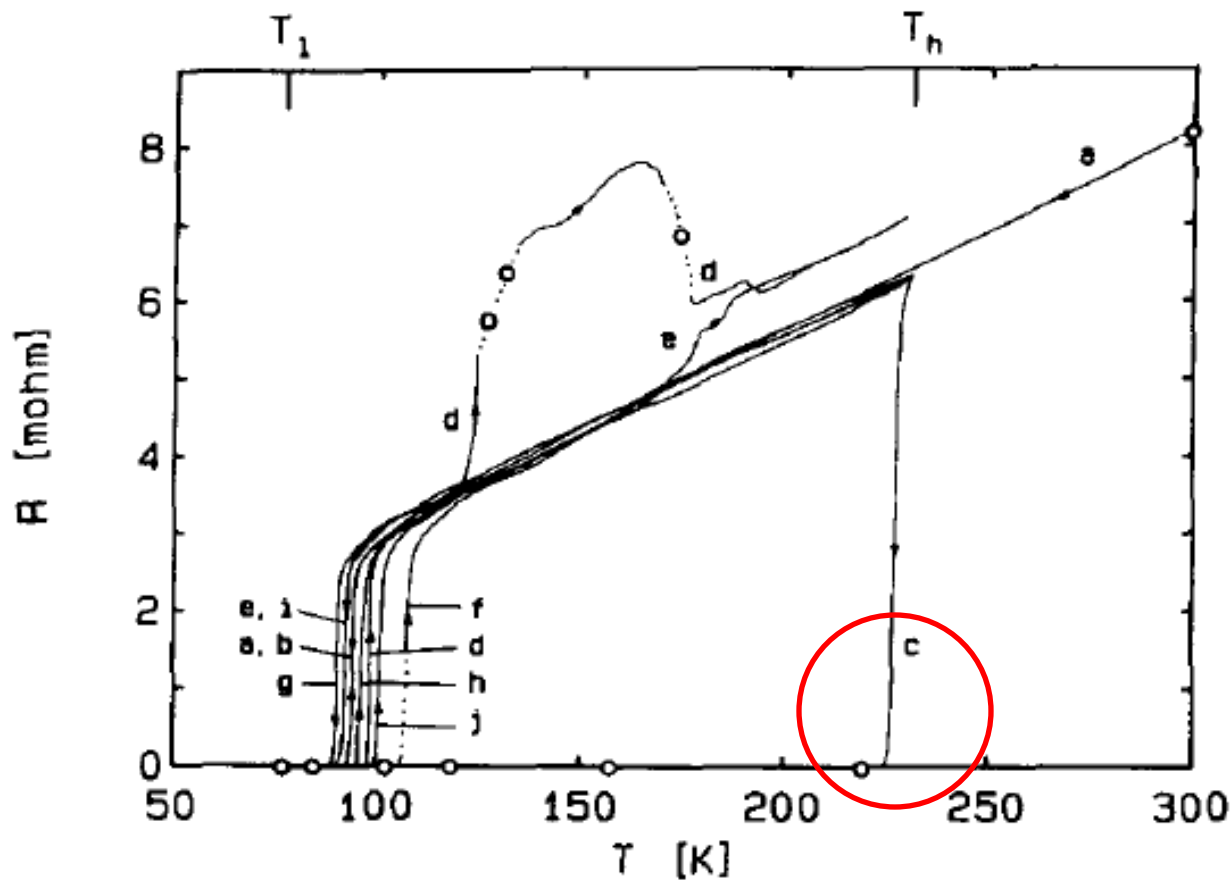




UNSTABLE HIGH TEMPERATURE SUPERCONDUCTIVITY AND MARTENSITIC EFFECTS IN YBaCuO

H.D.Jostarndt, M.Galfy, A.Freimuth and D.Wohlleben

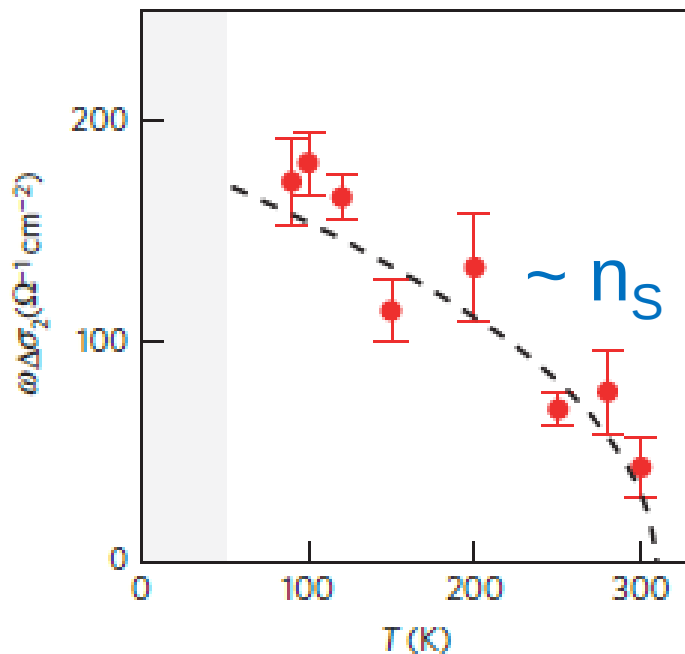
II.Physikalisches Institut der Universität zu Köln
Zùlpicher Str. 77, 5000 Köln 41, FRG



Optically enhanced coherent transport in $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ by ultrafast redistribution of interlayer coupling

W. Hu^{1†}, S. Kaiser^{1†}, D. Nicoletti^{1†}, C. R. Hunt^{1,2†}, I. Gierz¹, M. C. Hoffmann¹, M. Le Tacon³, T. Loew³, B. Keimer³ and A. Cavalleri^{1,4*}

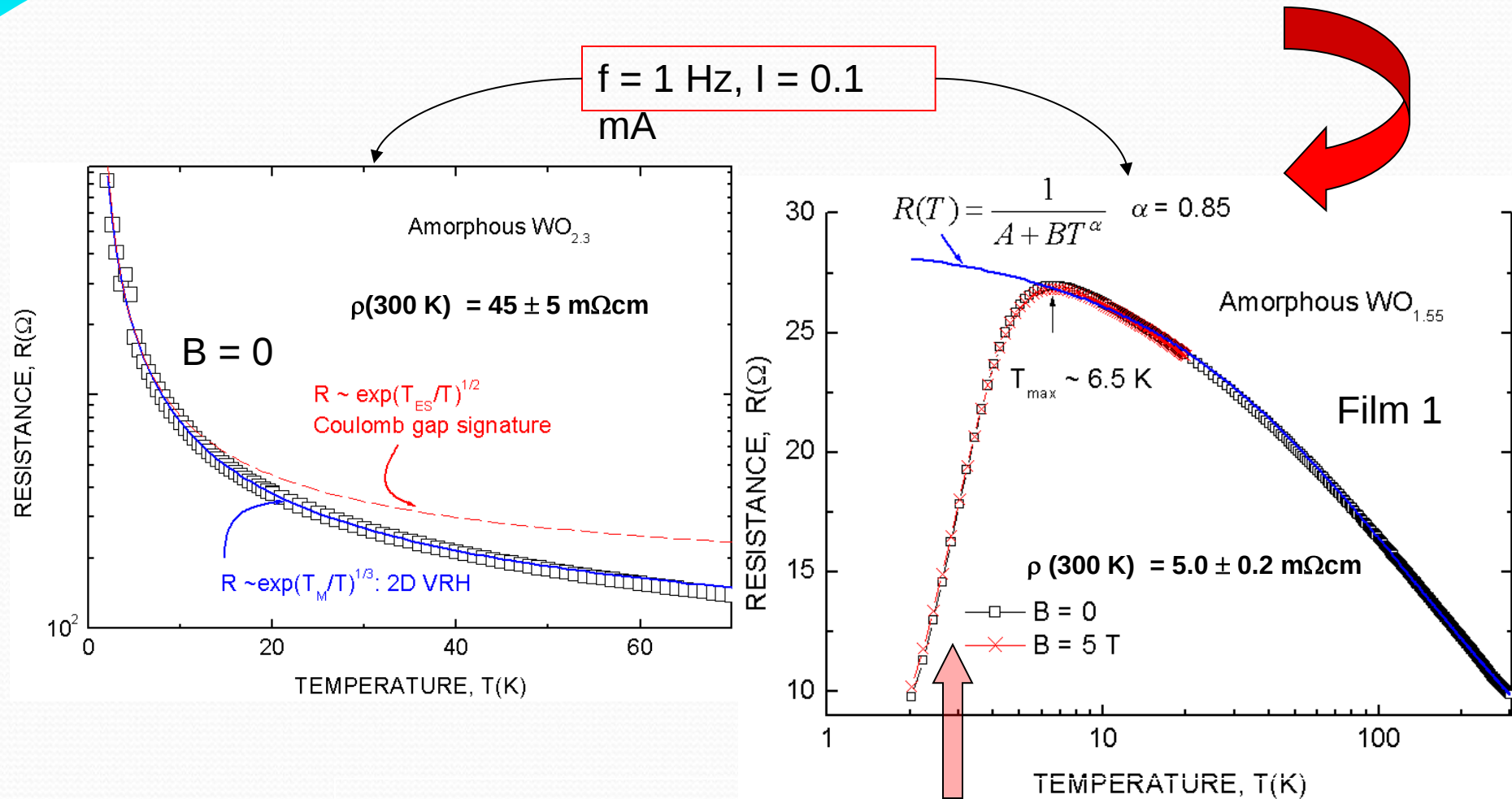
“...light stimulation redistributes Interlayer Josephson coupling in the superconducting state , enhancing inter-bilayer coupling at the expense of the coupling within the bilayers. Above T_c , a similar phenomenology is observed “



Previously, conclusions on the enhanced coupling between neighboring Cu (2) – O (2) bi-layers caused by photo-assisted oxygen ordering were made.

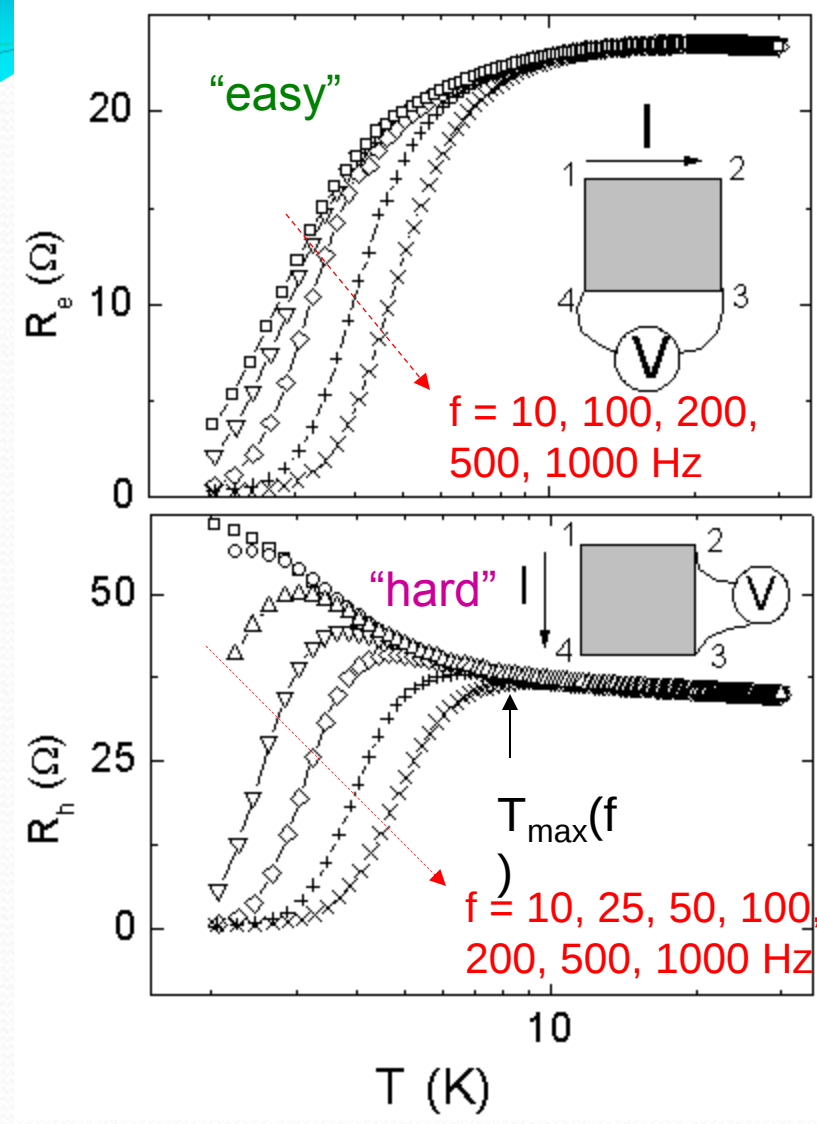
Hence, thermally unstable structures may be behind of transient Room Temperature Superconductivity in cuprates.

Charge Ordering in Amorphous WO_x Films

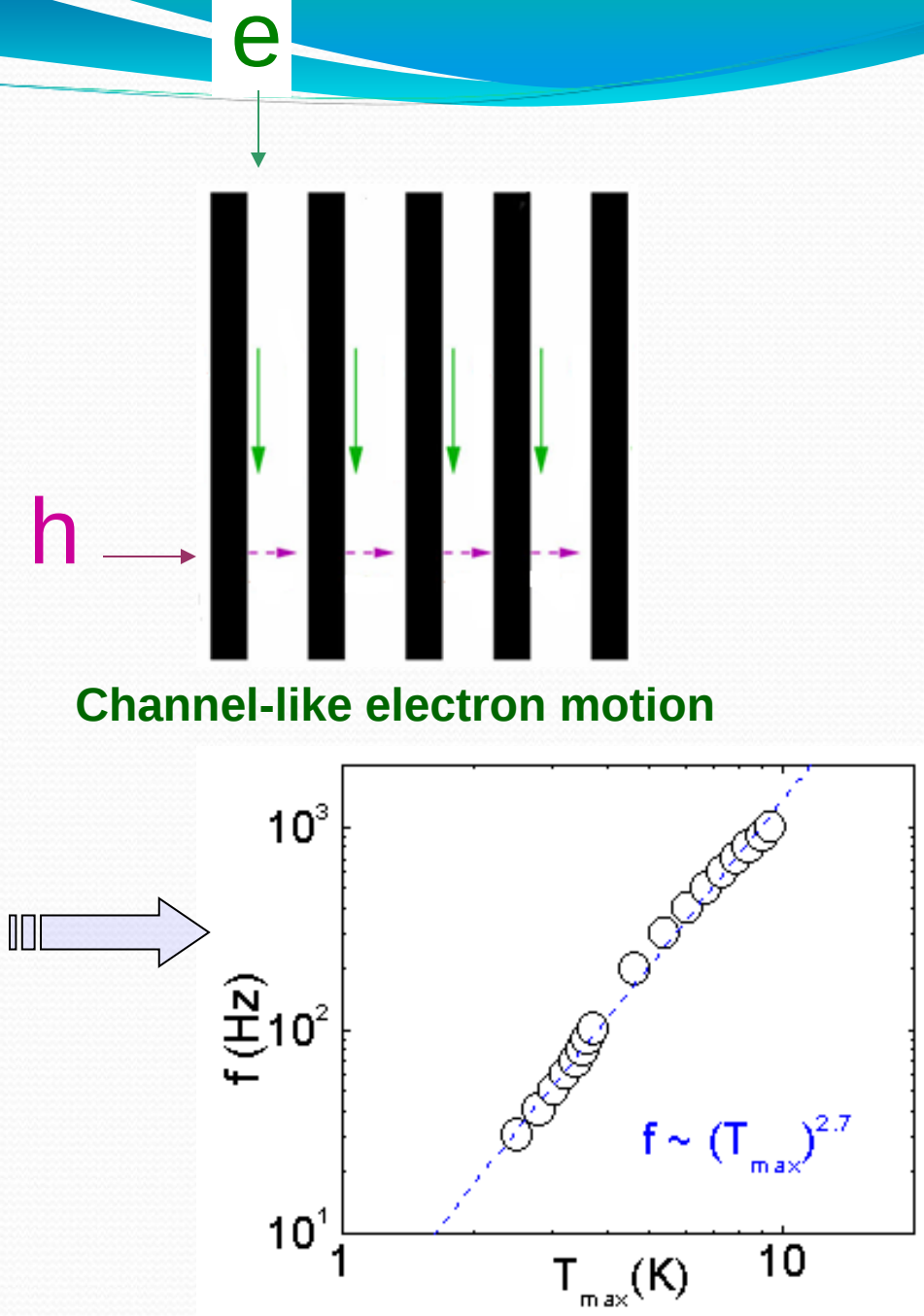


“anomalous” metallic state

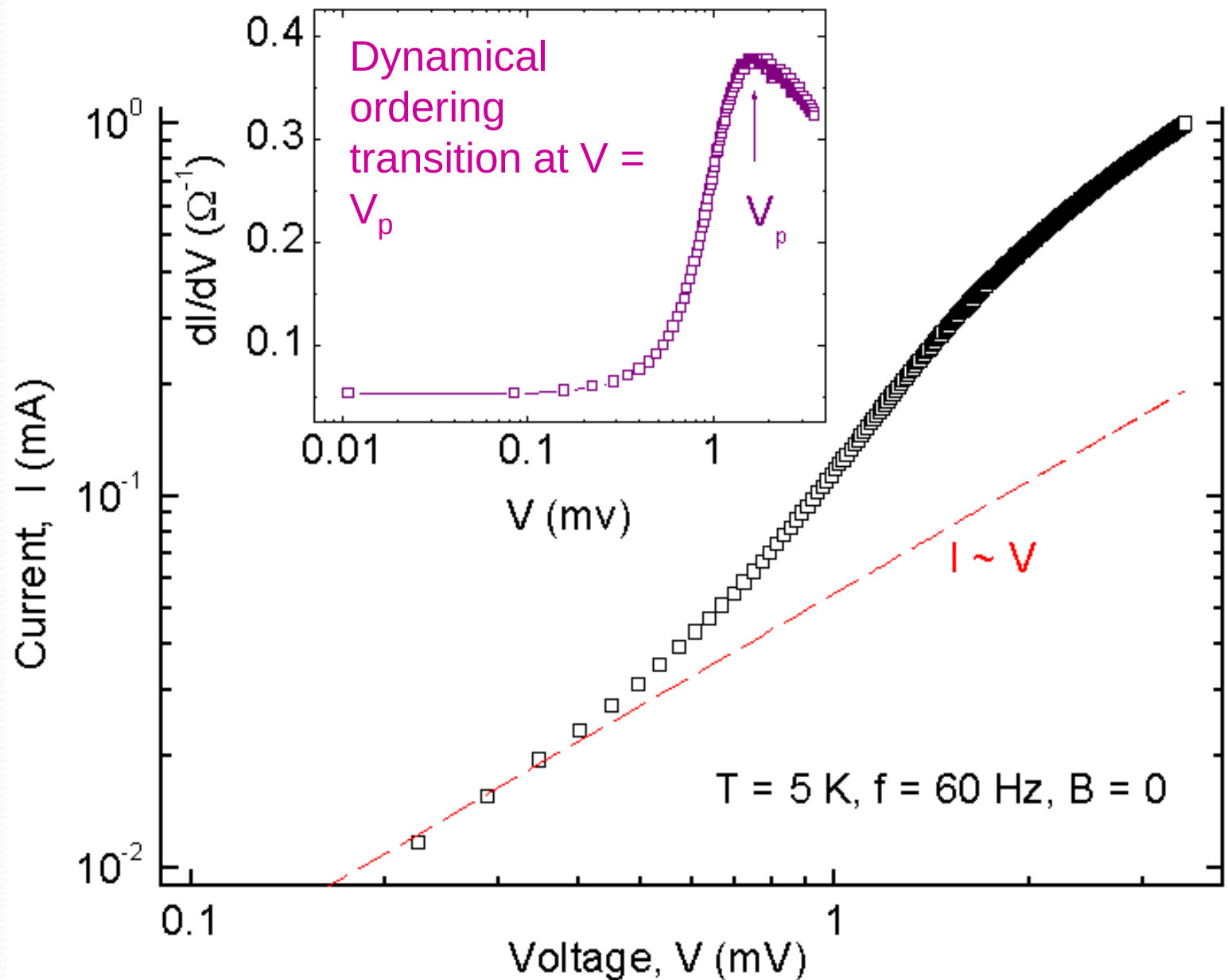
$B = 0, I_{12} = I_{14} = 10 \mu A$



Film 2: $0.72 \times 0.38 \times 0.0004 \text{ mm}^3$

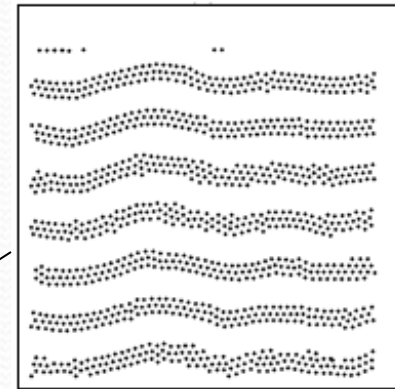
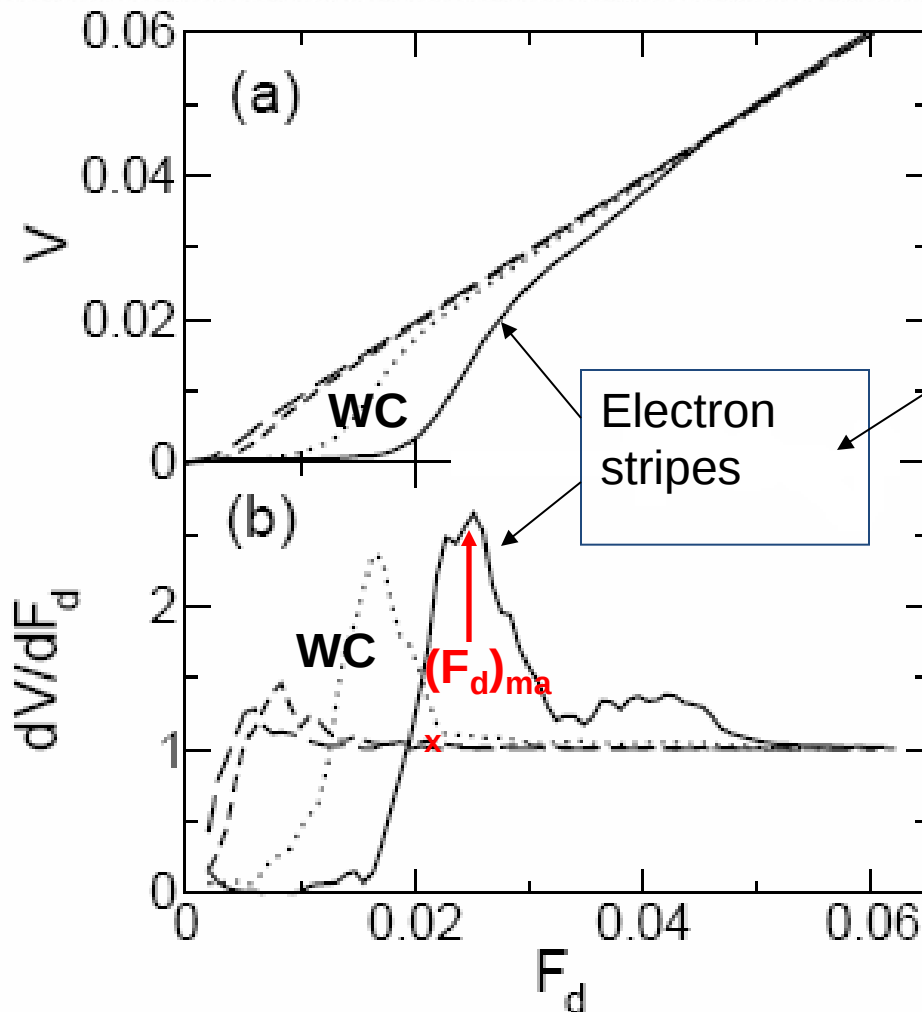


Non-Linear I-V Characteristics: “hard” direction



Numerical simulations by C. Reichhardt et al. (Europhys. Lett.' 2003)

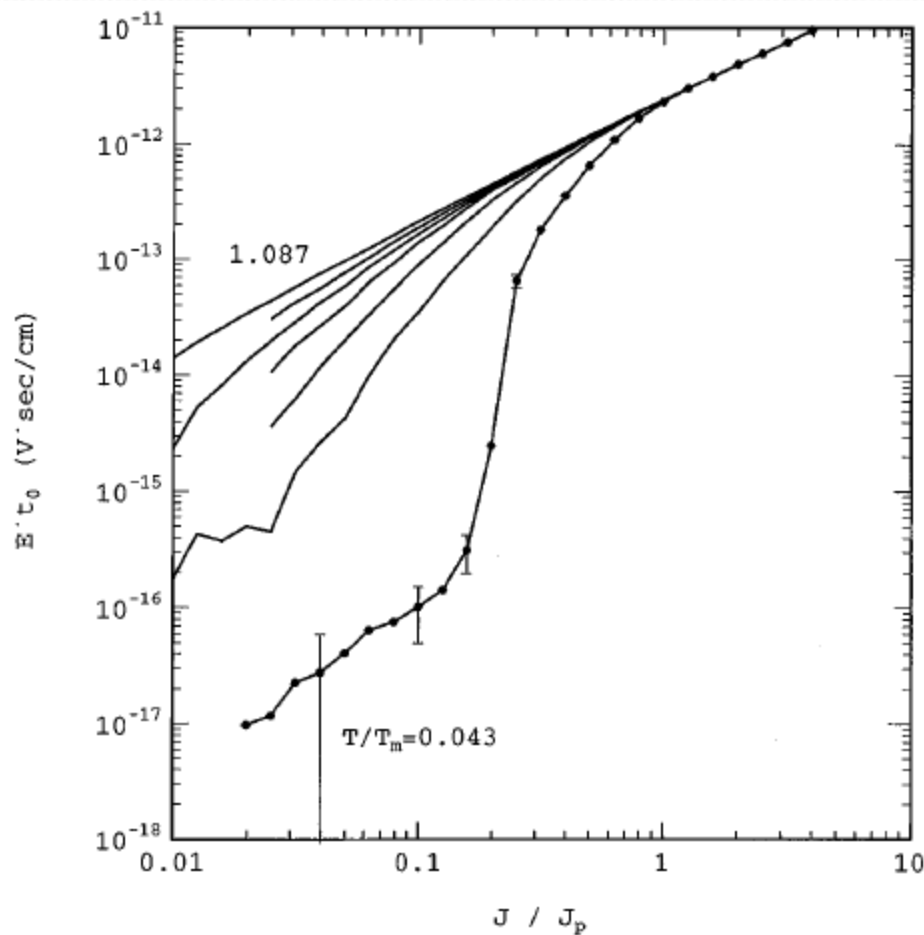
Velocity (V) vs. applied drive (F_d)



Peak in dV/dF_d , $(F_d)_{max}$, marks the **dynamical ordering transition**

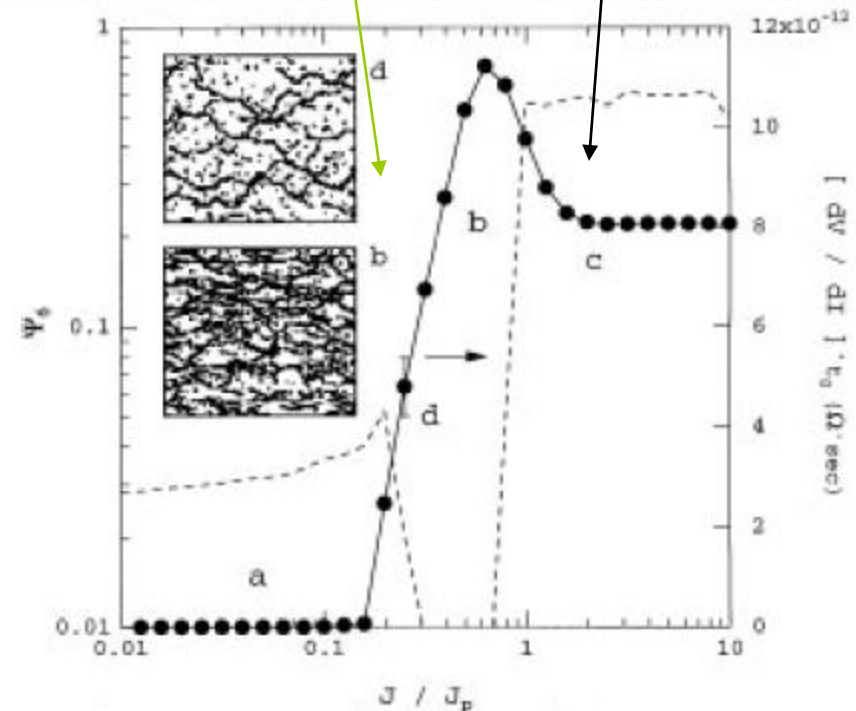
WC = Wigner crystal

Similar dynamical ordering transition is expected in vortex matter of type-II superconductors [S. Rui et al., PRL'1996]:

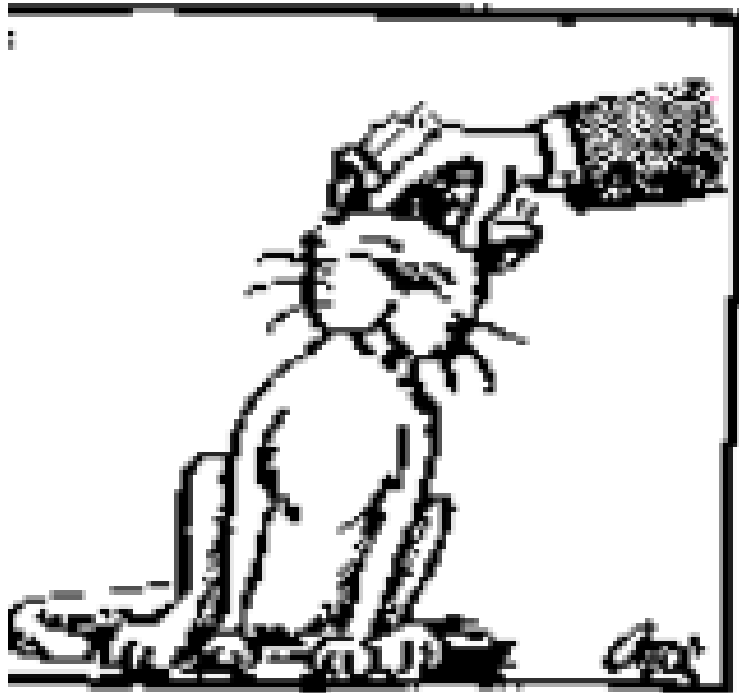


Plastic vortex motion

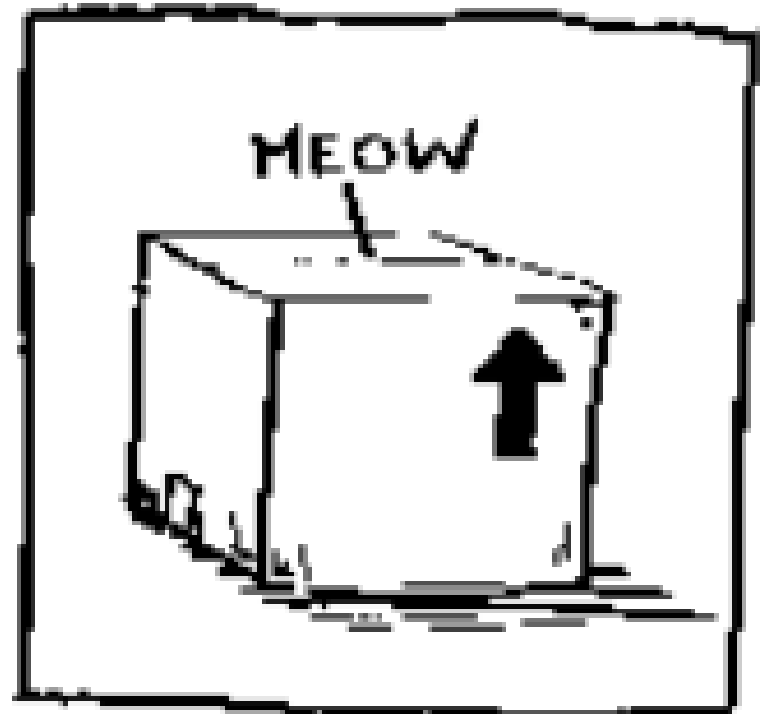
Moving vortex lattice



Fröhlich-like (super)conductivity ?

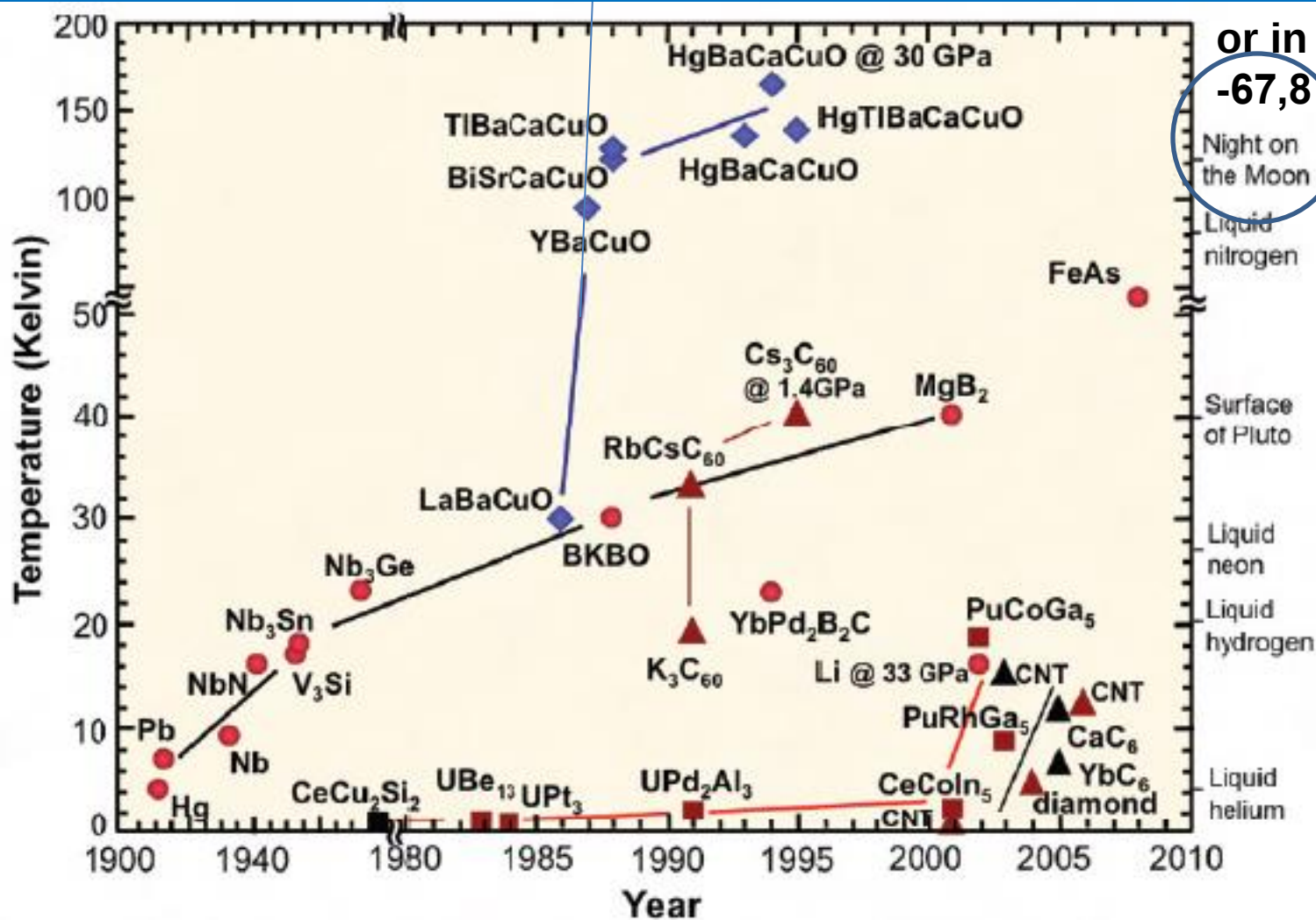


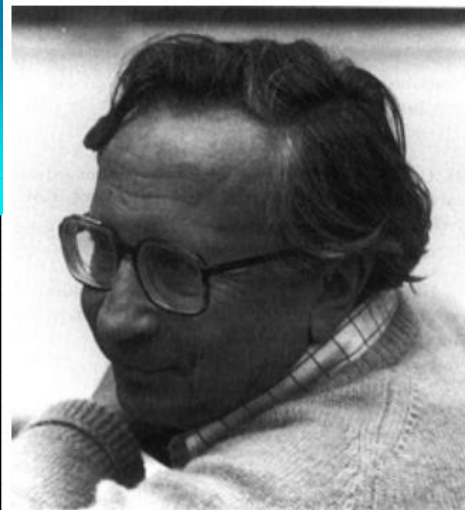
Theoretician's Cat



Experimentalist's Cat

Since the discovery in 1911 by Kamerlingh Onnes of the superconductivity in mercury (Hg) with the transition temperature $T_c = 4.2$ K, **an empirical approach in searching for new superconductors with higher T_c is still most successful one.**





Bernd Matthias

Bernd Matthias is known for having synthesized hundreds of new superconducting materials !

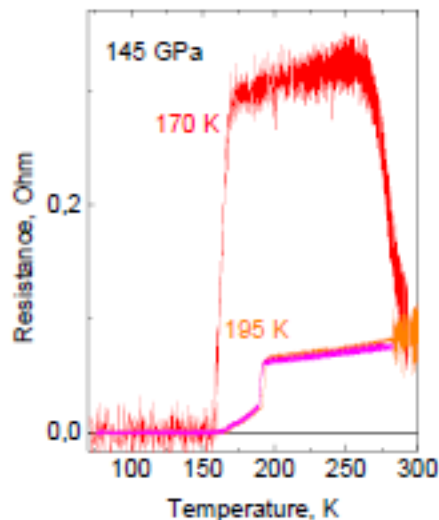
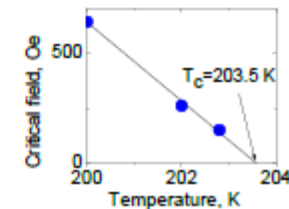
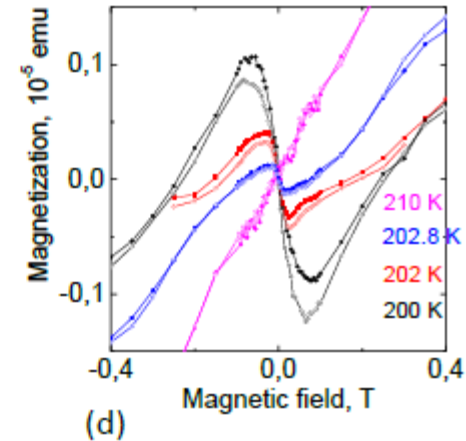
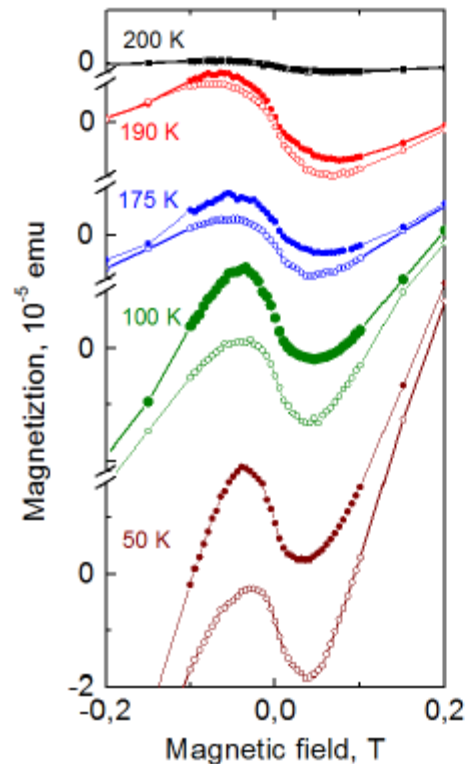
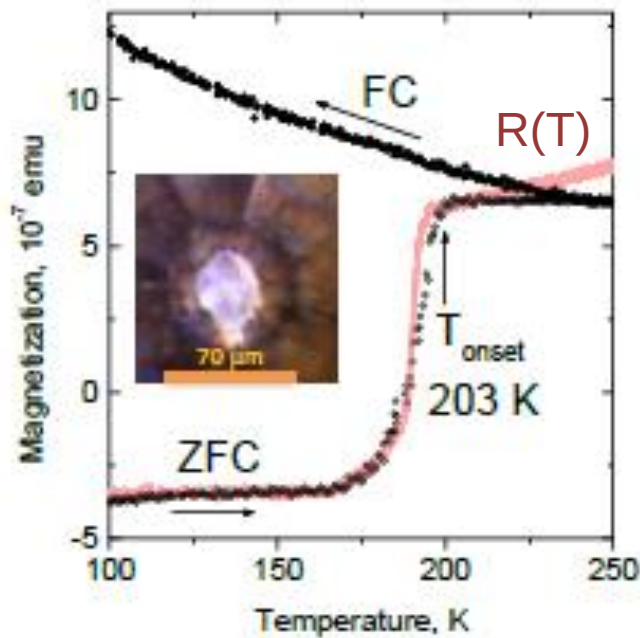
Brian Maple: “While it is indeed true that Matthias publicly railed against theorists, he did so to emphasize the fact that theory had not been useful in predicting where to find high- T_c superconductors...” (Physica C, 2015)

What is NEXT ?

Conventional superconductivity at 203 K at high pressures

A.P. Drozdov^{1*}, M. I. Erements^{1*}, I. A. Troyan¹, V. Ksenofontov, S. I. Shylin²

(H₂S)



The sample was pressurized to 145 GPa at 220 K and then cooled to 100 K. During next slow warming ~ 1 K/min $T_c = 170$ K was determined. At temperatures above ~ 250 K the resistance dropped sharply, and at the next temperature run T_c increased to ~ 195 K. This T_c remained nearly the same for next two runs.

Paul Chu (Physica C, 2015):

“The most recent report of detection of conventional electron–phonon mediated superconductivity up to 190 K in H₂S under ultrahigh pressures appears to have raised serious challenges to our present understanding in high temperature superconductivity, **if proven.”**

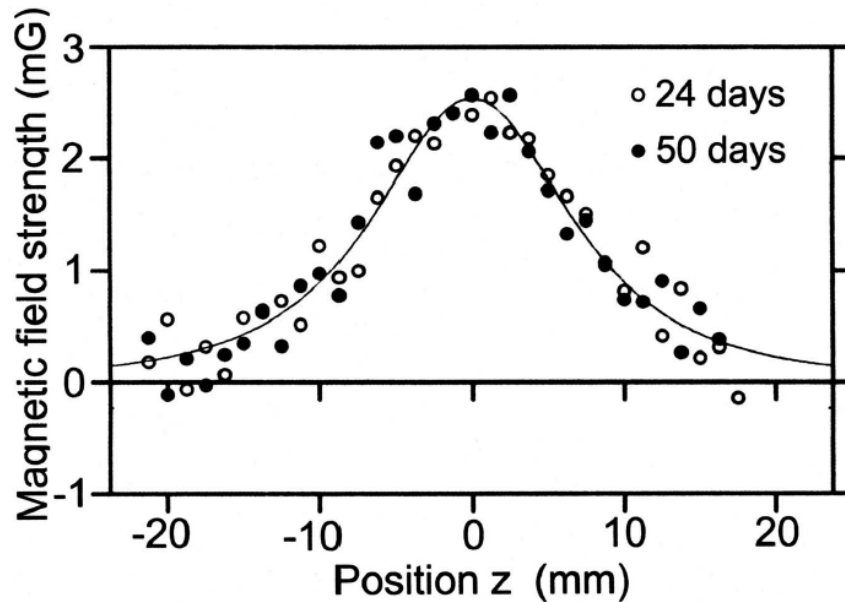
Possible room temperature superconductivity in conductors obtained by bringing alkanes into contact with a graphite surface

Yasushi Kawashima

Citation: [AIP Advances](#) 3, 052132 (2013); doi: 10.1063/1.4808207

“Ring current in a ring-shaped container into which n-octane-soaked thin graphite flakes were compressed did not decay for 50 days at room temperature.

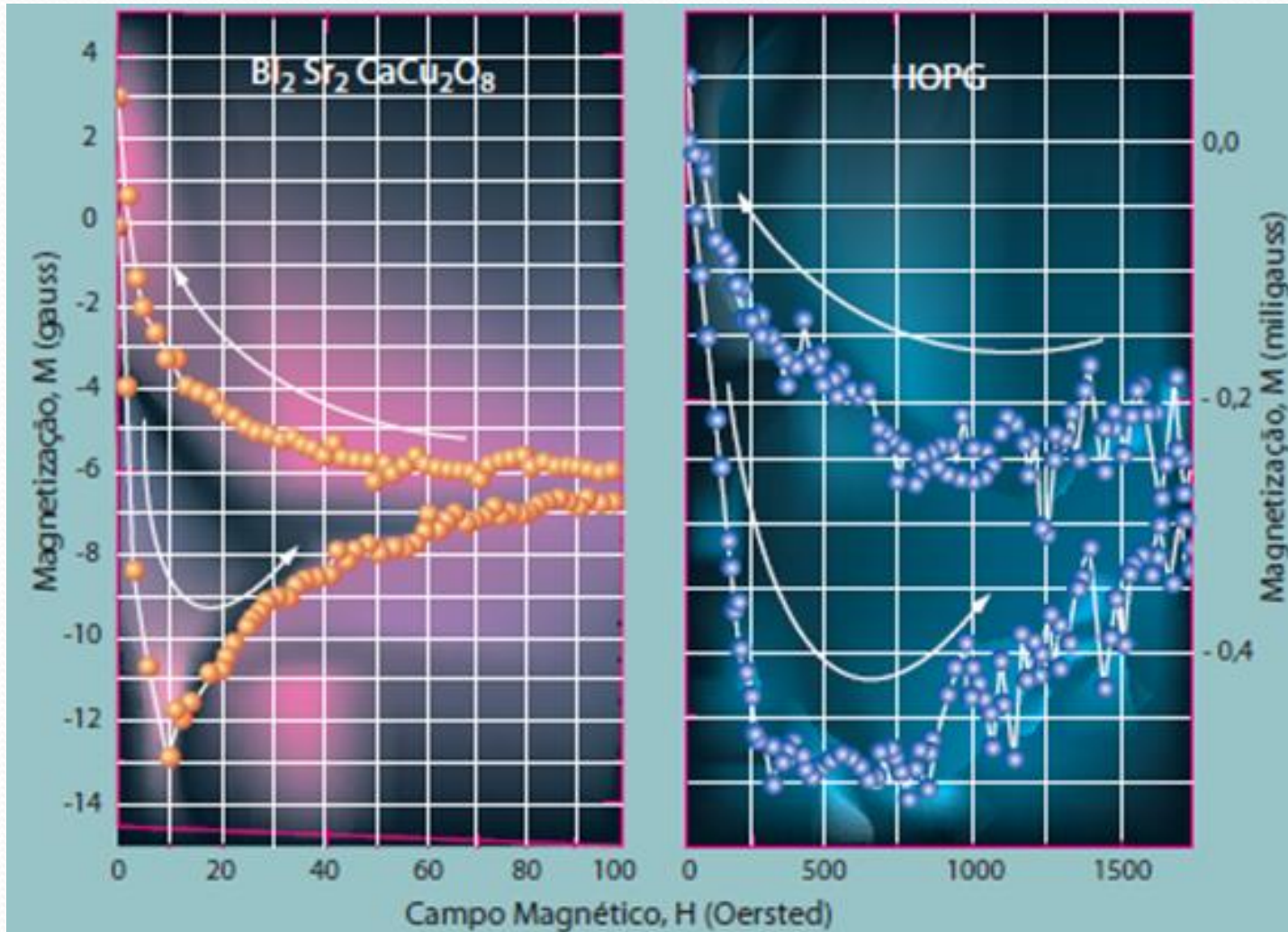
These results suggest that room temperature superconductor may be obtained by bringing alkanes into contact with a graphite surface.”



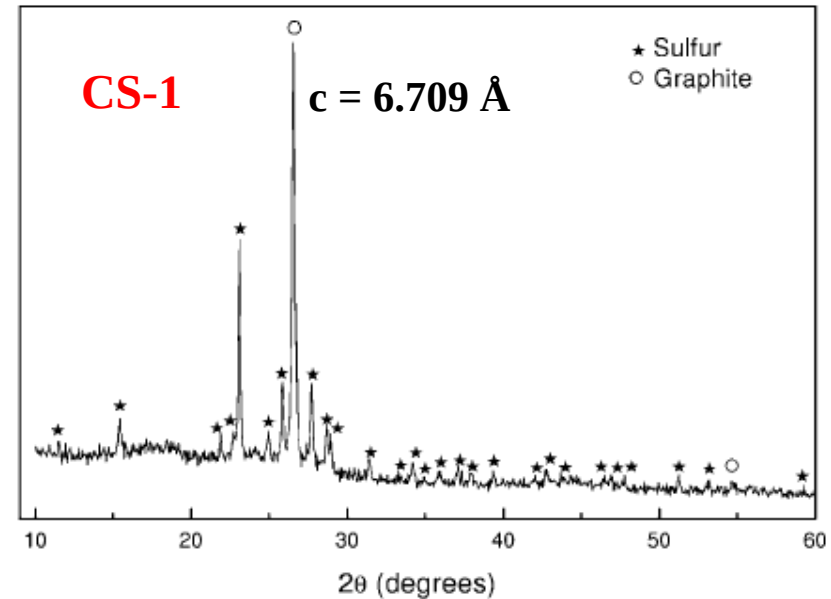
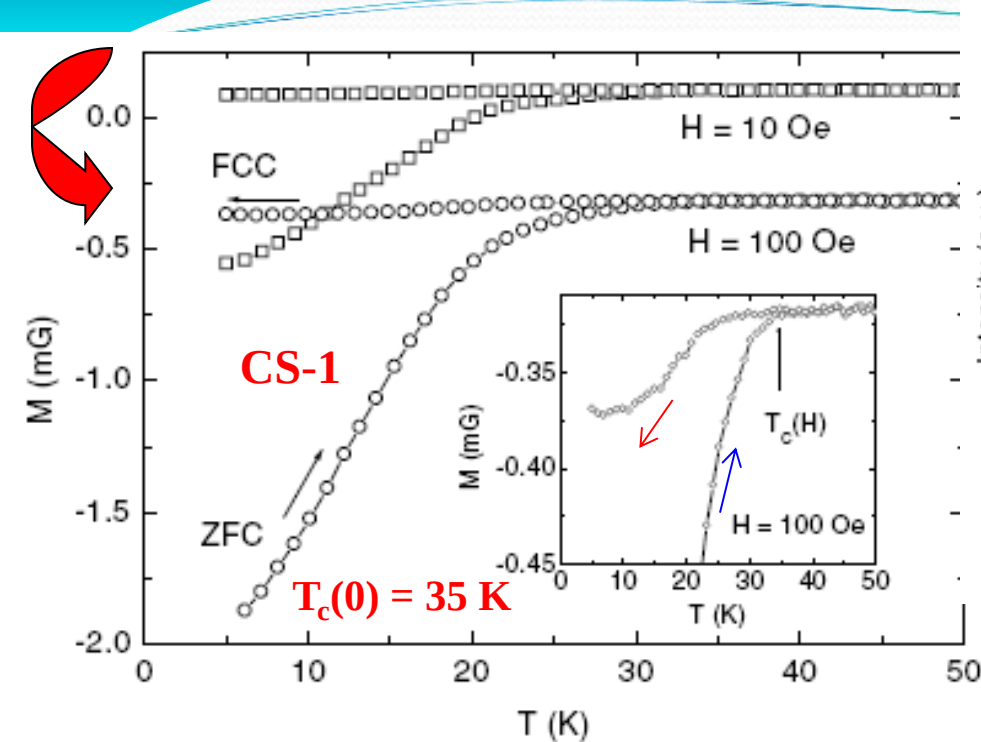
$T = 300 \text{ K}$

Superconductor
 $T < T_c = 90 \text{ K}$

GRAPHITE, $T = 300 \text{ K}$

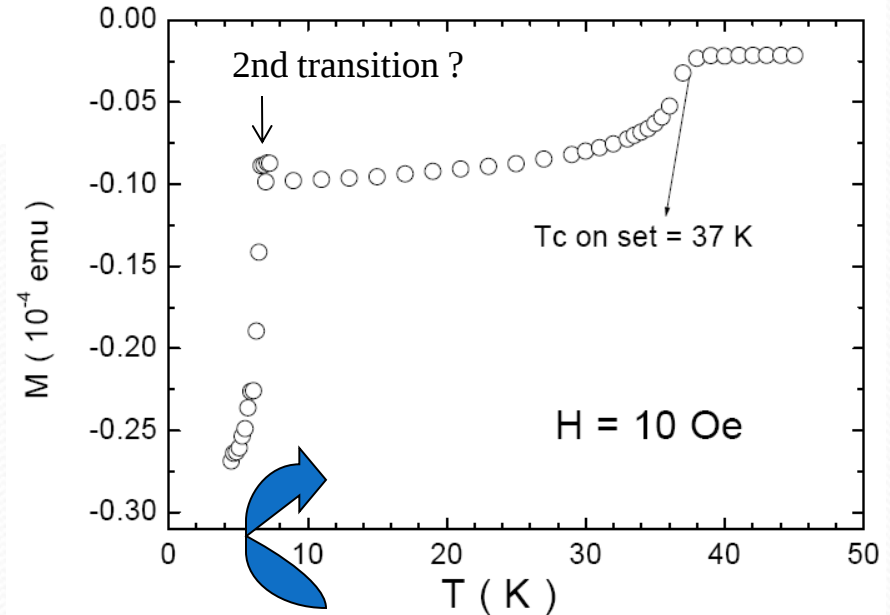


Enhanced local superconductivity in sulfur-doped graphite:



R. R. da Silva, J. H. S. Torres, and
Y. Kopelevich, Phys. Rev. Lett. 87,
147001 (2001)

Superconducting
volume fraction $\sim 0.02 \%$
 $\Rightarrow$ SURFACE ?



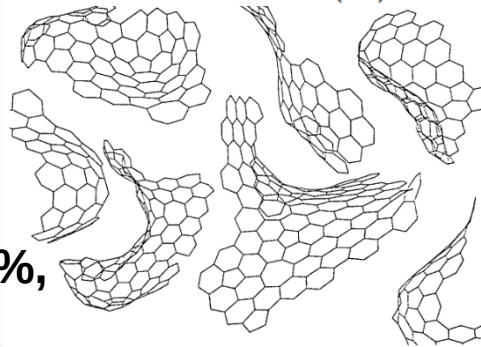
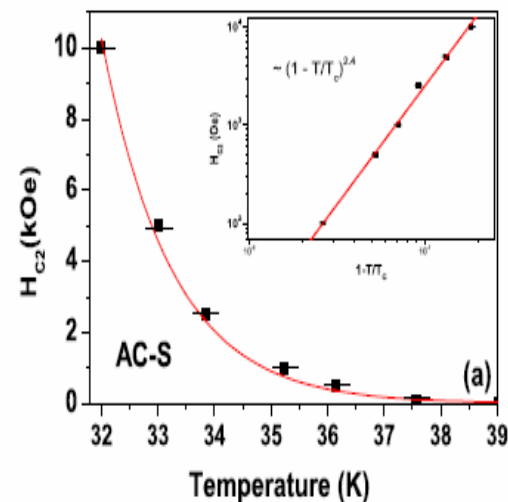
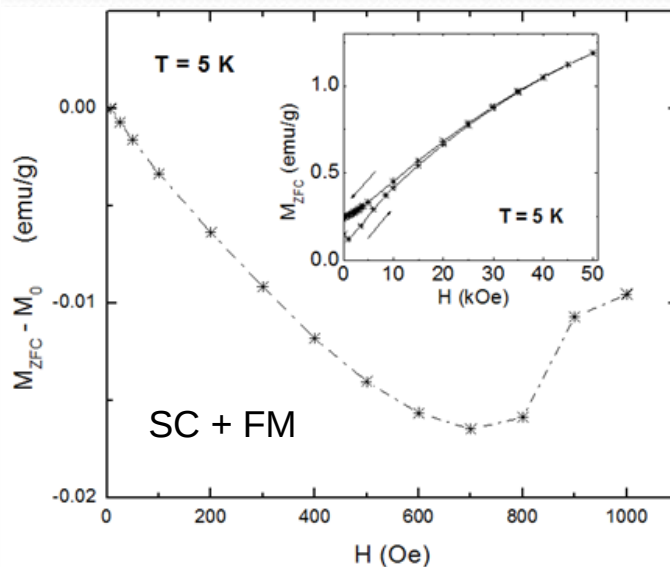
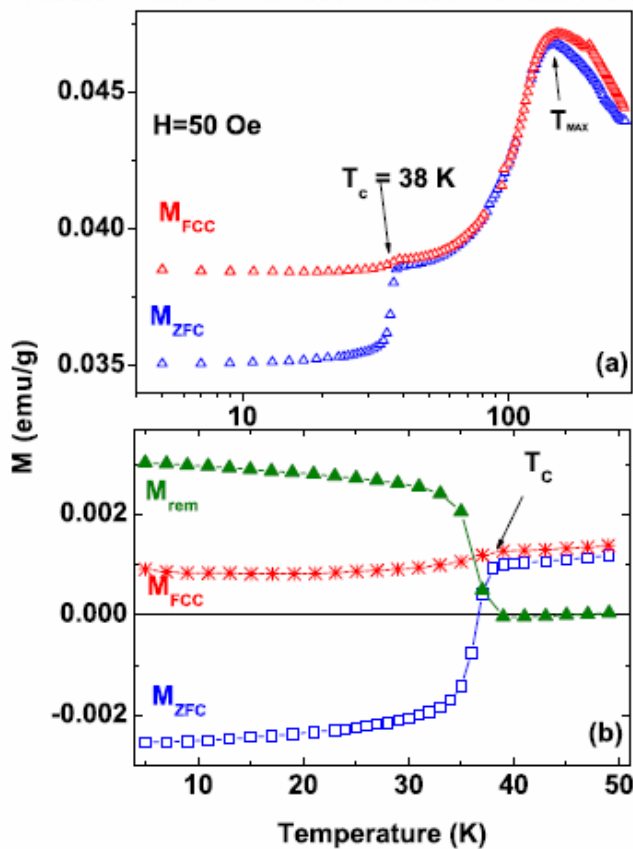
Y. Hai-Peng et al., Chin. Phys. Lett. 18, 1648 (2001)

Magnetization measurement of a possible high-temperature superconducting state in amorphous carbon doped with sulfur

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Non-graphitizing carbons;
P. J. F. Harris et al.,
Phil. Mag. Lett. 2000

SC shielding fraction ~ 0.15 %,
Meissner fraction ~ 0.02 %.

INSTEAD OF CONCLUSIONS:

(1) “Searching for new and enhanced Tc’s remains a promising and never ending fertile frontier.”



(2) “Almost half a century passed between the discovery of superconductivity by Kamerlingh Onnes and the theoretical explanation of the phenomenon by Bardeen, Cooper and Schrieffer. During the intervening years the brightest minds in theoretical physics tried and failed to develop a microscopic understanding of the effect. A summary of some of those unsuccessful attempts to understand superconductivity not only demonstrates the extraordinary achievement made by formulating the BCS theory, but also illustrates that **mistakes are a natural and healthy part of the scientific discourse, and that inapplicable, even incorrect theories can turn out to be interesting and inspiring.** “

Jörg Schmalian, “Failed theories of superconductivity”, arXiv: 1008.0447

