



Fullereni

M. Riccò



La scoperta dei fullereni



HAROLD KROTO, ROBERT CURL E RICHARD SMALLEY (1985)

hanno studiato gli spettri di massa di vapori di carbonio ottenuti da cristalli di grafite con laser ad alta energia (Nobel per la chimica 1996)





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La scoperta dei fullereni



LETTERSTONATURE

C₆₀: Buckminsterfullerene

H. W. Kroto^{*}, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells¹, graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C₆₀ molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic. Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.



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graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise



La scoperta dei fullereni





Macchina di Kratschmer e Huffman (1990) per la produzione di fullereni su larga scala

Struttura cristallina della grafite





Huffman Krätschmer

W. Krätschmer, L.D. Lamb,K. Fostiropoulus, D.R. Huffman,*Nature* 347 (1990) 354.

Reactor operating conditions:

DC current:	100 A							
Voltage:	32 V							
Temp.:	~ 4000 K							
Pressure:	200 Torr He							



Sintesi in reattore a plasma





Pumping station Arc reactor

Power, control, and cooling



La famiglia dei fullereni





Il più piccolo fullerene possibile è il C_{20} , che contiene 20 pentagoni e nessun esagono; comunque questo tipo di struttura ha forti tensioni interne perché la forma di ogni molecola di carbonio è fortemente non planare.

http://www.nanoscienceworks.org/nanopedia/fullerene



Altri possibili fullereni sono C₂₈, C₃₂, C₄₄, C₅₀, C₅₈, C₇₀, C₇₆, C₈₄, C₂₄₀, C₅₄₀, C₉₆₀ e molte altre.

http://www.nanoscienceworks.org/nanopedia/fullerene



La molecola di C₆₀





Cupola geodetica progettata da Buckmister Fuller



- Il C₆₀ è la molecola più stabile della famiglia dei fullereni.
- Icosaedro troncato con gli atomi di carbonio ibridizzati sp²
- Orbitali π delocalizzati determinano le proprietà elettroniche



La molecola di C₆₀





Figura 2: Molecola di C₆₀ e rappresentazione dei legami a cui partecipa ogni atomo: tutti i carboni sono equivalenti dal punto di vista del circondario elettronico locale. Gli angoli di legame interni agli esagoni sono sempre di ~ 120°, come nella grafite, mentre il terzo angolo (interno alla faccia pentagonale) è di 108°, data la sensibile deviazione dalla geometria piana. Il raggio molecolare è 3.55 Å, ma, nel caso si considerino anche i gusci elettronici, arriva a 5.02 Å.



Il cristallo di C₆₀







Struttura elettronica





K₃C₆₀

C₆₀



Struttura elettronica



- Caratteristica peculiare del C₆₀: ha numerosi stati redox stabili.
- Nel C₆₀ puro la banda LUMO originata dall'orbitale t_{1u} è vuota. → composto isolante
- Nelle fullerti gli elettroni ceduti dagli atomi intercalati riempiono progressivamente la banda LUMO. Si presentano effetti dovuti all' alta correlazione elettronica







- Le molecole di C₆₀ legate allo stato solido formano un cristallo molecolare con struttura f.c.c.
- I composti ottenuti intercalando al C $_{60}$ solido ioni opportuni sono chiamati fulleriti
- I materiali più interessanti derivati dal C₆₀ sono:
- Fulleriti intercalate con metalli alcalini (K,Na,Rb) (A₃C₆₀: conduttori metallici e superconduttori a T~10-40K)
- Fullereni polimerizzati ad alta pressione
- Fulleriti di Litio (composti con struttura polimerica, conduttori superionici)
- Fulleriti cationiche
- Fullereni endoedrici





C₆₀: disordine meroedrico



nonostante il suo altissimo grado di simmetria (gruppo spaziale icosaedrico, I_h), la struttura del C₆₀ non è compatibile con le simmetrie puntuali del reticolo *fcc*; da questo trae origine il disordine orientazionale intrinseco del solido :

disordine meroedrico





Le Fulleriti



stechiometria	proprietà elettroniche	struttura
A_1C_{60}	isolante	struttura polimerica
A_3C_{60}	metallico e super-c. T_c compresa fra 10 e 40 K	fcc
A_4C_{60}	non metallico piccola gap	bct
A_6C_{60}	isolante	bcc

Tabella 1: Caratteristiche delle principali fulleriti. A seconda della stechiometria degli alcalini si riscontrano strutture e proprietà elettroniche completamente diverse, molte delle quali interpretabili in base alla "banda di conduzione" formata da LUMO: ad esempio è evidente che le fulleriti di tipo A_6C_{60} , avendo tale banda completamente piena, devono essere isolanti.



Materiali superconduttori: parametr BCS caratteristici



La teoria BCS (Bardeen, Cooper, Schrieffer) ha fornito una descrizione "ab initio" dei primi superconduttori scoperti in termini di:

- λ : costante d'accoppiamento: indice della forza dell'accoppiamento elettronico ($\lambda \ll 1$)
- λ_p : lunghezza di penetrazione.
- ξ : lunghezza di coerenza.

 $\kappa = \lambda_p / \xi = rapporto di Ginzburg-Landau$



Superconduttività di I e II tipo



$$\kappa = \frac{\lambda_p}{\xi}$$

la sua importanza è legata al calcolo dell'energia libera dello stato superconduttore:

- $\kappa > 1/\sqrt{2} \implies$ è conveniente la penetrazione del campo con flussoni, quindi il superconduttore risulta essere di tipo II.
- $\kappa < 1/\sqrt{2} \Longrightarrow$ la formazione di flussoni non è più una condizione di minimo dell'energia libera, quindi si ha un superconduttore di tipo I.





Superconduttività nelle fulleriti







Rappresentazione schematica dei vari fononi nei composti del tipo A_3C_{60} : (a) librazioni; (b) fononi ottici C_{60} - C_{60} ; (d) ed (e) modi intra-molecolari H_g . La figura mette in evidenza come $H_g(7)$ sia più di carattere tangenziale, mentre $H_g(1)$ sia prevalentemente radiale.

 $k_{B}T_{c} \approx \frac{\hbar\omega_{D}}{1.45}e^{-\frac{1}{N(E_{F})V}}$

 $N(E_{_F})V = \lambda$

 $N(E_F)$ = densità di portatori al livello di Fermi

V = pseudopotenziale di Coulomb



Le Fulleriti superconduttive



Composto	Costante reticolare (Å)	T_c (K)		
Na_2RbC_{60}	14.028	2.5		
Na_2CsC_{60}	14.133	11		
K_3C_{60}	14.253	19.2		
K_2RbC_{60}	14.299	21.8		
K_2CsC_{60}	14.292	24		
$\mathrm{KRb}_{2}\mathrm{C}_{60}$	14.364	26		
Rb_3C_{60}	14.436	29.4		
$(NH_3)_4Na_2CsC_{60}$	14.473	29.6		
Rb_2CsC_{60}	14.493	31.3		

composti superconduttori





- meccanismo d'accoppiamento convenzionale, l'interazione elettrone-fonone.
 - Accoppiamento mediato da fononi intra-molecolari: oscillazioni della molecola di C₆₀ (modi H_q ~ 0.2 eV).
 - Larghezza banda di conduzione ~0.5 eV => Energia di Fermi E_F ~ 0.25 eV.

Caduta dell'approssimazione adiabatica: Dinamica elettronica e reticolare non più indipendenti

Fenomenologia non convenzionale , alte temperature critiche (fino a 40K). Previsioni scorrette delle teorie classiche (BCS, M-E) sui parametri caratteristici.



Le Fulleriti superconduttive







SC nel Cs₃C₆₀ (2008)



LETTERS

Bulk superconductivity at 38 K in a molecular system

ALEXEY Y. GANIN¹*, YASUHIRO TAKABAYASHI²*, YAROSLAV Z. KHIMYAK¹, SERENA MARGADONNA³, ANNA TAMAI³, MATTHEW J. ROSSEINSKY^{1†} AND KOSMAS PRASSIDES^{2†}

¹ Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK ² Department of Chemistry, University of Durham, Durham DH1 3LE, UK ³ School of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, UK *These authors contributed equally to this work [†]e-mail: M.J.Rosseinsky@liverpool.ac.uk; K.Prassides@durham.ac.uk

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C60-based solids1 are archetypal molecular superconductors with transition temperatures (T_c) as high as 33 K (refs 2-4). T_c of face-centred-cubic (f.c.c.) A₃C₆₀ (A = alkali metal) increases monotonically with inter C₆₀ separation, which is controlled by the A^+ cation size. As Cs^+ is the largest such ion, Cs_3C_{60} is a key material in this family. Previous studies revealing trace superconductivity in Cs_xC₆₀ materials have not identified the structure or composition of the superconducting phase owing to extremely small shielding fractions and low crystallinity. Here, we show that superconducting Cs₃C₆₀ can be reproducibly isolated by solvent-controlled synthesis and has the highest T_c of any molecular material at 38 K. In contrast to other A₃C₆₀ materials, two distinct cubic Cs₃C₆₀ structures are accessible. Although f.c.c. Cs₃C₆₀ can be synthesized, the superconducting phase has the A15 structure based uniquely among fullerides on body-centred-cubic packing. Application of hydrostatic pressure controllably tunes A15 Cs₃C₆₀ from insulating at ambient pressure to superconducting without crystal structure change and reveals a broad maximum in T_c at ~7 kbar. We attribute the observed T_c maximum as a function of inter C₆₀ separation—unprecedented in fullerides but reminiscent of the atom-based cuprate superconductors-to the role of strong electronic correlations near the metal-insulator transition onset.

use methylamine¹¹⁻¹³ to prepare solvated precursors with a suitable Cs distribution and structure to nucleate the bulk formation of superconducting Cs_3C_{60} .

Reaction of three equivalents of caesium with C_{60} in rigorously dried methylamine at $-65 \,^{\circ}$ C followed by removal of the solvent under dynamic vacuum at room temperature and heating at $180 \,^{\circ}$ C for 48 h yields a material of composition $C_{53.08(10)}C_{60}$ (see Supplementary Information, Scheme S1). Diffraction shows that body-centred anion packing is dominant with 13.4(1)%of a body-centred-orthorhombic (b.c.o.) phase (Fig. 1a) and 77.7(6)% of a cubic phase with the so-called A15 structure (a = 11.78282(8) Å, space group $Pm\bar{3}n$) in which the fulleride anion at the body centre is rotated by 90° about the [100] direction relative to the anion at the origin (Fig. 1b). A second cubic phase (8.9(2)% phase fraction) is observable with f.c.c. symmetry and a lattice constant (14.802(2) Å) comparable to that predicted for Cs_3C_{60} by Vegard's law extrapolation of the $Cs_{3-x}Rb_xC_{60}$ family¹⁴.

Low-field (20 Oe) zero-field-cooling and field-cooling d.c. magnetization, M, measurements reveal no superconductivity at 1 atm, but application of hydrostatic pressure (11.6 kbar) produces bulk superconductivity with a shielding fraction of 67% and an onset T_c of 37 K (Fig. 2a). The superconducting response of the sample is then followed by gradually releasing the external pressure.



SC ↔ AF (2009)



The Disorder-Free Non-BCS Superconductor Cs₃C₆₀ Emerges from an Antiferromagnetic Insulator Parent State

Yasuhiro Takabayashi,¹* Alexey Y. Ganin,²* Peter Jeglič,³ Denis Arčon,^{3,4} Takumi Takano,⁵ Yoshihiro Iwasa,⁵ Yasuo Ohishi,⁶ Masaki Takata,^{6,7} Nao Takeshita,⁸ Kosmas Prassides,¹† Matthew J. Rosseinsky²†

The body-centered cubic A15-structured cesium fulleride Cs_3C_{60} is not superconducting at ambient pressure and is free from disorder, unlike the well-studied face-centered cubic A_3C_{60} alkali metal fulleride superconductors. We found that in Cs_3C_{60} , where the molecular valences are precisely assigned, the superconducting state at 38 kelvin emerges directly from a localized electron antiferromagnetic insulating state with the application of pressure. This transition maintains the threefold degeneracy of the active orbitals in both competing electronic states; it is thus a purely electronic transition to a superconducting state, with a dependence of the transition temperature on pressure-induced changes of anion packing density that is not explicable by Bardeen-Cooper-Schrieffer (BCS) theory.

Superconductivity requires an attractive interaction between electrons to form Cooper pairs, which form a condensate that can move without electrical resistance. In simple metals and alloys, the Bardeen-Cooper-Schrieffer

(BCS) theory explains how electron-phonon coupling overcomes the repulsion between negatively charged electrons (1). In high-temperature superconductors, such as the copper oxides and iron oxyarsenides, the origin of the attraction is less clear. Beyond the theoretical challenges, the experiments are complicated by imperfections within the materials, such as structural disorder, low symmetry and dimensionality, and variations in chemical valence at the electronically active sites. Here we show that in the cubic alkali metal fulleride Cs₃C₆₀, which is completely ordered and for which precise valences can be assigned, the 38 K superconducting state (2) emerges directly from a localized electron antiferromagnetic insulating (AFI) state with the application of pressure as the anion packing density increases. This transition maintains the threefold degeneracy of the active orbitals in both competing electronic states, and is thus a purely electronic transition to a superconducting state. The transition temperature T_c depends on the anion packing density in a way that is not explicable within a simple BCS approach.

In systems where the bands in which the electrons move are narrow, there are electronelectron correlation energies associated with interelectron repulsion, which are comparable to the electronic bandwidth. These electron correlation effects (3) need to be taken into account in understanding the mechanisms for formation of the Cooper pairs (4). These concepts have been developed primarily in d-electron–based systems



 $Cs_3C_{60} \leftrightarrow HTC$







$K_3C_{60} \leftrightarrow \text{light induced HTC (2016)}$



LETTER

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Possible light-induced superconductivity in K_3C_{60} at high temperature

M. Mitrano¹, A. Cantaluppi^{1,2}, D. Nicoletti^{1,2}, S. Kaiser¹, A. Perucchi³, S. Lupi⁴, P. Di Pietro³, D. Pontiroli⁵, M. Riccò⁵, S. R. Clark^{1,6,7}, D. Jaksch^{7,8} & A. Cavalleri^{1,2,7}

The non-equilibrium control of emergent phenomena in solids is an important research frontier, encompassing effects such as the optical enhancement of superconductivity¹. Nonlinear excitation^{2,3} of certain phonons in bilayer copper oxides was recently shown to induce superconducting-like optical properties at temperatures far greater than the superconducting transition temperature, T_{c} (refs 4-6). This effect was accompanied by the disruption of competing charge-density-wave correlations^{7,8}, which explained some but not all of the experimental results. Here we report a similar phenomenon in a very different compound, K₃C₆₀. By exciting metallic K₃C₆₀ with mid-infrared optical pulses, we induce a large increase in carrier mobility, accompanied by the opening of a gap in the optical conductivity. These same signatures are observed at equilibrium when cooling metallic K_3C_{60} below T_c (20 kelvin). Although optical techniques alone cannot unequivocally identify non-equilibrium high-temperature superconductivity, we propose this as a possible explanation of our results.

at 7µm wavelength (180 meV photon energy), which is tuned to the T_{1u}(4) vibration (see Fig. 2 for measurements at 1 ps time delay). For all temperatures between $T_c = 20$ K and T = 100 K, photo-excitation drove transient changes in the optical properties, which were very similar to those observed when cooling at equilibrium (see also Extended Data Fig. 5). At a 1 ps pump–probe time delay, we observed a saturated reflectivity (R = 1; Fig. 2a and d), gapped $\sigma_1(\omega)$ (Fig. 2b and e), and divergent $\sigma_2(\omega)$ (Fig. 2c and f).

Furthermore, all transient optical spectra could be fitted with the same function used for the low-temperature superconductor at equilibrium. An extension of the Mattis–Bardeen model was used, applicable to superconductors of arbitrary purity and taking into account both an optical gap (a superconducting component) and a fluid of normal quasi-particles (a Drude component)²¹. The non-equilibrium fits evidenced an 11 meV gap in the non-equilibrium $\sigma_1(\omega)$, nearly twice as large as the 6 meV superconducting gap at equilibrium.

Figure 3 reports similar measurements taken at higher temperatures,



$K_3C_{60} \leftrightarrow \text{light induced HTC}$







SC nel picene



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nature

LETTERS

Superconductivity in alkali-metal-doped picene

Ryoji Mitsuhashi¹, Yuta Suzuki², Yusuke Yamanari², Hiroki Mitamura¹, Takashi Kambe², Naoshi Ikeda², Hideki Okamoto^{3,4}, Akihiko Fujiwara⁵, Minoru Yamaji⁶, Naoko Kawasaki¹, Yutaka Maniwa⁷ & Yoshihiro Kubozono¹







Superconductivity at 52K in holedoped C_{60} . Nature 408, 549-552 (2000).



Batlogg-Schon story





High-Temperature Superconductivity in Lattice-Expanded C₆₀

J. H. Schön,^{1,2*} Ch. Kloc,¹ B. Batlogg^{1,3}

 $\rm C_{60}$ single crystals have been intercalated with CHCl₃ and CHBr₃ in order to expand the lattice. High densities of electrons and holes have been induced by gate doping in a field-effect transistor geometry. At low temperatures, the material turns superconducting with a maximum transition temperature of 117 K in hole-doped C₆₀/CHBr₃. The increasing spacing between the C₆₀ molecules follows the general trend of alkali metal– doped C₆₀ and suggests routes to even higher transition temperatures.

The superconducting properties of various materials can be modulated by the application of an electric field, and a variety of field-effect devices es have been studied lately (1–9). We recently demonstrated the switching between insulating and superconducting behavior in single crystals of C_{60} . The gate-induced superconductivity is observed for electron doping (5) as well as hole doping (7). The higher superconducting transition temperature (T_{c}) for hole doping may be ascribed to a larger density of states at the Fermi level and stronger coupling to phonons (8, 10, 11). C₆₀ is a particularly interesting superconductor because the dominant electron-phonon

interaction, being an on-site intramolecular property, can be conceptually separated from the electronic density of states, which is given by the distance between adjacent molecules. Expanding the lattice, therefore, increases the density of states, and the resulting increase of $T_{\rm c}$ is well documented in alkali metal–doped bulk samples (A₃C₆₀) (*12*, *13*). The observation of gate-induced hole doping of C₆₀ resulting in a $T_{\rm c}$ of 52 K suggests that significantly higher $T_{\rm c}$'s could be anticipated in suitably "expanded" C₆₀ crystals. Indeed, here we report on raising $T_{\rm c}$ to 117 K with such methods.

Undoped C_{60} single crystals have been grown from the vapor phase in a stream of hydrogen (14). CHCl₃ and CHBr₃ are interca-

¹Bell Laboratories, Lucent Technologies, 600 Mountain Avenue, Murray Hill, NJ 07974, USA, ²University of Konstanz, Department of Physics, D-78457 Konstanz, Germany, ³Solid State Physics Laboratory, Eidgenössische Technische Hochschule, CH-8093 Zürich, Switzerland

*To whom correspondence should be addressed. Email: hendrik@lucent.com

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Batlogg-Schon story 2002....primi sospetti



- Physicists from inside and outside Bell Labs called management's attention to several sets of figures, published in different papers, that bore suspiciously strong similarities to one another (see Physics Today, July 2002, page 15). Much of the suspicion focused on Jan Hendrik Schön, a key participant in the research and the one author common to all the papers in question. With a few exceptions, Schön had applied crucial aluminum oxide insulating layers to the devices, had made the physical measurements, and had written the papers. Moreover, the sputtering machine that Schön used to apply the Al2O3 films was located, not at Bell Labs, but in his former PhD lab at the University of Konstanz in Germany.
- In particular, scientists found the data seemed overly precise, and that some of it contradicted the prevailing understanding of physics. Professor Lydia Sohn, of the University of California, Berkeley, noticed that two experiments carried out at very different temperatures had identical noise. When the editors of Nature pointed this out to Schön, he claimed to have accidentally submitted the same graph twice. Professor Paul McEuen of Cornell University then found the same noise in a paper describing a third experiment. More research by McEuen, Sohn, and other physicists uncovered a number of examples of duplicate data in Schön's work. In total, 25 papers by Schön and 20 coauthors were considered suspect.



Batlogg-Schon story 2002....primi sospetti









Batlogg-Schon story

• Bell Labs released the committee's 127-page report in late September, 2002. The committee had examined 24 allegations (involving 25 papers) and concluded that Schön had committed scientific misconduct in 16 of those cases. "The evidence that manipulation and misrepresentation of data occurred is compelling," the report concluded. The committee also found that six of the remaining eight allegations were "troubling" but "did not provide compelling evidence" of wrongdoing. Bell Labs immediately fired Schön.



Batlogg-Schon story articoli ritirati



On October 31, 2002, Science withdrew eight papers written by Schön:

http://www.sciencemag.org/cgi/content/full/sci;298/5595/961b

- * J. H. Schön, S. Berg, Ch. Kloc, B. Batlogg, Ambipolar pentacene field-effect transistors and inverters, Science 287, 1022 (2000)
- * J. H. Schön, Ch. Kloc, R. C. Haddon, B. Batlogg, A superconducting field-effect switch, Science 288, 656 (2000)
- * J. H. Schön, Ch. Kloc, B. Batlogg, Fractional quantum Hall effect in organic molecular semiconductors, Science 288, 2338 (2000)
- * J. H. Schön, Ch. Kloc, A. Dodabala-pur, B. Batlogg, An organic solid state injection laser, Science 289, 599 (2000)
- * J. H. Schön, A. Dodabalapur, Ch. Kloc, B. Batlogg, A light-emitting field-effect transistor, Science 290, 963 (2000)
- * J. H. Schön, Ch. Kloc, H. Y. Hwang, B. Batlogg, Josephson junctions with tunable weak links, Science 292, 252 (2001)
- * J. H. Schön, Ch. Kloc, B. Batlogg, High-temperature superconductivity in lattice-expanded C60, Science 293, 2432 (2001)
- * J. H. Schön, H. Meng, Z. Bao, Field-effect modulation of the conductance of single molecules, Science 294, 2138 (2001)

On December 20, 2002, the Physical Review journals withdrew six papers written by Schön: http://www.aps.org/media/pressreleases/122002.cfm (no longer available)

- * J. H. Schön, Ch. Kloc, R. A. Laudise, and B. Batlogg, Electrical properties of single crystals of rigid rodlike conjugated molecules, Phys. Rev. B 58, 12952-12957 (1998)
- * J. H. Schön, Ch. Kloc, and B. Batlogg, Hole transport in pentacene single crystals, Phys. Rev. B 63, 245201 (2001)
- * J. H. Schön, Ch. Kloc, D. Fichou, and B. Batlogg, Conjugation length dependence of the charge transport in oligothiophene single crystals, Phys. Rev. B 64, 035209 (2001)
- * J. H. Schön, Ch. Kloc, and B. Batlogg, Mobile iodine dopants in organic semiconductors, Phys. Rev. B 61, 10803-10806
- * J. H. Schön, Ch. Kloc, and B. Batlogg, Low-temperature transport in high-mobility polycrystalline pentacene field-effect transistors, Phys. Rev. B 63, 125304 (2001)
- * J. H. Schön, Ch. Kloc, and B. Batlogg, Universal Crossover from Band to Hopping Conduction in Molecular Organic, Phys. Rev. Lett. 86, 3843-3846 (2001)

On March 5, 2003, Nature withdrew seven papers written by Schön:

http://www.nature.com/nature/journal/v422/n6927/index.html

- * Schön, J. H., Kloc, Ch. & Batlogg, B. Superconductivity at 52K in hole-doped C60. Nature 408, 549-552 (2000).
- * Schön, J. H. et al. Gate-induced superconductivity in a solution-processed organic polymer film. Nature 410, 189- 192 (2001).
- * Schön, J. H., Meng, H. & Bao, Z. Self-assembled monolayer organic field-effect transistors. Nature 413, 713-716 (2001).
- * Schön, J. H. et al. Superconductivity in single crystals of the fullerene C70. Nature 413, 831-833 (2001).
- * Schön, J. H. et al. Superconductivity in CaCuO2 as a result of field-effect doping. Nature 414, 434-436 (2001).



C₆₀

C_{60} ridotto \leftrightarrow ossidato





K₃C₆₀



Sali di Fullerenio









 $J|A_{RT}|C_{L}|S_{T}$

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Fullerenium Salts: A New Class of C60-Based Compounds

Mauro Riccò,*,1 Daniele Pontiroli,1 Marcello Mazzani,1 Fabio Gianferrari,1 Massimo Pagliari,1 Angelo Goffredi,1 Michela Brunelli,2 Giorgia Zandomeneghi,9 Beat H. Meier,9 and Toni Shiroka¹¹

Dipartimento di Fisica, Università di Parma, Via G. Usberti 7/a, 43100 Parma, Italy, Institut Laue Langevin, BP 156, 6, rue Jules Horowitz, 38042 Grenoble Cedex 9, France, Physical Chemistry Laboratory, ETH-Zurich, Wolfgang-Pauli-Strasse 10, CH-8093 Zurich, Switzerland, and Laboratorium für Festkörperphysik, ETH-Zurich, Schafmattstrasse 16, CH-8093 Zurich, Switzerland

Received November 12, 2009; E-mail: Mauro.Ricco@fis.unipr.lt



Magnetismo nel C₆₀



TDAE











Orthorhombic (1D)	Tetragonal (2D)	Rhombohedral (2D)				
a=9.26Å b=9.88Å c=14.22Å	a=9.09Å c=14.95Å	a=9.19Å c=24.5Å				
Sp. gr: I m m m	S. g.: ?	Sp. Gr.: R -3 m				
1-8 GPa 300°C	3 GPa 600°C (mixed phase)	4 GPa 700°C				











Rh-C₆₀



 Osservata per la prima volta nel 1994 (Y. Iwasa *et al.*, Science 264, 1570 (1994))

Single crystal

a=9.17 Å c=24.57 Å Sp. Gr.: R-3m 5 GPa 500°C





Rh-C₆₀ magnetico?





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RETRACTION doi:10.1038/nature04622 Magnetic carbon

T. L. Makarova, B. Sundqvist, R. Höhne, P. Esquinazi, Y. Kopelevich, P. Scharff, V. Davydov, L. S. Kashevarova & A. V. Rakhmanina

Nature 413, 716-718 (2001)

In this Letter we reported high-temperature ferromagnetism in a polymeric phase of pure carbon that was purportedly free of ferromagnetic impurities¹. Since then, however, measurements made on the same or similar samples using particle-induced X-ray emission (PIXE) with a proton microbeam have indicated that these contained up to 10% iron^{2–4}. Also, polymerized C₆₀ samples mixed with iron before polymerization had a similar Curie temperature (500 K) to those we described¹, owing to the presence of the compound Fe₃C (cementite) (A. Talyzin, A. Dzwilewski, L. Drubovinsky, A. Setzer and P.E., manuscript in preparation). In addition, it has since been shown that the pure rhombohedral C₆₀ phase is not ferromagnetic⁵.

Nevertheless, magnetic order in impurity-free carbon structures at room temperature has been demonstrated independently⁶. Ferromagnetic properties may yet be found in polymerized states of C_{60} with different structural defects and light-element (H, O, B, N) content, or with carbon nanomodifications resulting from destruction of these polymerized states.

T.L.M. and P.S. decline to sign this retraction because they do not believe that the earlier results¹ are totally invalidated by these subsequent findings^{2–5}.

- Makarova, T. L. et al. Magnetic carbon. Nature 413, 716–718 (2001); corrigendum 436, 1200 (2005).
- 2. Höhne, R. & Esquinazi, P. Adv. Mater. 14, 753 (2002).
- 3. Spemann, D. et al. Nucl. Instr. Meth. B 210, 531 (2003).
- 4. Han, K. H. et al. Carbon 41, 785 (2003).
- 5. Boukhvalov, D. W. et al. Phys. Rev. B 69, 115425 (2004).
- Murakami, Y. & Suematsu, H. Magnetism of C₆₀ induced by photo-assisted oxidation. Pure Appl. Chem. 68, 1463–1467 (1996).

tion, large hysteresis and attachment to a magnet at room temperature. The temperature dependences of the saturation and remanent magnetization indicate a Curie temperature near 500 K.



Carbonio magnetico?





The FERROCARBON project brings together an array of European scientific talents from Italy, Spain, Germany, Sweden, Russia and the United Kingdom. Their skills cover the broad competencies in both theoretical and experimental chemistry and physics, plus material science and engineering, which are needed to achieve the challenging task of understanding how to produce magnetic carbon routinely and in bulk.

"The important thing in science is not so much to obtain new facts as to discover new ways of thinking about them." - Sir William Bragg



Ferrocarbon Consortium Parco Area delle Scienze, 7a - 43100 Parma, ITALY - Tel.: +39-0521-905-217 E-mail: ferrocarbon@fis.unipr.it

Scientific Coordinator: M. Riccò - Secretary: A. Goffredi - Web Designer: T. Shiroka

http://www.ferrocarbon.it/



Fulleriti polimeriche A₁C₆₀



























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100

110

220

















Fullerite Li₄C₆₀

- Polimerica a T = 300 K: cicloaddizione 2 + 2
- I legami del polimero si rompono a circa 300 °C, e si forma una fase monomerica di struttura cubica → fase metallica



S. Margadonna, D. Pontiroli, M. Belli, T. Shiroka, M. Riccò, M. Brunelli, J. Am. Chem. Soc. 126, 2004, 15032

M. Riccò, T. Shiroka, M. Belli, D. Pontiroli, M. Pagliari, G. Ruani, D. Palles, S. Margadonna, M. Tomaselli, *Phys. Rev. B* 72, 2005, 155437



Conducibilità superionica nel Li₄C₆₀



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Phys. Rev. Lett. **102**, 145901 (issue of 10 April 2009) <u>Title and Authors</u>

hysical Review

10 April 2009

Parma.

Dipartime

"Superionic" Buckyball Crystal

Depa

Ei

Materials that conduct electricity with ions rather than electrons are essential for batteries, fuel cells, and more exotic technologies. Providing enough space in the molecular structure for the movement of ions usually requires a disordered (non-crystalline) material. But a paper in the 10 April *Physical Review Letters* reports a crystalline compound with very high conductivity. It consists of positively-charged lithium ions flowing through a stacked structure of much larger, negatively-charged buckyballs (soccer-ball-shaped C₆₀ molecules). The results

suggest a new category of crystalline materials for researchers to study as they design new devices.

Highly ordered crystals are usually not the best starting point for researchers who want to make new materials with high ionic conductivity. Ionic conductors consist of molecules or groups of atoms of one charge that form a network, with space



M. Riccò/Univ. of Parma

Buckyworld. A new highly-conductive material consists of a crystalline network of negatively-charged buckyballs (black) with positively-charged lithium ions (blue) inhabiting the spaces between them (pink). The lithium ions move easily through the structure. (See animation of the rotating structure below.)





Fullereni endoedrici X@C₆₀





Metodi di produzione:

- Direttamente nel reattore ma in presenza della specie atomica da intrappolare
- Trattamento ad alte temperature e pressioni
 - Apertura della gabbia con un approccio di tipo chimico

Nanofarmaci, Quantum Computing ecc.





Fullereni endoedrici X@C₆₀

Reported Species

I	Π	Шb	IVb	Vb	VIb	VIIb		VIIIb		Ib	Пb	Ш	IV	V	VI	VII	0
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
Н																	He
Li	Be											В	С	N	0	F	Ne
Na	Mg											AI	Si	Р	S	CI	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Тс	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	1	Хе
Cs	Ba	La*	Hf	Та	W	Re	Os	lr	Pt	Au	Hg	TI	Pb	Bi	Po	At	Rn
Fr	Ra	Ac**	Rf	Db	Sg	Bh	Hs	Mt	Uun	Uuu	Uub		Uuq		Uuh		
Lan	thani	ides *	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Acti	nides	**	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	



 $LF - \mu SR$

 $ZF - \mu SR$

t

 $\overline{\nu}_{\mu}$

Forward positron detector



Schematic LF (ZF) µSR experiment









Schematic LF (ZF) µSR experiment

- <u>Muons</u> $(I = \frac{1}{2}, \tau \sim 2.2 \,\mu s)$:
 - Light isotope of proton
 - Implantation of polarized μ^+
 - Localise at an interstitial site
 - Decay: emitted positron to spin direction of μ^+
- <u>Muonium:</u>

Insulators:

Muonium (Mu $\equiv \mu^* e^*$)

Hydrogen

 $H/\hbar = -\gamma_{\mu} \mathbf{I} \cdot \mathbf{B} + \gamma_{e} \mathbf{S} \cdot \mathbf{B} + A \mathbf{S} \cdot \mathbf{I} = -\gamma_{\mu} I_{z} \mathbf{B} + \gamma_{e} S_{z} \mathbf{B} + A \mathbf{S} \cdot \mathbf{I}$



 $Mu@C_{60}$: presente anche negli A_3C_{60} nei quali mostra una particolare stabilità dovuta alla ad una debole interazione con la banda di conduzione