Evidence for Superconductivity at Graphite Interfaces

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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
Granular superconductivity

Microscopic superconducting grains in a non-superconducting matrix


- Anomalous thermally activated-like temperature dependence of the resistance, $R \sim e^{-T_1/T}$. García et al., NJP 14, 053015 (2012)


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 $n > 10^{13}\text{cm}^{-2}$ [3]-[6]-[10]
- High-Tc surface superconductivity in topological flat-band systems [8]


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

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

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)
The picture indicates the existence of ~30…150nm thick (c-axis direction) crystalline regions separated by 2D-interfaces.
BUT

2D-interfaces in some solids show 
SUPERCONDUCTIVITY
Superconductivity at the interfaces between two crystalline regions of Bi or BiSb

\[ T_c \approx 21 \text{ K} \]

Bi

\[ \text{Bi}_{1-x}\text{Sb}_x \ (x \leq 0.07) \text{ bicrystals of inclination type} \]

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

Shapira and Deutscher, PRB 27, 4463 (1983)

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

T. Scheike, P. Esquinazi, to be published
Evidence for Josephson coupled superconducting regions at the internal 2D interfaces in well ordered graphite samples
Lamella preparation

Bulk graphite

Lamella

Superconducting patches

Graphene

Josephson coupling?

J. Barzola, A. Ballestar, S. Dusari and P.E., Chapter 8 in Graphene (2011)
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 $\rightarrow$ typical for granular superconductivity
- Josephson-like I/V characteristics

A. Ballestar, J. Barzola-Quiquia and P.E., arXiv/1206.2463
Granular superconductivity in water-treated graphite powder

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

- 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)
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 °C overnight
- packed in polymer foils of less than 1 mg mass
ZFC-FC Hysteresis in water-treated graphite powder
Evidence for pinning of magnetic entities

Low-field hysteresis in granular superconductors


YBaCuO pellet
Anomalies of the Magnetic Properties of Granular Oxide Superconductor BaPb$_{1-x}$Bi$_x$O$_3$

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
Full remanence width of magnetization vs. maximum applied field
Remanent magnetization, lower critical fields and surface barriers in an YBa$_2$Cu$_3$O$_7$ 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

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

DyBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} superconducting crystal

\[ \mu_0 H = 1 \, \text{T} \]
Flux creep in RTS graphite powder
T. Scheike, W. Böhlmann, P. E., J. Barzola-Quiquia, A. Ballestar and A. Setzer
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. ....
- ....