Evidence for Superconductivity at Graphite Interfaces

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„Correlations and coherence in quantum systems"
Évora, Portugal, 8 - 12 October 2012

BASICS I
Main experimental evidence for the phenomenon of superconductivity

- Field expulsion (Meissner state, perfect diamagnetism)
- Zero resistance state
- Existence of vortices or fluxons
- Josephson effect

BASICS II
Granular superconductivity

Microscopic superconducting grains in a non-superconducting matrix

- Josephson tunnelling between the grains influences the I-V curves, R → zero at low T and I (current). Barzola et al., "Graphene" (2011). Ballestar et al., arXiv/1206.2463
- Anomalous thermally activated-like temperature dependence of the resistance, $R \sim e^{-T_1/T}$. García et al., NJP 14, 053015 (2012)
- Andreev scattering: peculiarities in the I/V curves or periodic oscillations of the magnetoresistance. Esquinazi et al., Phys. Rev. B 78, 134516 (2008)
- Anomalous field hysteresis loops of the magnetoresistance. Esquinazi et al., Phys. Rev. B 78, 134516 (2008), Dusari et al., J Supercond Nov Magn 24, 401405 (2011)
- Anomalous field hysteresis loops of the magnetization. Scheike et al, Adv.Mat. Suppl Inf. (2012) and to be published.

All these phenomena were observed recently in graphite samples

From all the evidence obtained in the last 38 years on high-T_c granular superconductivity in graphite I restrict to the following observations

- (1) Giant field driven Metal-Insulator transition in bulk ordered graphite samples (2001-2011) → An effect due to internal interfaces
- (2) Zero-resistance state due to Josephson coupled superconducting patches at internal interfaces in ordered graphite: measurements of lamellae (2009-2012)
- Anomalous field hysteresis in the magnetoresistance of thin graphite samples (2008-2011)
- Quantum resonances assigned to Andreev reflections in the magnetoresistance (2008)
- Electric field induced resistance transition in thin graphene samples (2012)
- (3) Granular superconductivity in water-treated graphite powder (2012) → Magnetization measurements

Theoretical work 2001-2012 on possible superconductivity in graphite/graphene

– SC predicted in inhomogeneous regions of graphite structure [1]
– RVB Superconductivity [2,7]
– SC possible if the carrier density $n>10^{13}cm^{-2}$ [3]-[6]-[10]
– High-Tc surface superconductivity in topological flat-band systems [8]

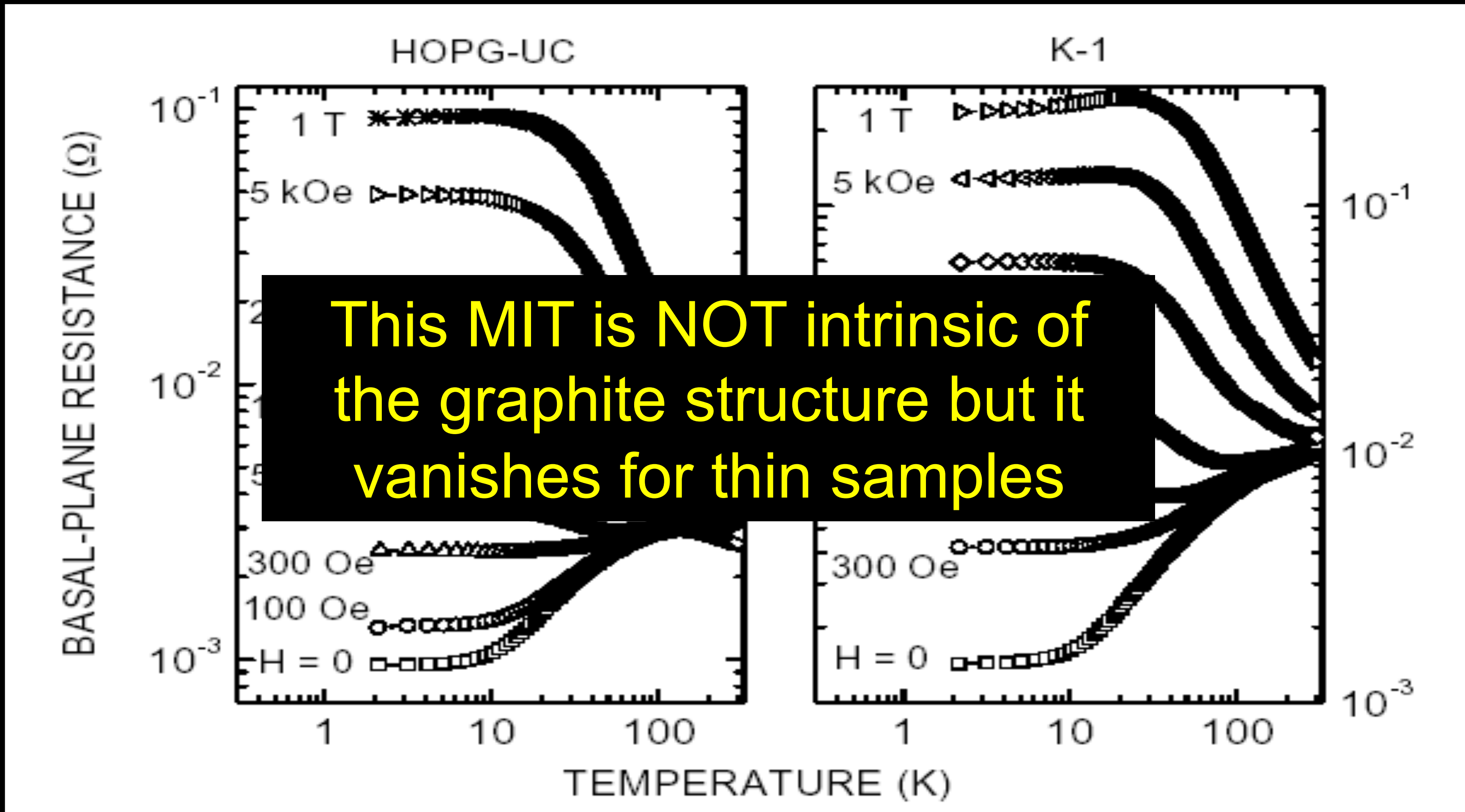
[1] J. Gonzalez, M. Vozmediano, F. Guinea, Phys. Rev. B, **63**, 134421 (2001)
[2] G. Baskaran, Phys. Rev. B **65**, 212505 (2002)
[3] A. M. Black-Schaffer and S. Doniach, Phys. Rev. B, **75**, 134512 (2007)
[4] N. Garcia and P. Esquinazi, J. Supercond. Nov. Magn., **22**, 439 (2009): "2D Superconductivity"
[5] B. Uchoa and A.H.C. Neto, Phys. Rev. Lett., 98, 146801 (2007)
[6] N.B. Kopnin and E.B. Sonin, Phys. Rev. Lett., **100**, 246808 (2008)
[7] S. Pathak, V. Shenoy and G. Baskaran, Phys. Rev. B 81, 085431 (2010): "d+id pairing"
[8] Savini et al., PRL 105, 037002 (2010): Doped graphane as a high-temperature electron-phonon superconductor.
[9] N. B. Kopnin, T. T. Heikkilä, and G. E. Volovik, Phys. Rev. B **83,** 220503(R) (2011)
[10] R. Nandkishore et al., Nature Physics 8, 158 (2012): „Chiral d-wave superconductivity"
[11] G. Profeta et al., Nature Physics 8, 131 (2012): „e-ph coupling and Li adatoms"
[12] Hosseini and Sareyan, Phys. Rev. Lett. 108, 147001 (2012): "Exotic Chiral Superconducting Phase in a Graphene Bilayer"
and continues …

Further experimental evidence for granular superconductivity in doped graphite or disordered carbon (other papers in literature)

- K.Antonowicz, Possible superconductivity at room temperature, *Nature* 247, 358 (1974)
- I. Felner and Y. Kopelevich, Magnetization measurement of a possible high-temperature superconducting state in amorphous carbon doped with sulfur. *Phys. Rev. B* 79, 233409 (2009) .
- R. Ricardo da Silva, J. H. S. Torres, and Y. Kopelevich, Indication of superconductivity at 35 k in graphite-sulfur composites. *Phys. Rev. Lett.* 87, 147001 (2001).
- H.-P. Yang, H.-H. Wen, Z.-W. Zhao, and S.-L. Li. Possible superconductivity at 37 k in graphite-sulfur composites, *Chin. Phys. Lett.* 18, 1648 (2001).
- S. Moehlecke, P. C. Ho, and M. B. Maple. Coexistence of superconductivity and ferromagnetism in the graphite sulphur system. *Phil. Mag. B* 82, 1335 (2002).

(1)

Giant „Metal-Insulator Transition“ in BULK graphite for fields perpendicular to graphene planes

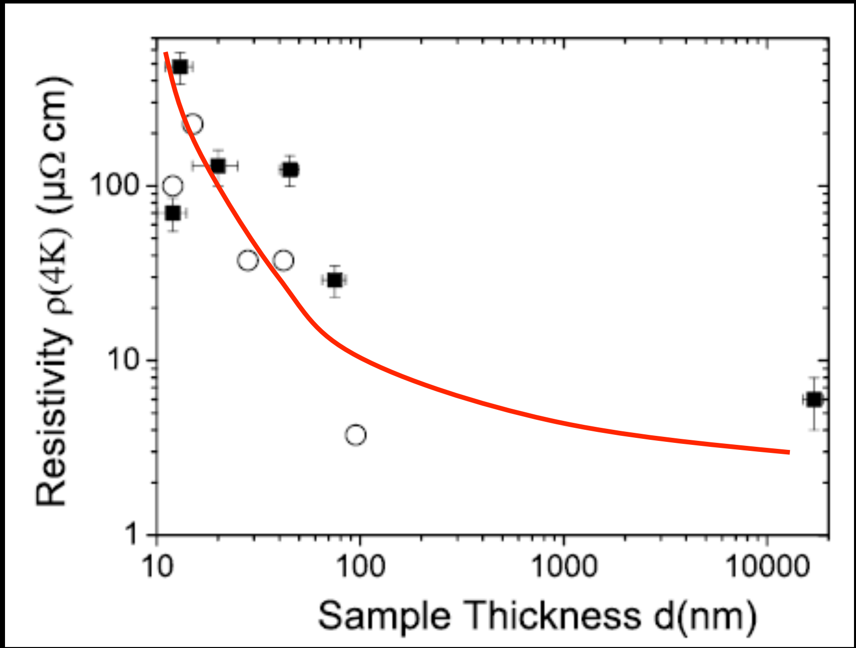


This MIT is NOT intrinsic of the graphite structure but it vanishes for thin samples

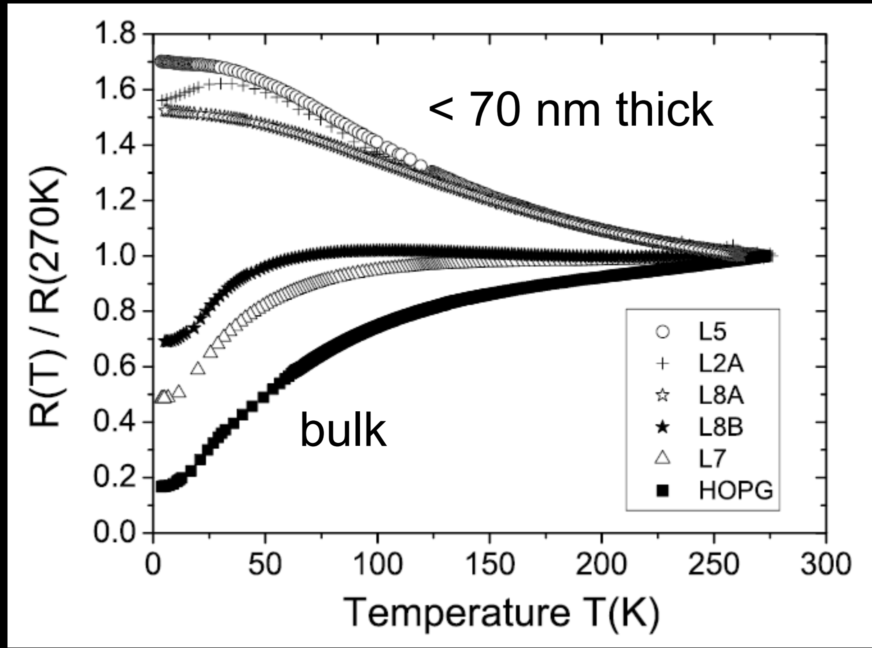
Y. Kopelevich, P. Esquinazi, J. Torres, R. da Silva and H. Kempa, Adv. Solid State Physics **43,** 207 (2003)

The metallic-like properties and the MIT are NOT intrinsic of ideal graphite

Resistivity grows the thinner the graphite sample

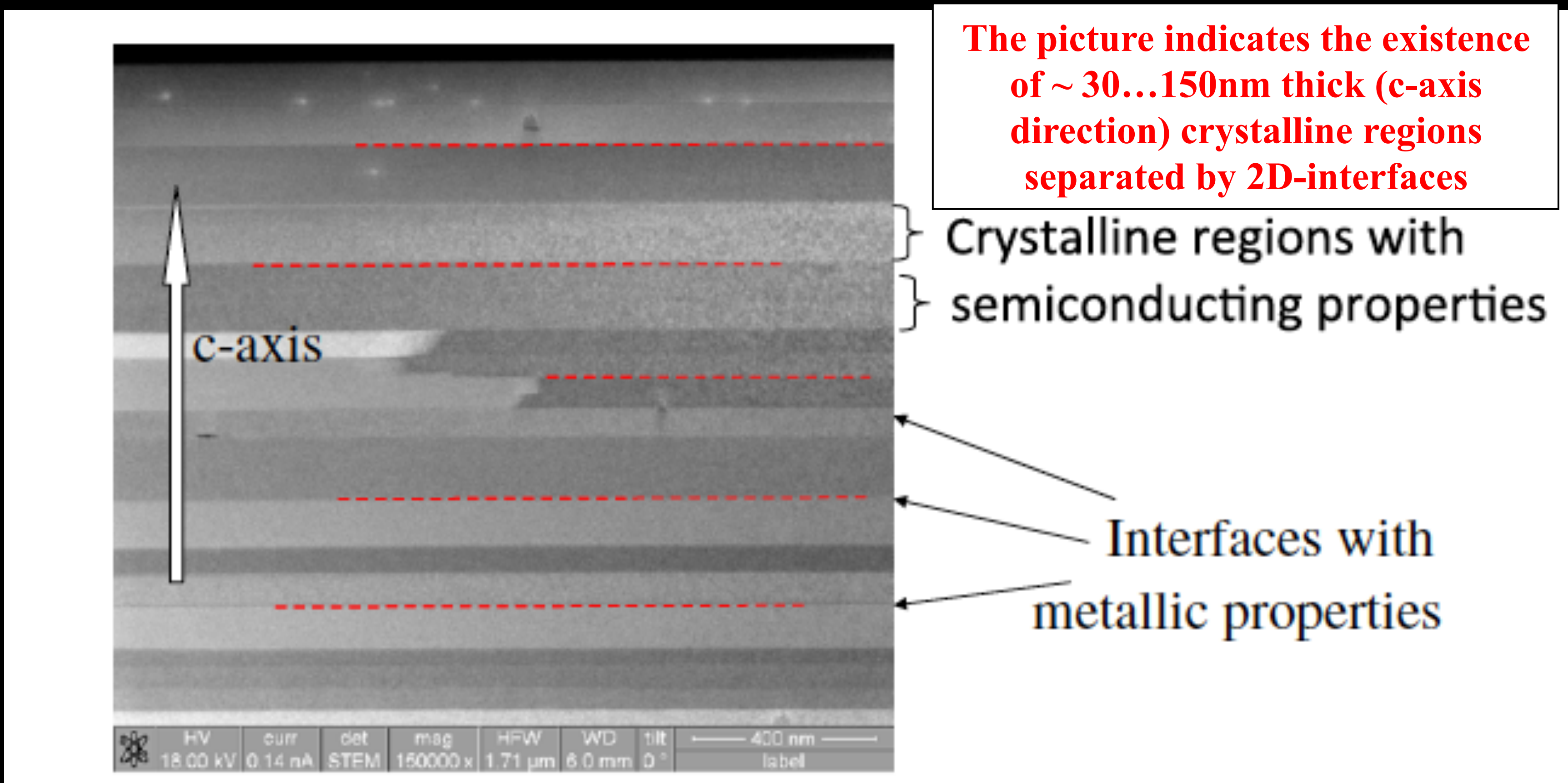


The metallic behavior of R(T) changes to semiconducting the thinner the sample



J. Barzola-Quiquia, et al., phys. stat. sol. (a) **205**, 2924 (2008)

Internal Structure of oriented pyrolytic graphite measured with TEM 18keV



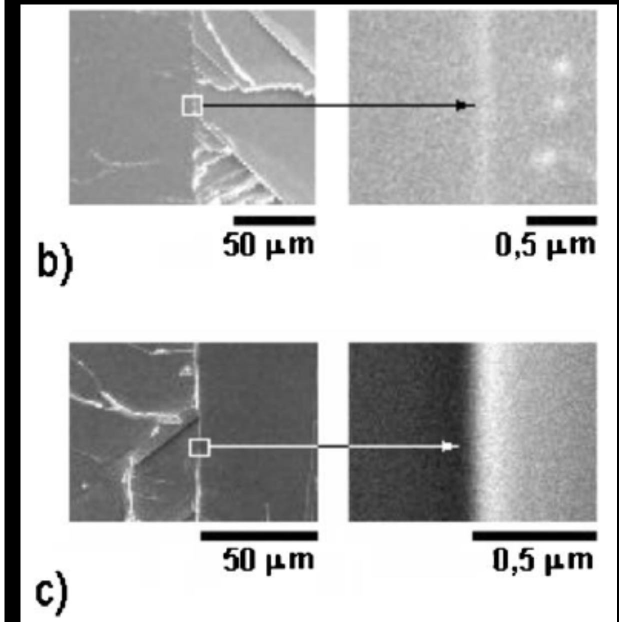
J. Barzola-Quiquia, et al., phys. stat. sol. (a) **205**, 2924 (2008)
N. García et al., New Journal of Physics **14** (2012) 053015

BUT

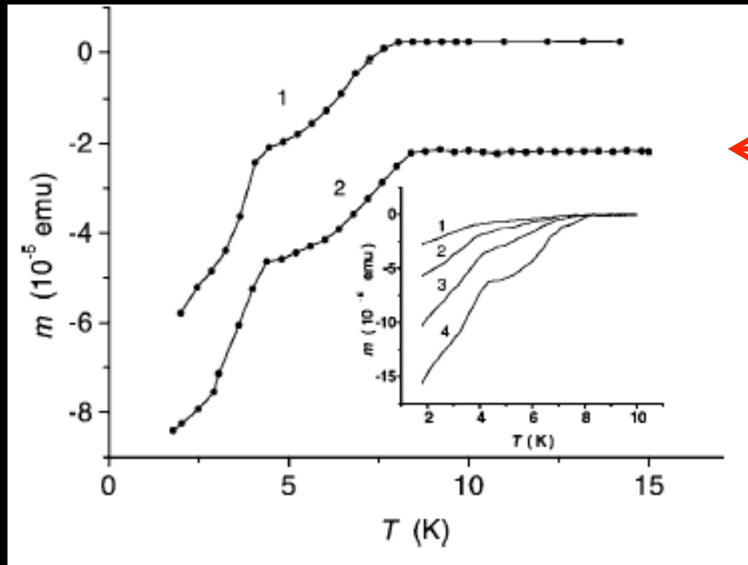
2D-interfaces in some solids show

SUPERCONDUCTIVITY

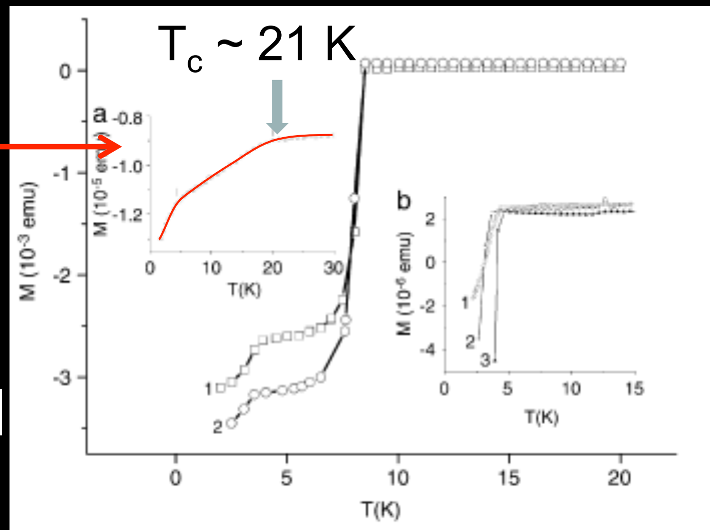
Superconductivity at the interfaces between two crystalline regions of Bi or BiSb



PHYSICAL REVIEW B 73, 132507 (2006)

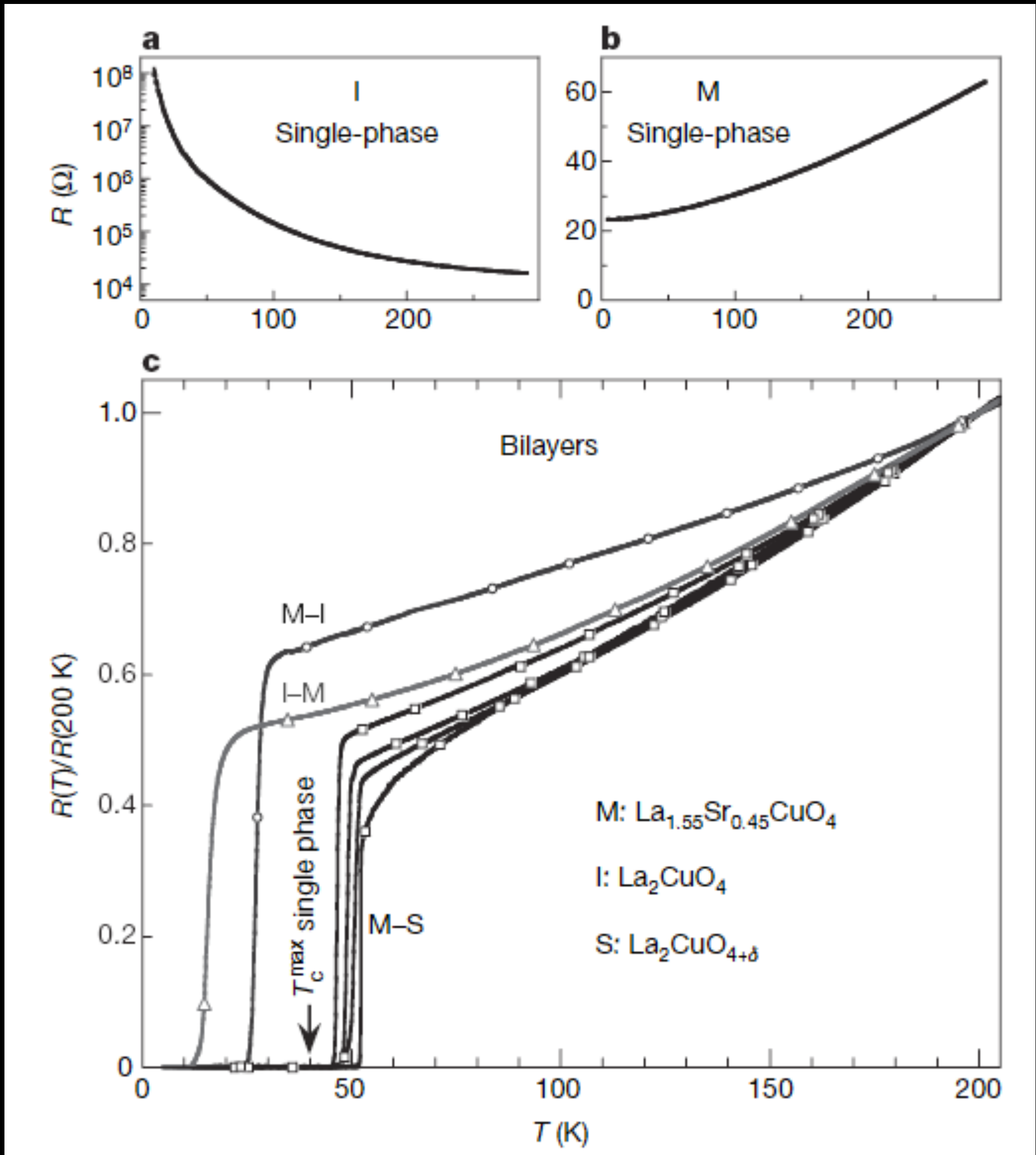


Bi

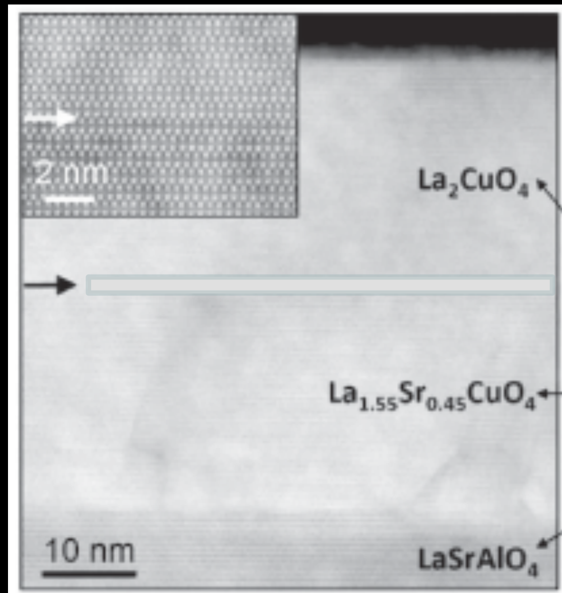


Bi_{1-x}–Sb_x ($x \leq 0.07$) bicrystals of inclination type

F. M. Muntyanu et al., Solid State Commun. **147**, 183 (2008)



High-Temperature interface Superconductivity between metallic and insulating copper oxides

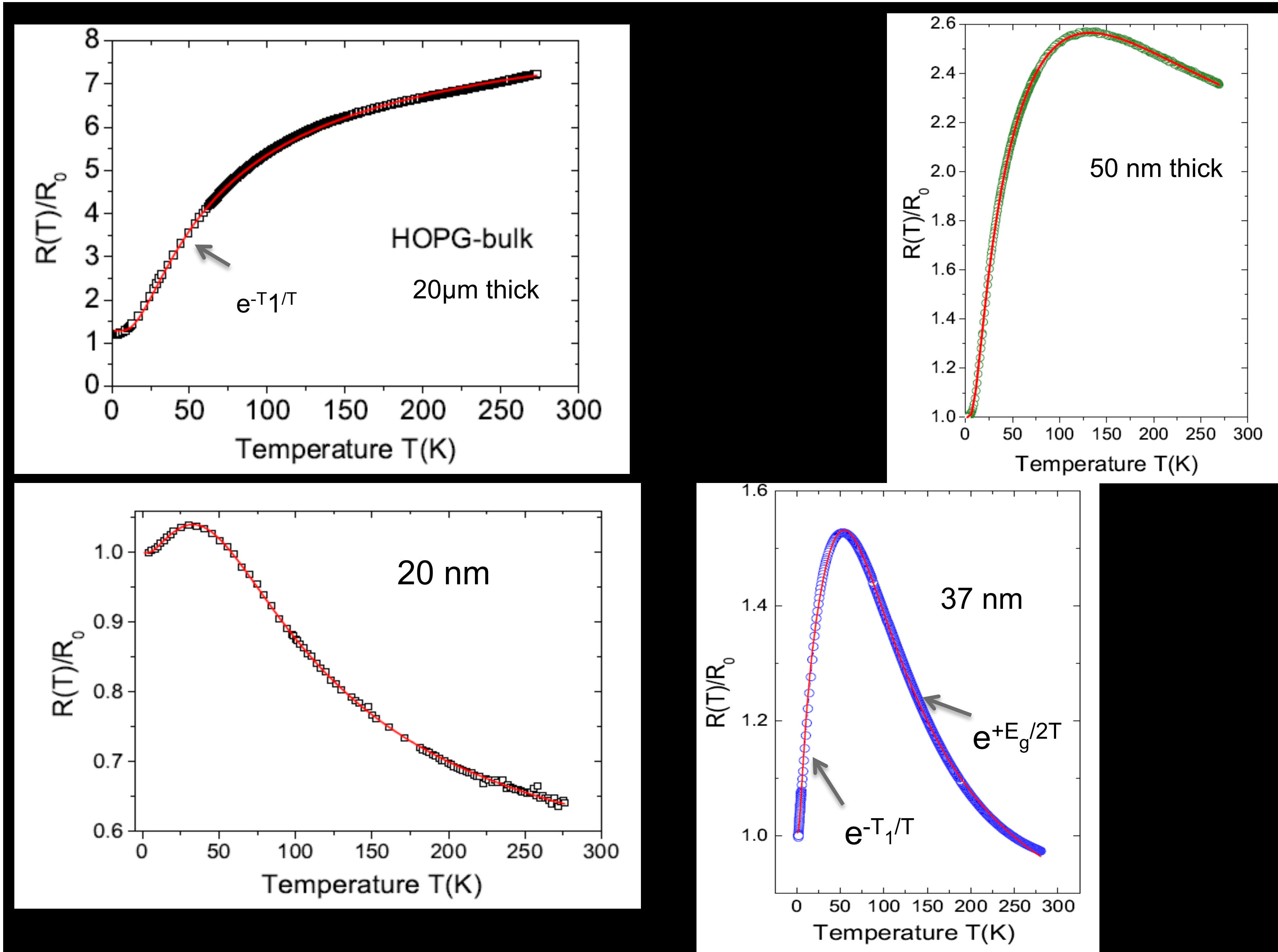


Gozar et al., Nature 455, 782 (2008)

The temperature dependence of the resistance in bulk graphite ordered samples can be understood under the following basic assumptions

(1) Metallic-like behavior in the resistivity is not intrinsic but mainly due to the parallel contribution from internal interfaces

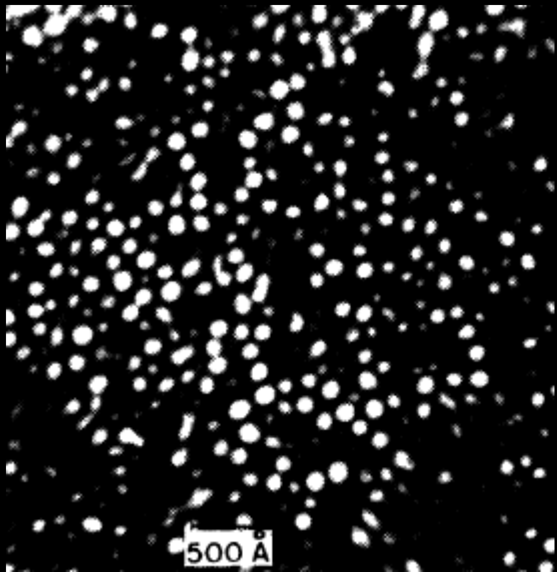
(2) Non-percolative superconducting regions, „granular superconductivity“, are located at the interfaces, i.e. at regions with high carrier density.



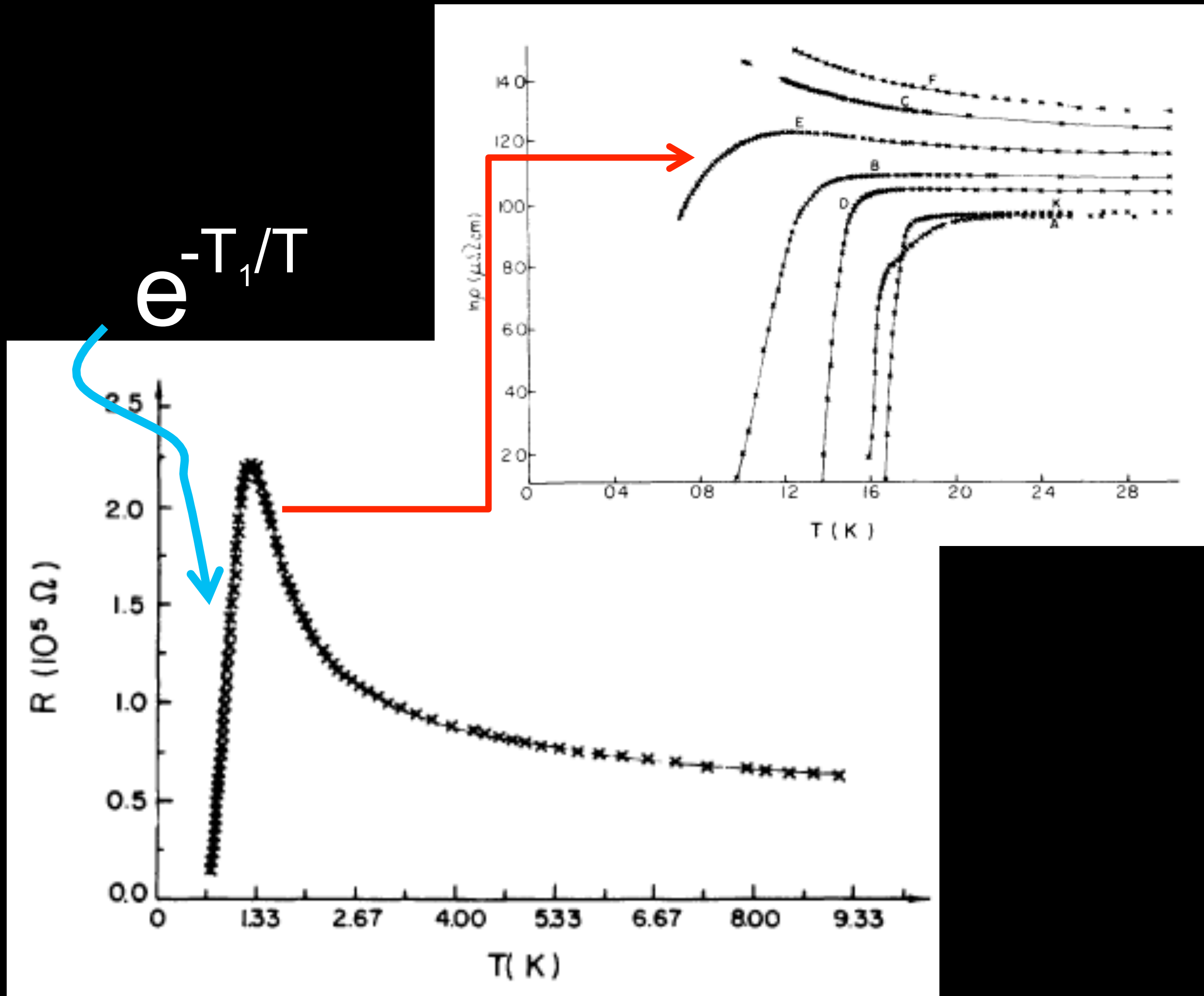
N. García et al., New Journal of Physics **14** (2012) 053015

Behavior similar to the superconducting-semiconducting transition in granular Al-Ge

Shapira and Deutscher, PRB 27, 4463 (1983)

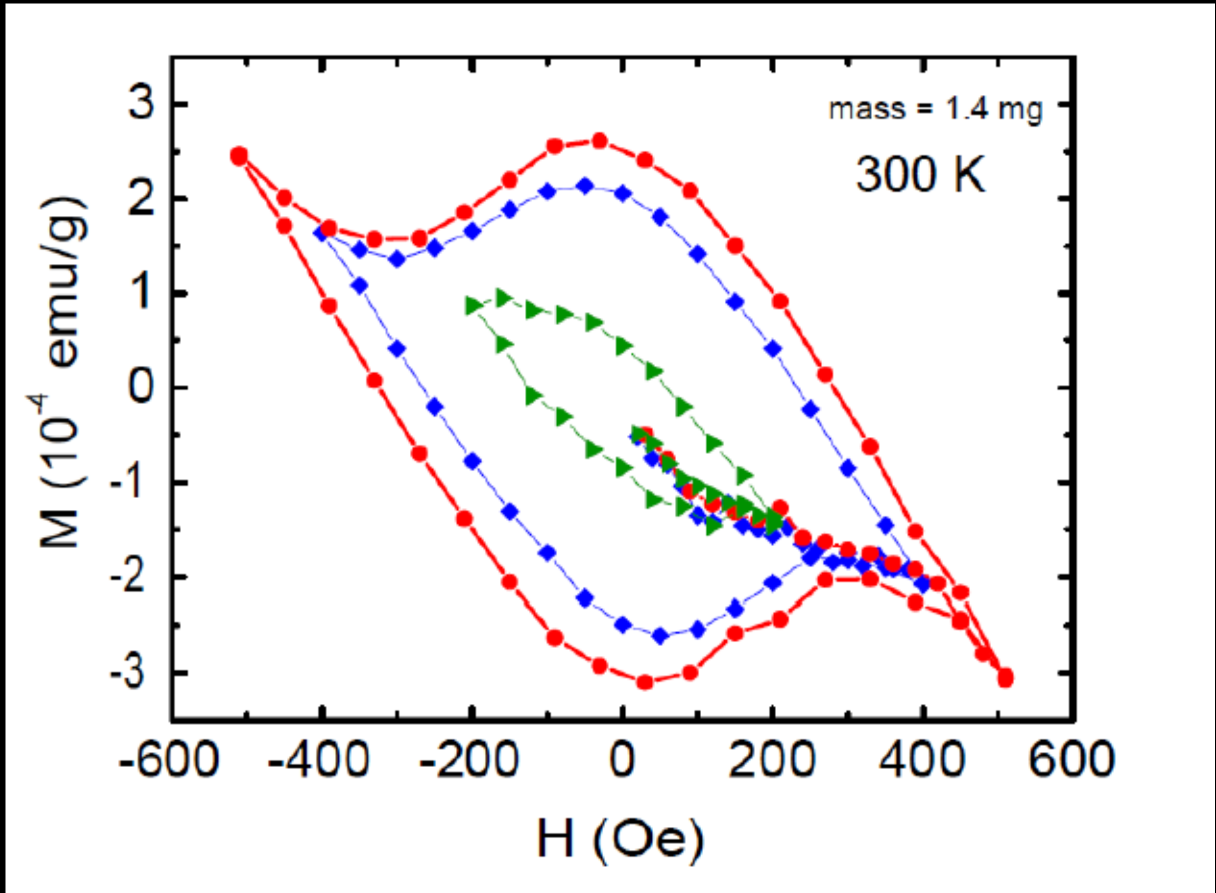


$e^{-T_1/T}$



J. S. Langer and V. Ambegaokar, Phys. Rev. 164, 498(1967)
D. E. McCumber and B. I. Halperin, Phys. Rev. B1, 1054 (1970)

Magnetization measurements of bulk HOPG samples for fields normal to the internal interfaces

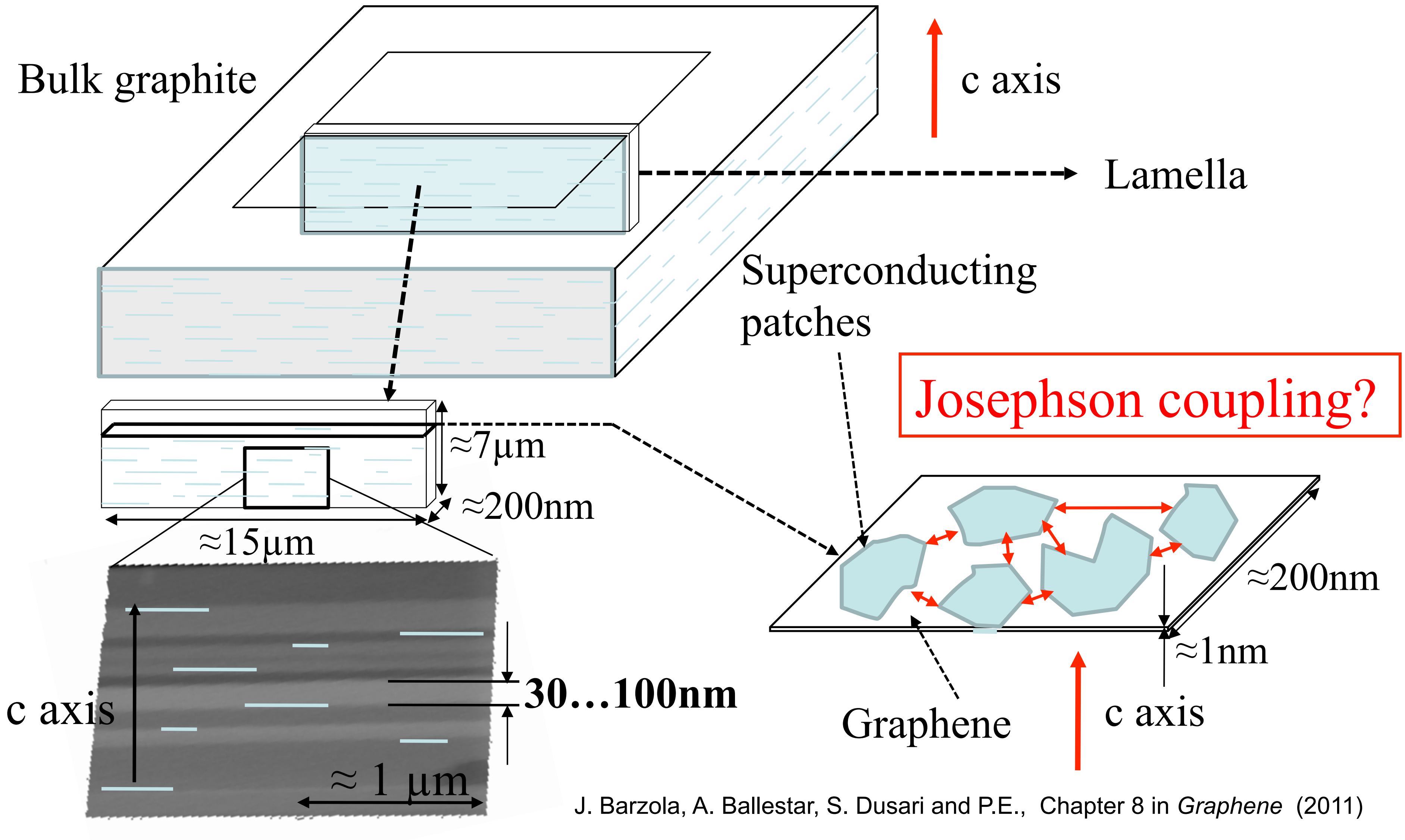


T. Scheike, P. Esquinazi, to be published

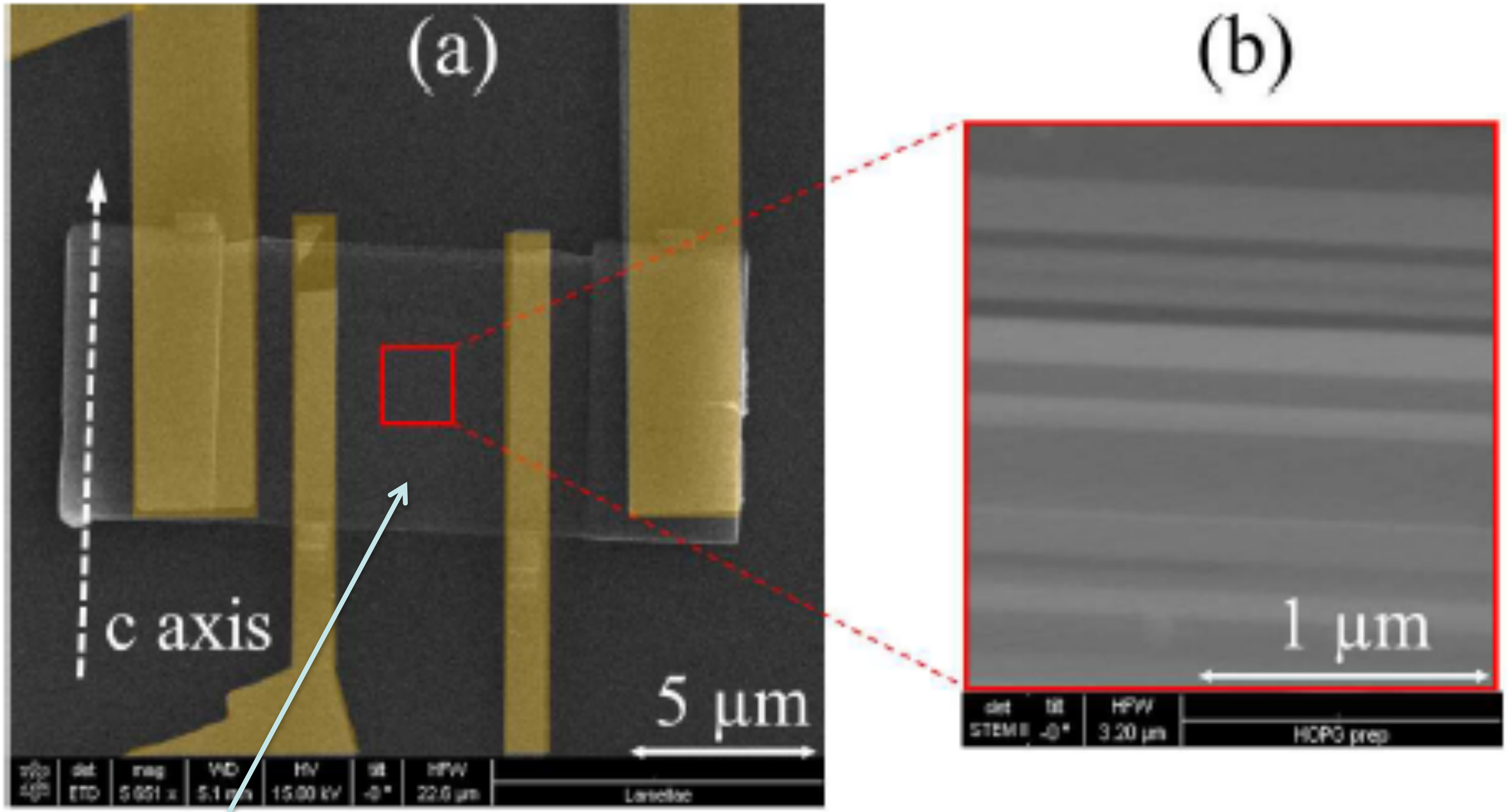
(2)

Evidence for Josephson coupled superconducting regions at the internal 2D interfaces in well ordered graphite samples

Lamella preparation



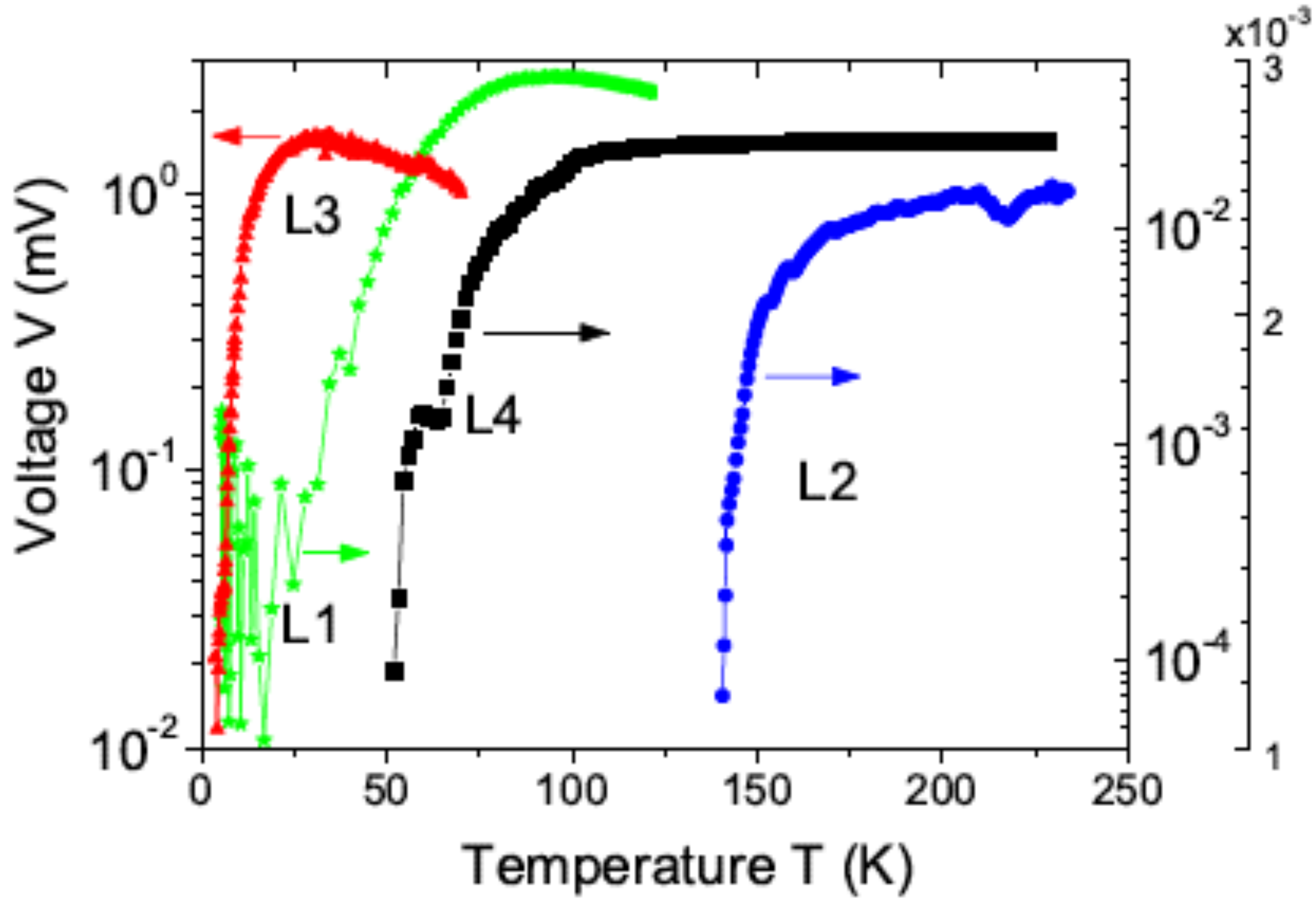
J. Barzola, A. Ballestar, S. Dusari and P.E., Chapter 8 in *Graphene* (2011)



Lamella

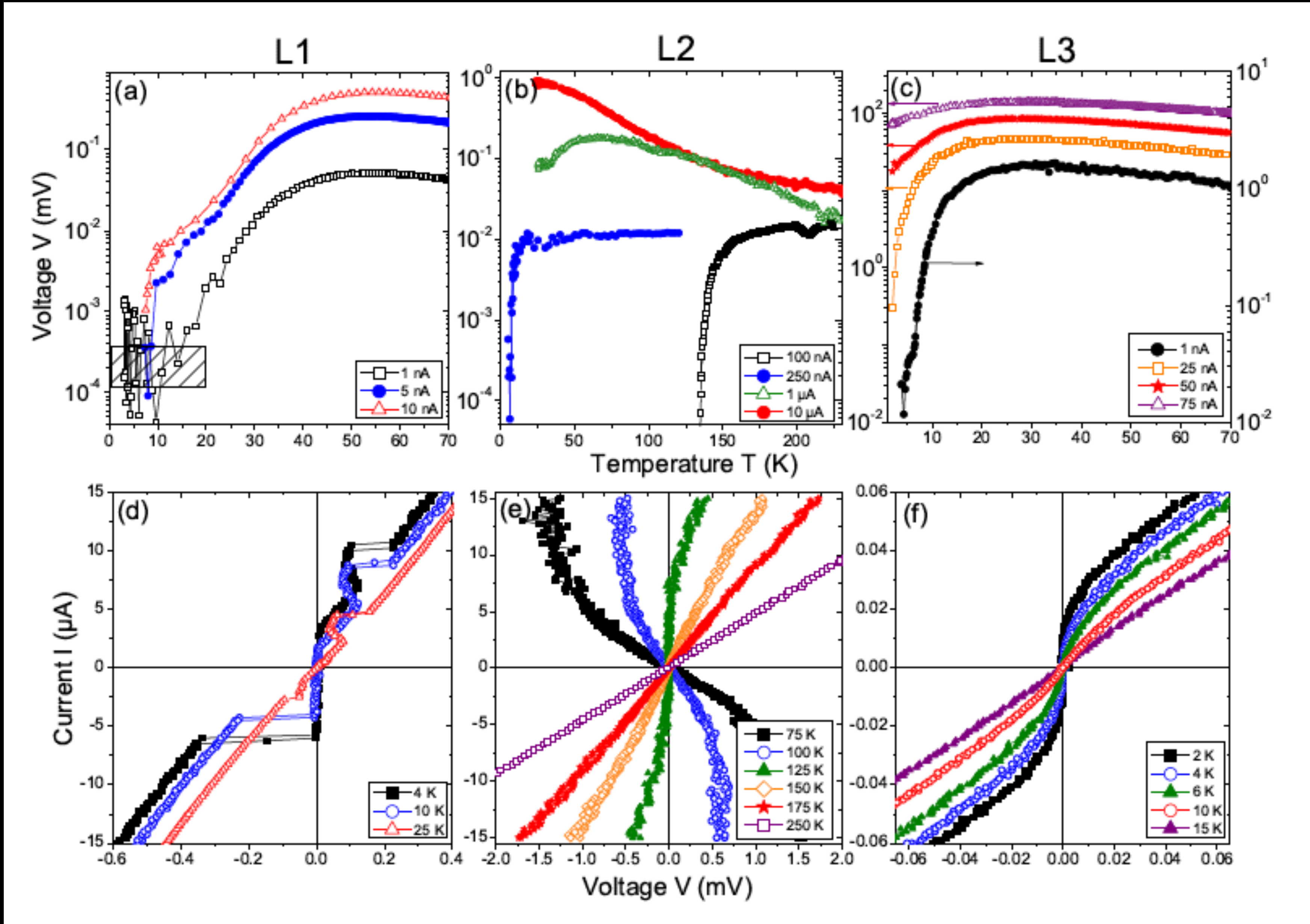
A. Ballestar, J. Barzola-Quiquia and P.E., arXiv/1206.2463

Temperature dependence of the voltage at constant current for different lamellae



A. Ballestar, J. Barzola-Quiquia and P.E., arXiv/1206.2463

- Clear current dependence of the resistance → typical for granular superconductivity
- Josephson-like I/V characteristics



A. Ballestar, J. Barzola-Quiquia and P.E., arXiv/1206.2463

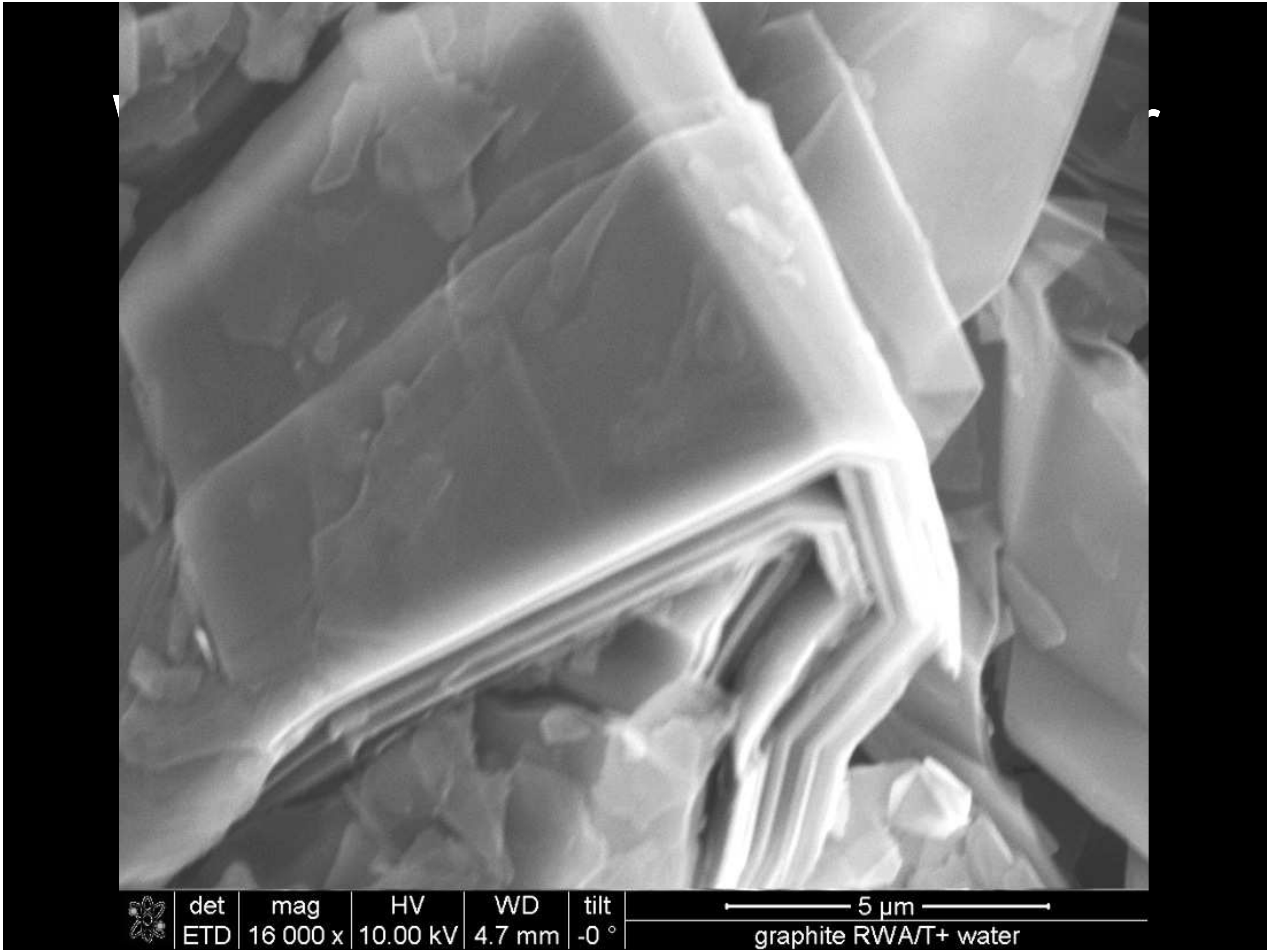
(3) Granular superconductivity in water-treated graphite powder

- “Doping” through water ?
- Effects of water to the “hydrophobic” nature of a graphite surface is non-trivial

- K. Suzuki et al., *Applied Physics Express* 4, 125102 (2011): Existence of a uniform structured-water layer at the graphite/water interface
- Several papers report on the existence of different kinds of gas bubbles at the graphite surface in water: Zhang et al., *Langmuir* 25, 8860 (2009)
- Understanding controls on interfacial wetting at epitaxial graphene: Experiment and theory: Zhou et al., Phys. Rev. B 85, 035406 (2012)

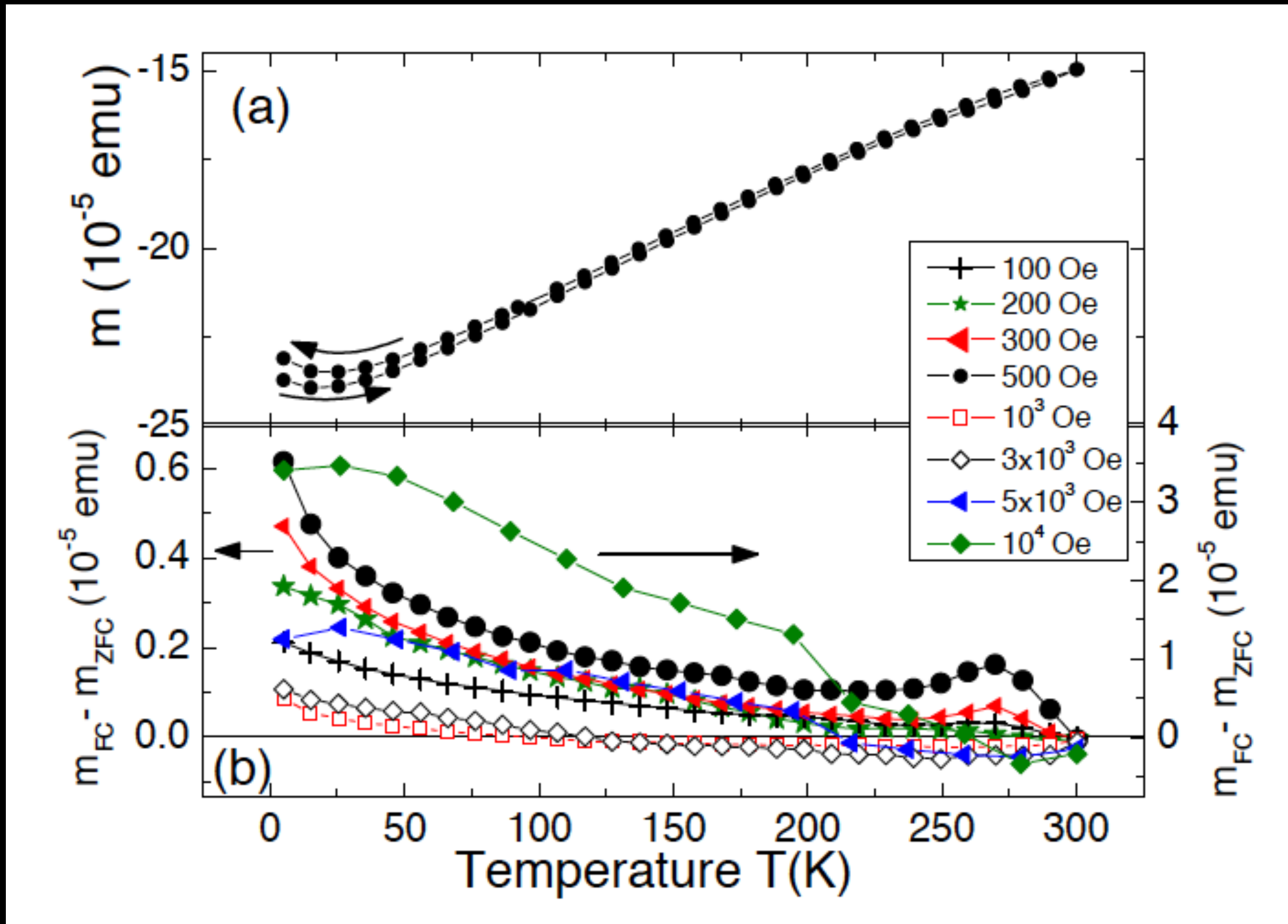
Preparation

- 100 mg ultra pure graphite powder was mixed into 20 mL distilled water and this mixture is continuously stirred at room temperature for one day
- Powder recovered by filtration
- dried at 100 ^{o}C overnight
- packed in polymer foils of less than 1 mg mass


det
ETD
mag
16 000 x
HV
10.00 kV
WD
4.7 mm
tilt
-0 °
5 µm
graphite RWA/T+ water

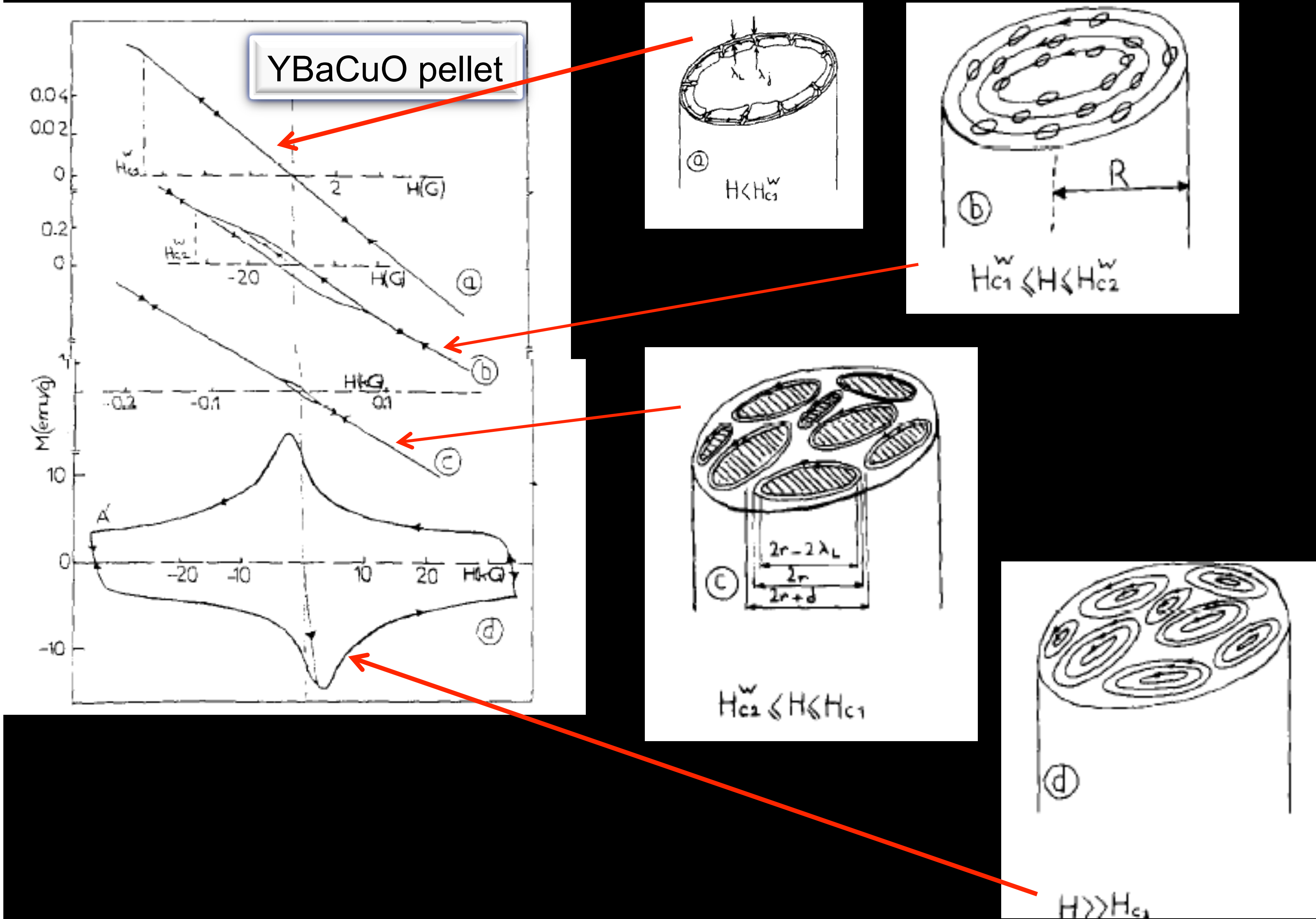
ZFC-FC Hysteresis in water-treated graphite powder Evidence for pinning of magnetic entities

T. Scheike, W. Böhlmann, P. E., J. Barzola-Quiquia, A. Ballestar and A. Setzer, Adv. Mat. (2012)



Low-field hysteresis in granular superconductors

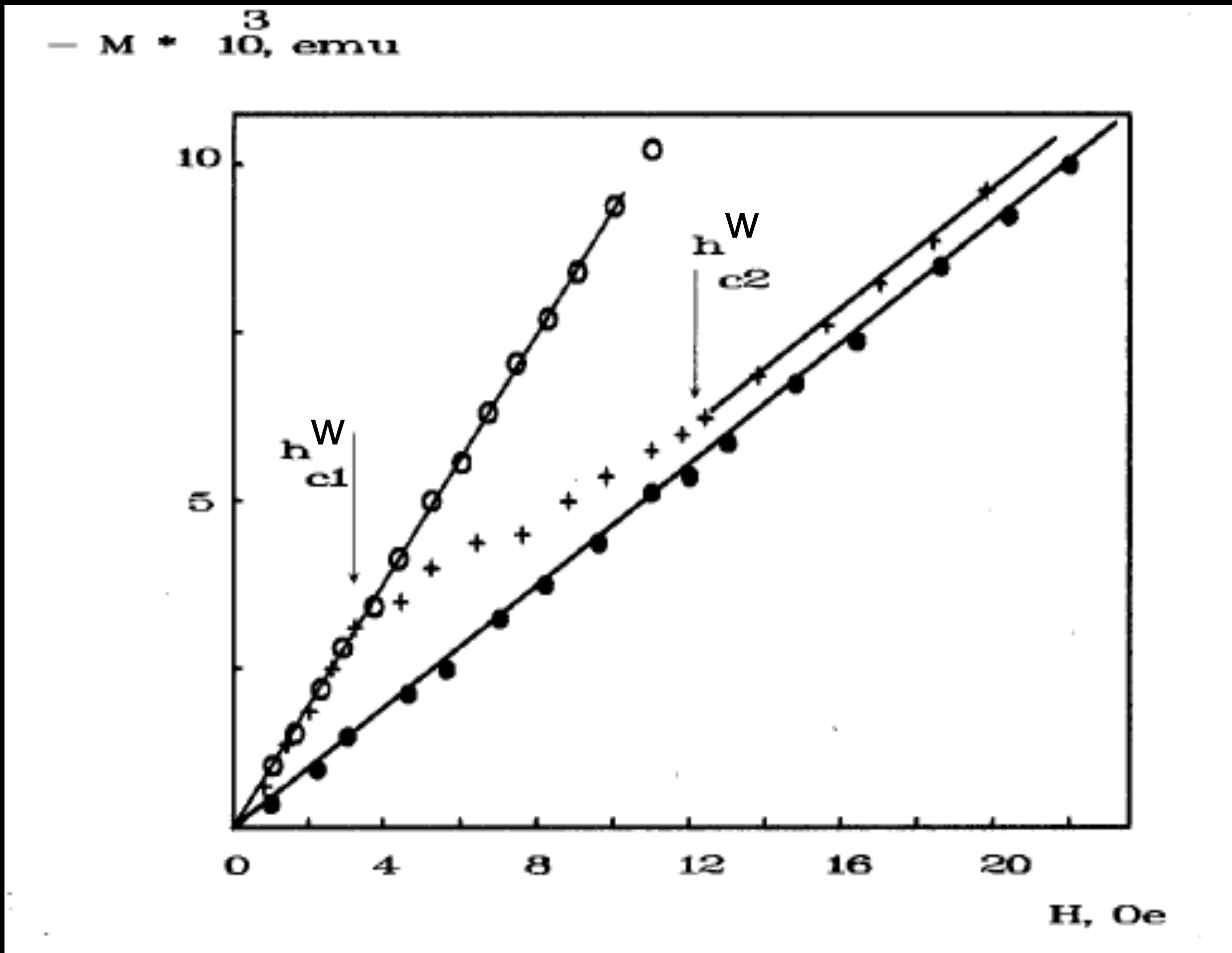
See for example: Senoussi et al, Physica C 175 (1991) 215–225



Anomalies of the Magnetic Properties of Granular Oxide Superconductor $BaPb_{1-x}Bi_xO_3$

M. Borik, M. Chernikov, V. Veselago, and V. Stepankin

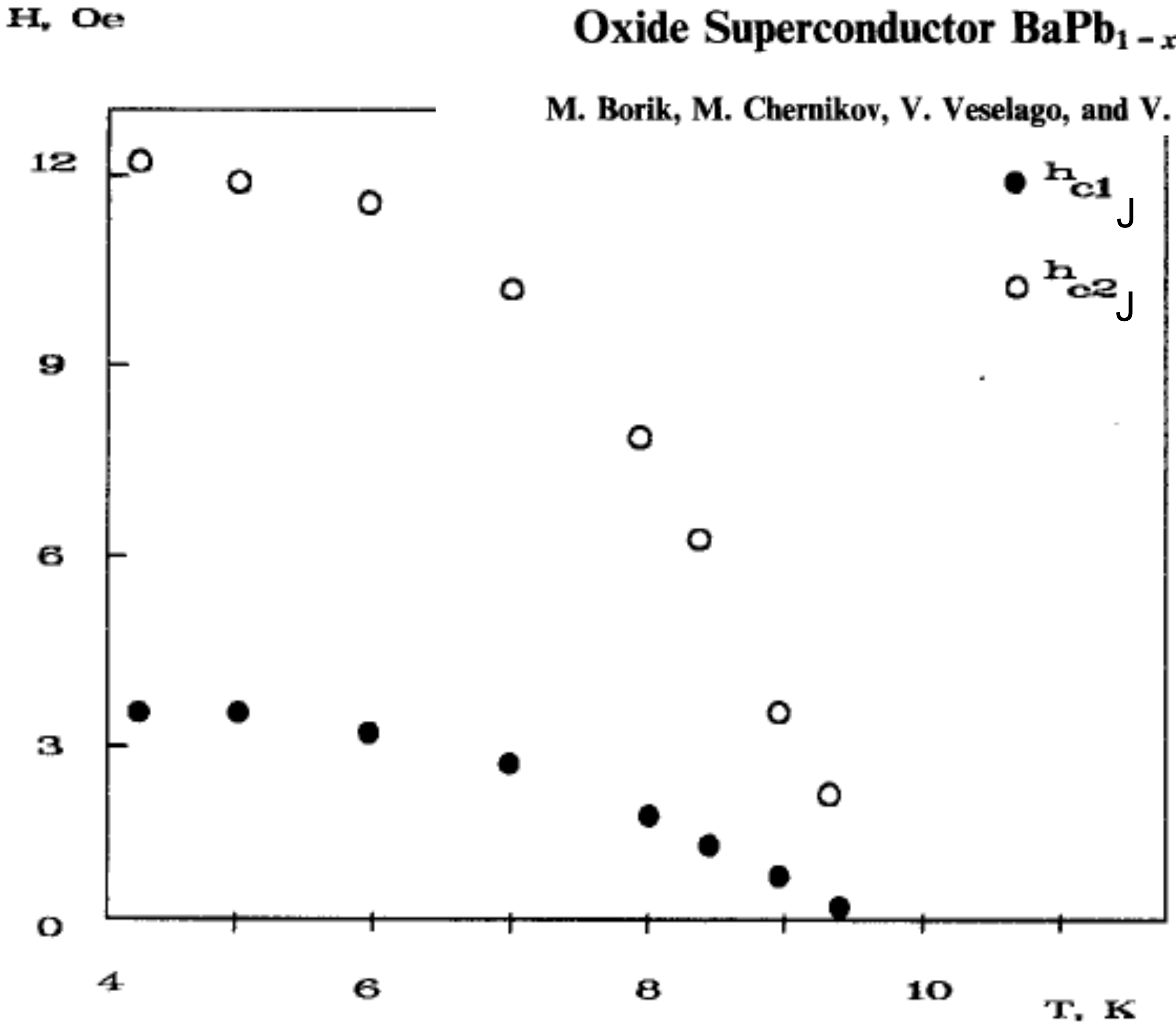
Journal of Low Temperature Physics, Vol. 85, Nos. 3/4, 1991



The T-dependence of the Josephson critical fields

Anomalies of the Magnetic Properties of Granular Oxide Superconductor $BaPb_{1-x}Bi_xO_3$

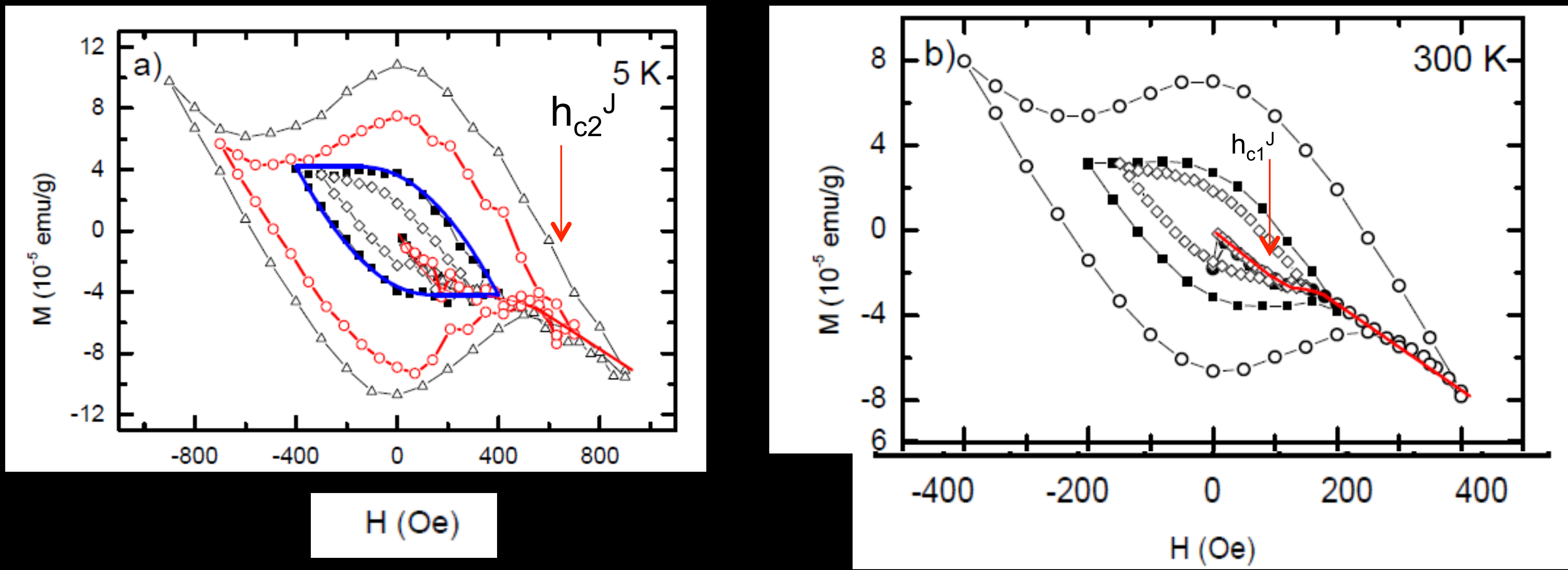
M. Borik, M. Chernikov, V. Veselago, and V. Stepankin



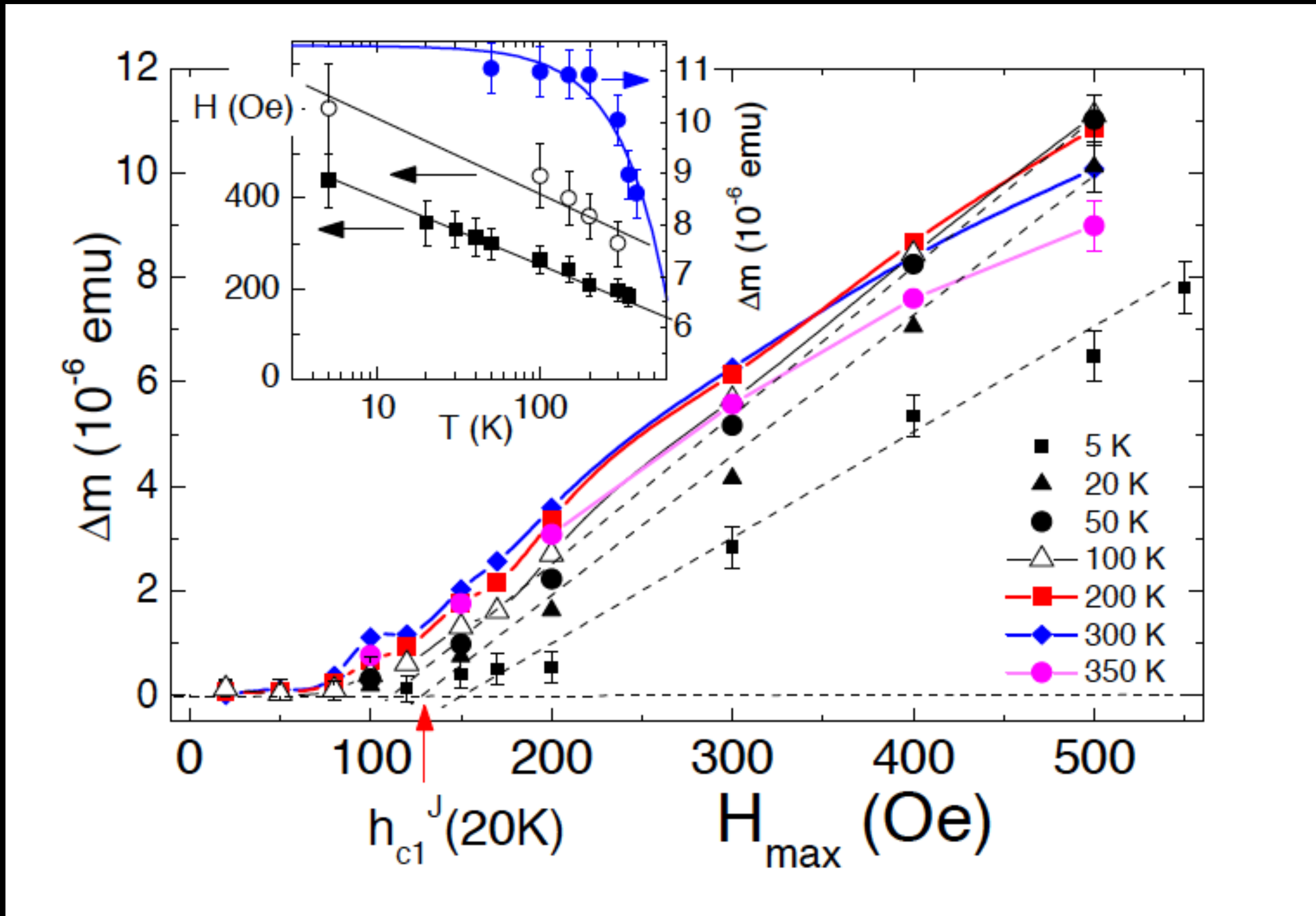
Low field Hysteresis in water-treated graphite powder

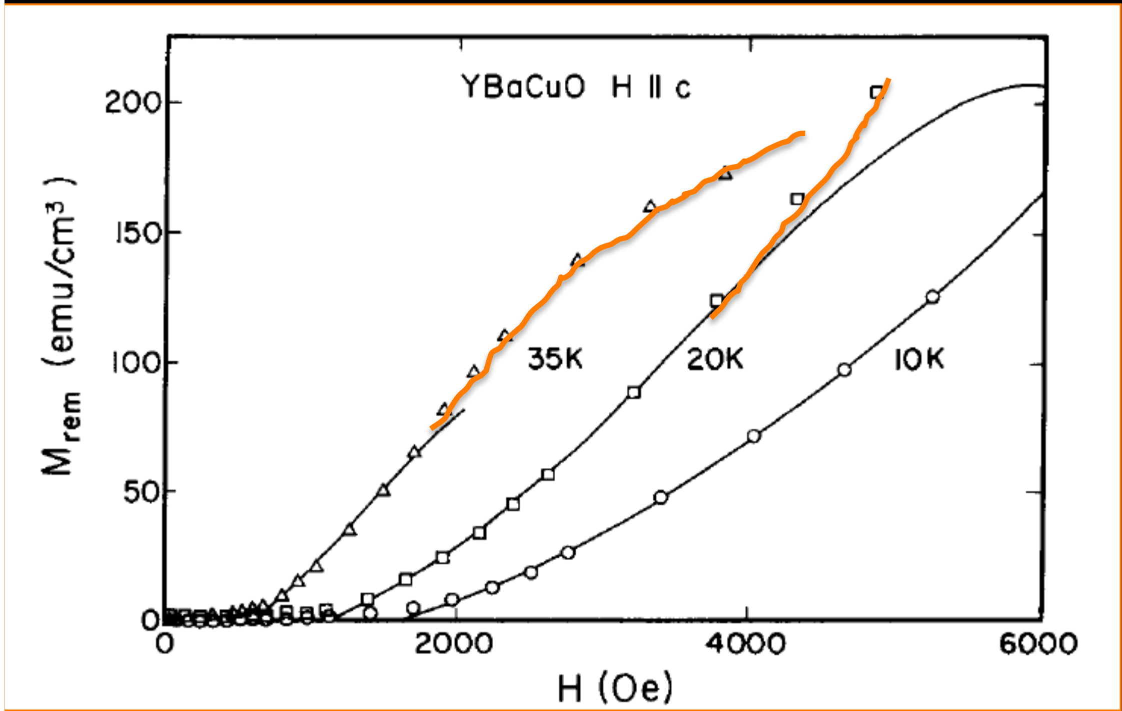
T. Scheike, W. Böhlmann, P. E., J. Barzola-Quiquia, A. Ballestar and A. Setzer

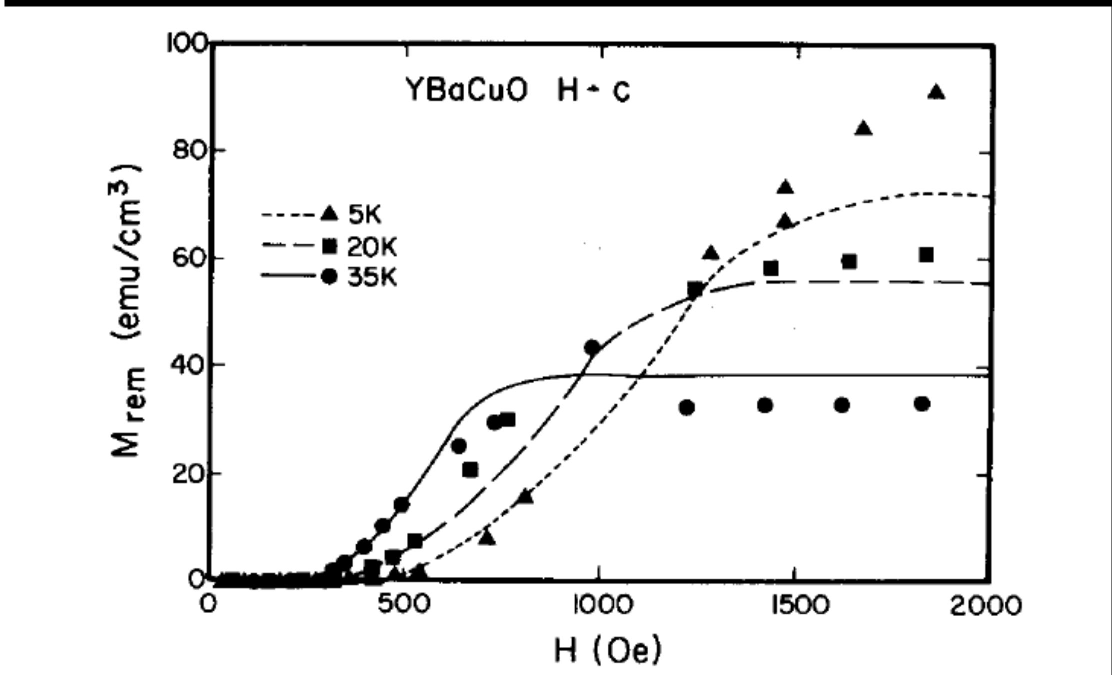
Adv. Mat. (2012)



Full remanence width of magnetization vs. maximum applied field







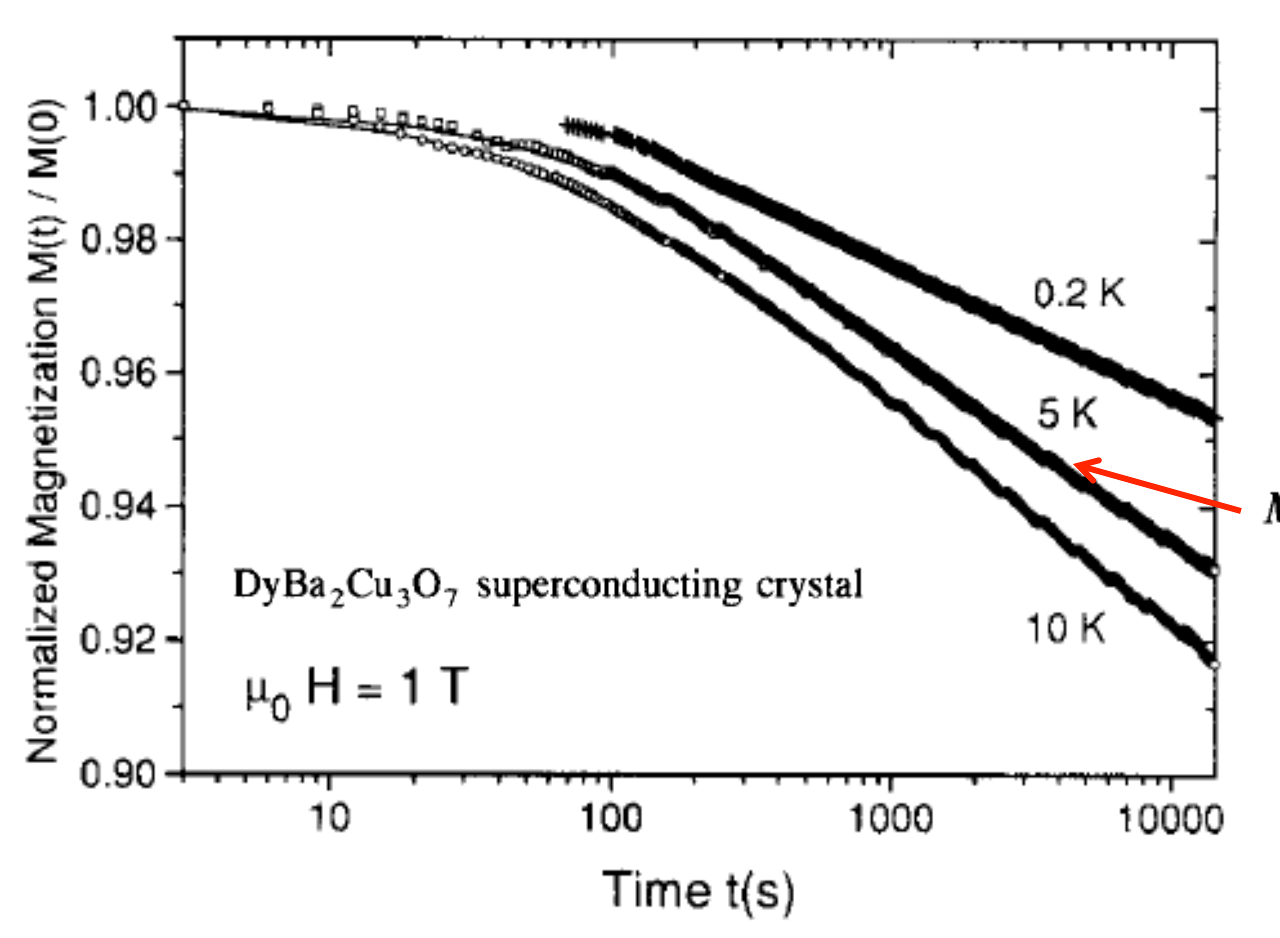
Remanent magnetization, lower critical fields and surface barriers in an $YBa_2Cu_30_7$ crystal

M.W. Mcelfresh,
Y. Yeshurun,
A. R. Malozemoff, and
F. Holtzberg

Physica A 168 (1990)
308-318

Time dependence of the magnetization: flux creep

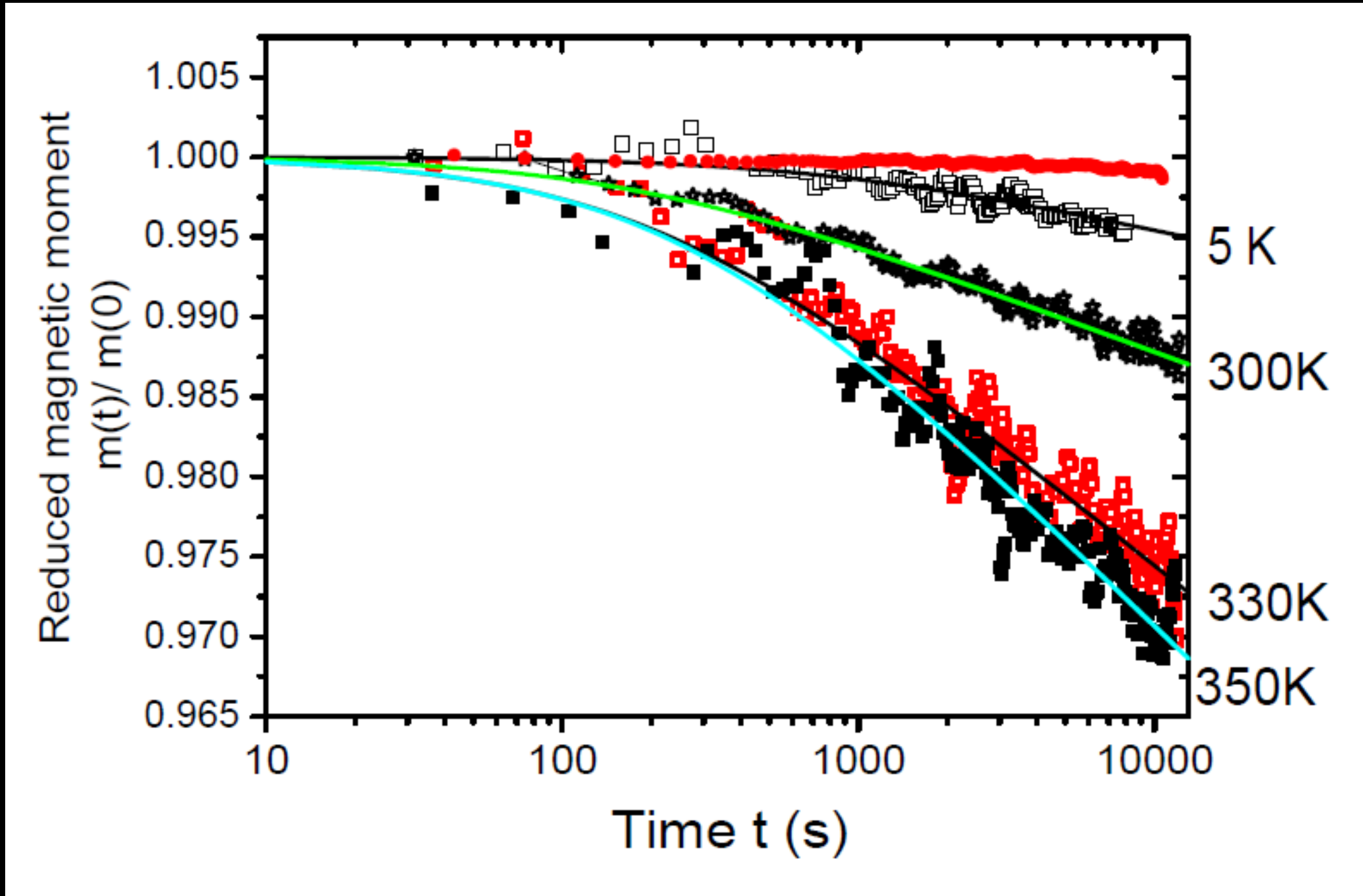
K. Rogacki et al. / Physica C 246 (1995) 123–132



$$M(t) = M_0 - M_1 \ln\left(1 + \frac{t}{\tau_0}\right)$$

Flux creep in RTS graphite powder

T. Scheike, W. Böhlmann, P. E., J. Barzola-Quiquia, A. Ballestar and A. Setzer
Adv. Mat. (2012)



38 years of speculations on the existence of high-temperature superconductivity in graphite

- Anomalous temperature dependence of the resistivity of bulk HOPG of high quality at zero field
- Giant field-induced Metal-Insulator Transition
- Anomalous, superconducting-like hysteresis loops in SQUID measurements
- Anomalous hysteresis loops and "Andreev-like" quantum oscillations in the magnetoresistance of thin graphite flakes
- Resistivity increases the thinner the sample → TEM evidence for the influence of interfaces
- Field-induced transition in the resistance near an interface
- Josephson-like IV curves in specially prepared lamellae
- Evidence for granular superconductivity above 300K in the hysteresis loops, ZFC-FC and flux creep experiments of specially prepared graphite powders

Open questions and experimental tasks for the future

- ✓ Evidence indicates that interfaces play a role, but is there a especial “misalignment angle” or stacking fault?
- ✓ Is it enough a bilayer or the Bernal multigraphene structure at both sides is necessary?
- ✓ Is it simply due to an increase of the carrier concentration, or special defects and/or hydrogen play a role?
- ✓ Is there a single superconducting phase? Which?
- ✓ How to produce it in large enough amount?
- ✓ Is magnetic order playing some role in it?
- ✓ Basic parameters remain unknown like T_c, H_{c1}, H_{c2}, etc. ….
- ✓ ….